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EVALUATION OF REGENERABLE FLUE GAS DESULFURIZATION PROCESSES

Volume II

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NOTICE

ABSTRACT

Eleven regenerable flue gas desulfurization (FGD) processes have been evaluated on a common design and cost basis to assess their future potential and make recommendations regarding the level of additional developmental activities. One throwaway FGD process, lime/limestone wet scrubbing, was also considered to provide a "base-line" for process comparisons. Because of the preliminary development status of many of the processes, capital investment costs were not estimated in this study. Additional topics considered in the study were reducing gas production, lime/limestone sludge regeneration, and sulfur versus sulfuric acid production.

Four major conclusions can be drawn from this study. First, although capital costs were not estimated during this study, it is clear that they will represent a major factor in the total annualized cost of these processes and will become the key to selecting one process over another. Second, designs and operating data currently available for most second-generation FGD processes do not appear adequate for scale-up to commercial sized (100 MW) units. Third, the choice of sulfur or sulfuric acid production is a criterion which will have a major impact on the cost of an FGD system and will have to be evaluated on a site-specific basis. Finally, the use of reducing gas produced from coal or heavy fuel oil results in technical and economic penalties when compared to the use of methane as a reductant.

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INTRODUCTION

Volume II contains Radian's detailed process evaluations which were prepared to investigate the future potential of second generation FGD processes for the Electric Power Research Institute. The important features of this investigation are that it compares twelve processes ranging from the most developed to the still developing second generation processes on a common basis and in a consistent manner, that it is based on detailed heat and material balances for each process, and that a thorough technical evaluation was performed for each process. Although other comparisons of flue gas desulfurization processes have been done, this study broadens the scope of the evaluation to include new and still developing systems and places all the processes on the same basis for more effective comparison. This volume contains detailed process descriptions and technical evaluations for the following twelve processes:

1) Westvaco Activated Carbon Process,

2) Shell/UOP Copper Oxide Adsorption Process,

3) Bergbau-Forschung/Foster Wheeler Dry Adsorption Process,

4) Atomics International Aqueous Carbonate Process,

5) Catalytic/IFP Ammonia Scrubbing Process,

6) Citrate/Phosphate Buffered Absorption Process,

7) Ammonia - Ammonium Bisulfate (ABS) Process,

8) Ionics Electrolytic Regeneration Process,

9) Wellman-Lord Sulfite Scrubbing Process,

10) Cat-Ox Catalytic Oxidation Process,

11) Magnesia Slurry Scrubbing Process and

12) Lime/Limestone Wet Scrubbing Process.

Since several of the processes require an H_2/CO reducing gas, a section is included discussing various technical and economic considerations relating to four methods of H_2/CO production: steam methane reforming, steam-naphtha reforming, coal gasification, and partial oxidation. The study basis specified that the processes be designed for sulfur production. However, it was felt that recent developments indicate a strong potential market for sulfuric acid exists in some areas which may result in sulfuric acid being the desired by-product although more difficult to store and ship. Therefore, a section discussing sulfur and sulfuric acid production was prepared. Calcium sulfite/sulfate regeneration for the Lime/Limestone Process has been proposed on several occasions and a technical and economic evaluation of this idea is also presented.

The program had two objectives:

1) to assess the potential economic and technical viability of developing flue gas desulfurization processes, and

2) to provide EPRI with information to assist them in directing future research and development efforts.

To achieve these objectives Radian developed a technical approach which was followed for each process. A thorough literature search was made; then, the process vendors were contacted to gain access to information which was sufficiently detailed to permit the calculation of energy and material balances. Non-disclosure (secrecy) agreements were obtained where necessary to acquire this information. Key design and scale-up factors were identified and the technical feasibility of the processes was assessed with emphasis on pointing out areas where further development is needed or potential problems exist. The energy and material balances allowed Radian to arrive at independent estimates of the processes' raw material and utility costs. At various points during the project, the validity of Radian calculations and assessments was checked by consultation with process vendors and a consultant knowledgeable in the field.

Once this sequence of steps had been followed for each process, the systems were compared on a common basis. From the investigations and the comparison, several conclusions and recommendations were made. The detailed comparison and the conclusions and recommendations were presented in Volume I.

1.0 WESTVACO ACTIVATED CARBON PROCESS

The Westvaco Process is similar to the Reinluft, Bergbau-Forschung, Lurgi and Hitachi Processes in that it uses activated carbon as an adsorbent and catalyst to remove SO_2 from flue gas. The primary differences among these processes are in the methods of gas-solid contacting and adsorbent regeneration.

Westvaco is one of the United States' largest makers of active carbon products. The emphasis in their research work on flue gas desulfurization has been to develop a system which utilizes high grade, commercially producible activated carbon to obtain high rates of adsorption over long periods of time and which does not consume this more expensive material during the regeneration step.

1.1 Process Description

Adsorption System

The Westvaco Process employs a multi-stage fluidized bed unit to contact the SO_2-laden flue gas with the carbon adsorbent, a scheme unique among FGD systems. The sorber, when designed for 90 percent removal, consists of five shallow beds. The top four beds each contain approximately twelve inches of settled carbon and the bottom bed contains three inches. These beds are maintained in a highly agitated, fluidized state by the passage of the flue gas up through the unit. Figure 1-1 is a flow diagram illustrating the flow of carbon and gas throughout the system.

The lowest stage in the sorber is designed to remove all of the SO_3 in the flue gas. This first bed operates at 300°F

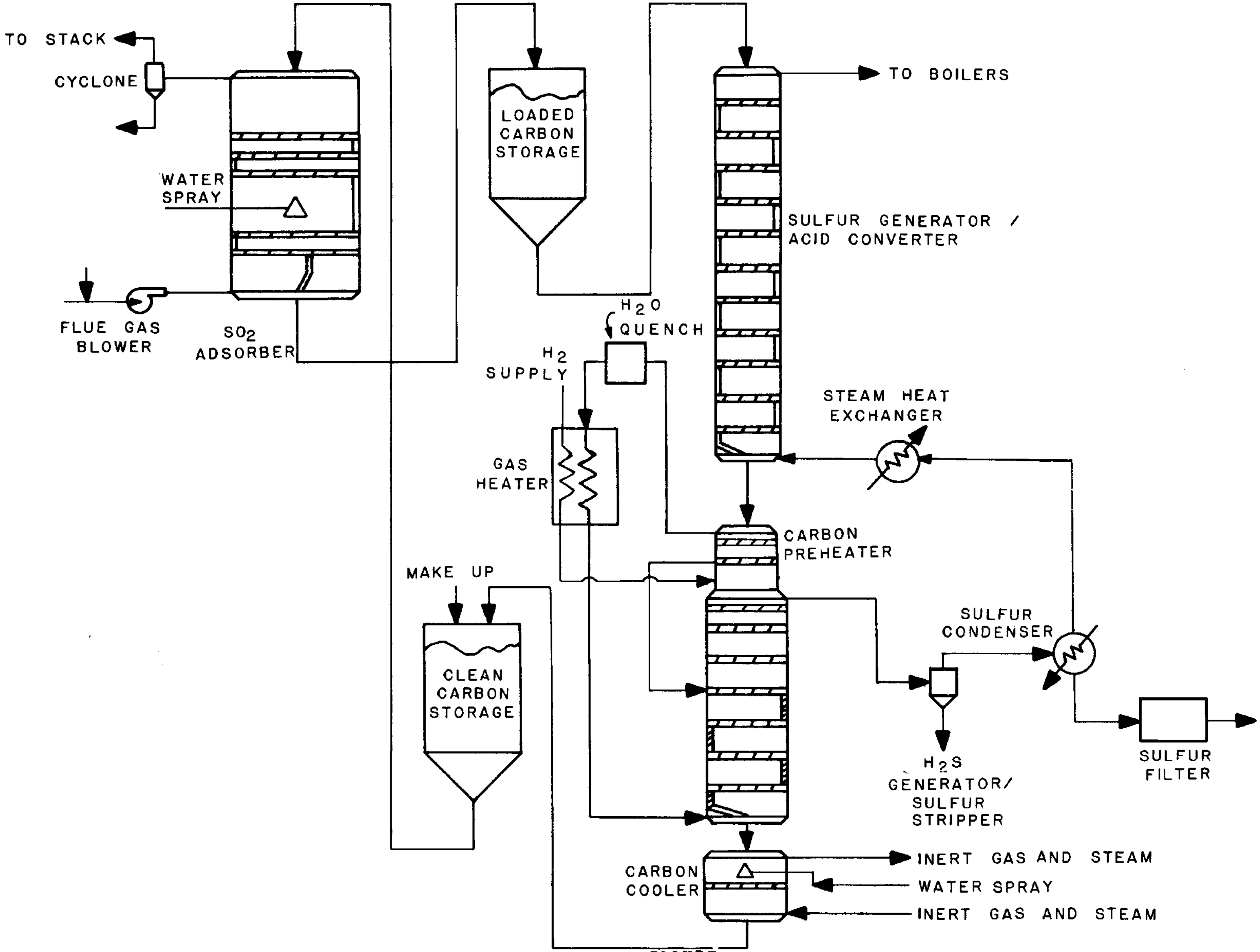

FIGURE 1-1
PROCESS FLOW DIAGRAM
WESTVACO
ACTIVATED CARBON PROCESS

while sorbing SO_3 to reduce dewpoint problems. With the SO_3 largely removed, the other four stages can operate at 150 to 250°F where the catalytic adsorption of SO_2 is more rapid. Water is sprayed onto the second stage to humidify the gas and cool it to the desired temperature (150 to 250°F). The top three stages of the sorber supply about 25°F reheat to the gas.

The basic adsorption mechanism is shown in Equation (1-1).

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \xrightarrow[\text{CARBON}]{} H_2SO_4 \qquad (1\text{-}1)$$

Carbon catalyzes the oxidation of SO_2 to SO_3 and adsorbs the sulfuric acid formed. The carbon can contain as much as 40 percent by weight of acid but to maintain efficient rates the design acid loading is about 0.22 lb acid/lb carbon. This loading value fixes the carbon circulation rate. The turbulent motion of the particles in the fluidized beds eliminates mass transfer limitations and also prevents the formation of hot spots.

Increased flue gas blower head is necessary to overcome the pressure drop incurred when fluidizing the carbon particles. The pressure drop depends on the total carbon depth which must be supported; one inch of settled carbon requires a pressure drop of approximately 0.5 inches of water for fluidization. A pressure drop must also be taken across the gas distributors (about 10 percent of that required across each bed) which is, however, not as large as might be suggested from a study of fluid cat crackers in the refining industry. Fluid cat crackers are generally several feet deep, single stage, and contain particles much smaller than the 12 x 40 mesh used here. Deep beds with small particles tend to form large bubbles. This tendency lends itself to occurrence of channeling and dead spots (KU-001). Therefore in deep beds, a larger pressure drop across the distributor is needed to get good distribution than will be necessary for the shallow beds and large particles in the Westvaco adsorber. The power requirement of the flue gas blowers was estimated based on a maximum total pressure drop of 40 inches of water. The normal drop is 30 inches across the absorber and 5 inches across the cyclone after the absorber.

Regeneration System

The acid laden carbon is regenerated by reducing the acid with hydrogen in several steps. In the first step the loaded carbon is fed to an eleven-stage fluidized bed contactor where most of the acid is reduced to sulfur by H_2S in the fluidizing gas stream at a temperature of 300°F. The reaction proceeds according to Equation (1-2).

$$H_2SO_4 + 3H_2S \rightarrow 4S + 4H_2O \qquad (1\text{-}2)$$

When the temperature gets above 350°F, one of the side reactions (1-3A) or (1-3B) begins to produce SO_2 which is recycled with the rest of the off-gas to the sorber, either directly or by way of the boilers where any residual H_2S is incinerated.

$$H_2SO_4 + \tfrac{1}{2}S \rightarrow 3/2\ SO_2 + H_2O \qquad (1\text{-}3A)$$

$$H_2SO_4 + \tfrac{1}{2}C \rightarrow \tfrac{1}{2}CO_2 + SO_2 + H_2O \qquad (1\text{-}3B)$$

Under normal operation the exothermic heat of reaction (1-2) is largely taken up by the evaporation of adsorbed water. The temperature in the unit can be controlled by spraying water over the carbon but the advantageous heat transfer characteristics of fluidized beds should eliminate any need for this except as an emergency backup. In performing the material balances it was assumed that 15 percent of the adsorbed acid is evolved as SO_2 and recycled to the adsorber. Each bed in the sulfur generator contains 17 inches of settled carbon and the fluidizing gas velocity is 3 feet per second.

The carbon next passes to a preheater, a two stage fluidized bed, where the temperature of the solids is raised from 300°F to 750°F by heat exchange with hydrogen-rich regeneration gas which has been preheated to about 1300°F. The hydrogen-rich gas, which has cooled to 500°F by contacting the carbon, is quenched with water to 200°F in order to protect the booster blower, compressed, and reheated to approximately 1300°F. It is then introduced into the H_2S generator/sulfur stripper where it passes up through a seven-stage fluidized bed. The carbon from the preheater is introduced on the fourth stage from the top. The temperature in the unit is around 1000°F and in this hot, hydrogen-rich environment two operations take place. The carbon is regenerated by thermally stripping the adsorbed sulfur from it and reacting the residual acid with hydrogen. At the same time hydrogen also reacts with three-fourths of the sulfur to produce hydrogen sulfide for use in the sulfur generator. The uppermost three beds of carbon are not part of the carbon flow loop, but rather are non-cycling fluidized beds present to catalyze the reaction of hydrogen and sulfur vapor to H_2S as in Equation (1-4).

$$H_2 + S \rightarrow H_2S \qquad (1\text{-}4)$$

After leaving the sulfur stripper, the carbon is cooled in another single stage bed fluidized by a mixture of inert gas and steam and further cooled by a water spray. After being cooled to 300°F the regenerated carbon is transported to the storage vessel feeding the SO_2 sorber. Because of rate limitations, the carbon has about four percent residual sulfur still adsorbed on it, but this small amount has been shown to have minimal effect on carbon activity, and is not re-oxidized in the adsorber, nor does it increase with time.

The gas from the sulfur stripper/H_2S generator is cooled to 250°F and the sulfur is condensed, filtered, and routed to storage. The H_2S-rich gas is reheated to 300°F and fed to the sulfur generator.

Additional parts of the system are the hydrogen production facility, inert gas generation system, and storage vessels for both clean and loaded carbon. The various possible reducing gas systems are discussed in Section 13. It should be noted, however, that Radian's calculations for the base case Westvaco material and energy balances assume a shifted reducing gas composition of 20 percent H_2. The inert gas generator, which produces a gas used to fluidize and cool regenerated carbon, will not be discussed because it is a rather minor part of the process. Cone bottom storage tanks for holding both laden and clean carbon are easily included in the system and provide valuable flexibility by isolating the adsorption and regeneration sections from each other. One penalty paid for this surge capacity, however, is the heat lost from the stored carbon. In one case this heat loss is beneficial since it is advantageous for clean carbon to enter the adsorber at a lower temperature (the reaction rate is faster at a lower temperature), but heat lost from the acid-laden carbon must be made up by adjusting the temperature of the H_2S-rich gas entering the acid converter.

Other auxiliary systems are needed for start-up. An air blower and heating system are needed to bring the adsorber up to temperature and a source of either H_2S or sulfur will be necessary to start up the regeneration section once the adsorber is running.

1.2 Environmental Considerations

The Westvaco Process has an advantage over many other processes because it is able to go to very high SO_2 removals with only moderate increases in adsorber size and pressure drop. Due to the multistage design and the fact that the kinetics of SO_2 adsorption on carbon are less than first order in SO_2 concentration (BA-254), the system can be designed to achieve 99 percent efficiency with only about a 20 percent increase in carbon depth and pressure drop over a system designed for 90 percent efficiency. In other words, while the carbon loading remains the same, the flow rate of carbon increases by 10 percent and the residence time of the carbon in the adsorber increases by 20 percent. Concurrently, because the regeneration and adsorption sections can be essentially decoupled by intermediate carbon storage, the regeneration section capacity need only be increased sufficiently to handle the additional 10 percent sulfur load. The primary limitation then, is the economic tradeoff between removal efficiency and the equipment costs and power required to overcome the pressure drop through the adsorber. These costs, however, do not go up as rapidly for Westvaco as they do for some other systems such as wet scrubbers.

A second area of major interest is the capability of the system for simultaneous removal of NO_x. Using a scheme for SO_2 recovery which could also remove NO_x at reasonable incremental cost would have definite capital cost advantages over using two separate systems, one for SO_2 and one for NO_x. There are some indications from research on other carbon adsorption systems that around 40 to 50 percent of NO_x in flue gas can be removed by activated carbon along with SO_3 removal (BA-003). The probable reaction is either the catalytic oxidation and hydrolysis of NO to HNO_3 with the acid being adsorbed on the carbon or the absorption of NO_x in the sulfuric acid in the pores. The thermodynamics of both the oxidation of NO to nitric acid and subsequent reduction of the acid to N_2 with H_2 are very favorable. Discussions with Westvaco researchers revealed that the Westvaco process has not demonstrated any NO_x reduction in pilot testing. However, since the adsorption media of the Reinluft and Bergbau-Forschung Processes are so similar to that used by Westvaco, the process may potentially be able to demonstrate some NO_x removal capability.

Carbon fines produced by attrition of adsorbent in the highly agitated fluid beds could cause a serious particulate problem in the cleaned stack gas as these fines are loaded with sulfuric acid. The use of sufficiently hard carbon and a reasonable gas velocity could, however, result in the need for only nominal control such as a cyclone to eliminate excessive particulate emissions. Any captured dust could be incinerated with the pulverized coal fuel. Federal standards limit particulate emissions to 0.1 lb/MM Btu, which is equivalent to about 0.05 gr/scf. The pilot plant data showed carbon fines being generated at a rate of 0.11-0.22 gr/scf. This value became stabilized at 0.11 gr/scf after several cycles. The carbon fines passing through the cyclone were constant at 0.05 gr/scf when the cyclone operated at 2 inches of water. However, Westvaco has manufactured samples of a harder carbon which has been shown to be more attrition resistant in special lab tests but has not been demonstrated in the pilot plant. On the basis of a carbon 7 times harder than that used in pilot studies and operating the cyclone near 4 inches of water pressure drop, particulate emissions to the stack due to carbon fines of less than 0.01 gr/scf are expected. Even with the less hard carbon a cyclone with 4 inches of water pressure drop would reduce particulates escaping to the stack below 0.015 gr/scf. Harder carbon decreases generation of fines and more efficient collection reduces stack emissions. Carbon attrition and fines control are discussed further in the section on design considerations.

The carbon particles in bench and pilot scale testing were unaffected by the particulate fly ash loading of the flue gas and no noticeable pickup of metals occurred. No recognizable accumulation of chlorides was observed either (WE-184). The lack of chloride accumulation can be explained by the flow scheme. Chlorides are generally present in flue gas as $HC\ell$ and any pickup of $HC\ell$ on carbon would be as an acid solution, in water adsorbed on the carbon. $HC\ell$ solution is very unstable with respect to temperature. The cooler conditions in the upper stages of the adsorber would encourage some adsorption of $HC\ell$ but as the carbon flows down, its temperature and the temperature of the gas around it increases to 300°F on the lowest stage and all the chlorides would be desorbed again when the carbon left the adsorber. In essence, an internal recycle of chlorides would be set up in the adsorber but it would be very unlikely, except in upset conditions, that the carbon leaving the sorber would be carrying any significant quantity of chlorides.

1.3 Material and Energy Balances

Considerable time and effort was spent performing material and energy balance calculations so that an independent estimate could be made of the process raw material and utility requirements. Also, these calculations permitted estimates of the size and quality of waste streams. In addition, estimates of the size of equipment and hence the difficulty in scaling as well as the probable maximum module size were made. Some of the items discussed under design considerations, environmental considerations and economics first came to attemtion through the balances. In particular, the importance of minimizing the carbon attrition problem came to the fore in the material balance study.

The utility and raw material requirements derived from the balances are presented in Table 1-1. These requirements are presented by usage in the main process sections. Power for the smaller pumps and blowers has not been included.

In general, the balances performed by Radian checked closely with Westvaco's information. There were discrepancies of a few percent, mostly in water content, partly because of the reaction of hydrogen with chemisorbed oxygen which is difficult to quantify. The only change from Westvaco's energy balance was an increase from 1200 to 1300°F in the temperature to which the reducing gas is reheated. This was necessary to close the heat balance for the H_2S generator/sulfur stripper. Additional calculations were made to estimate the power required by the flue gas blowers. The estimates made of pressure drops through the fluid bed units led to the discovery of an error in the Westvaco information. The original Westvaco proposal indicated a pressure drop of 60 inches of water across the sulfur generator but Radian's calculations suggested 90 to 100 inches would be more appropriate. This change has no major consequence in terms of energy usage because the gas flow through this unit is very much smaller than that through the main adsorber.

1.4 Design Considerations

One of the unique features of the Westvaco process is the use of multiple stage, fluidized bed gas-solid contacting in both adsorption of SO_2 from the flue gas and regeneration of the activated carbon adsorbent. Since experience with units of this type is not widespread and these units make up almost the entire process, any discussion of design considerations must necessarily focus on fluidized beds.

TABLE 1-1

RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE WESTVACO PROCESS

Basis: 500 Mw, 3.5 Percent Sulfur Coal

Processing Area	Electric Power (Mw)	Low Btu Fuel Gas (MM Btu/hr)	Reducing Gas (MM Btu/hr)	Carbon (lb/hr)	Steam (MM Btu/hr)	Process Water (M gal/hr)
Adsorption	13.2	-	-	128	-	20.4
Regeneration	-	76	210	152	6.5	6
Hydrogen Production	-	25*	-	-	-	-
TOTALS	13.2	76	210	280	6.5	26.4

* This can be recovered from the gas heater without additional fuel being burned.

Fluidized beds are highly agitated by the passage of gas through the solids, and the resultant turbulent mixing gives them excellent heat and mass transfer characteristics. Diffusion limitations are reduced and formation of hot spots is minimized as long as adequate gas flow distribution can be maintained to keep the bed evenly fluidized. In the Westvaco Process this ability to obtain even heat distribution is valuable in avoiding the carbon ignition problems which have hindered the Reinluft Process.

Although fluidized bed units are generally complex to scale up, they can be mathematically modeled with some success. The validity of various models, however, continues to be a point of academic controversy. Westvaco was able to successfully predict the performance of an 18-inch reactor from information gathered on a 6-inch diameter bench scale unit. This represented a 13-fold scale-up based on gas flow. A 25-Mw unit would entail a scale-up of almost 160-fold from the pilot plant unit. There has been a significant amount of potentially helpful experience in designing and operating units similar to the main adsorber by Courtaulds Ltd. of England (AV-011, RO-204). The Courtaulds units are multistaged with shallow beds (2 to 3 inches settled depth) and are used to adsorb solvent vapors from large air streams. At least one adsorber with a diameter over 50 feet, handling over 500,000 scfm, has been built and operated satisfactorily. Access to information from this source for aid in design and scale up, however, is restricted by the secretiveness of Courtaulds.

The fluid bed adsorber is at a certain disadvantage when compared to wet scrubbers because it operates at a lower gas velocity of 4 fps and a higher pressure drop of 20 to 30 inches of water. Characteristically, the contacting unit will be larger in diameter and the power requirement for pressure drop will be higher for the Westvaco Process than for a wet scrubber.

In order for a carbon adsorption process to function at an acceptable cost, adsorbent make up must be held to a low level. The Westvaco regeneration scheme was developed to minimize the chemical consumption of the carbon adsorbent which occurs in the Reinluft and the Bergbau-Forschung Processes. These two processes regenerate the adsorbent and evolve SO_2 by heating the loaded carbon. At an elevated temperature the carbon reduces the acid within the pores producing SO_2, CO_2 and H_2O. Chemisorbed oxygen is also removed by reaction with the carbon. By avoiding this carbon consumption, Westvaco is able to use a more expensive adsorbent with high activity toward SO_2 adsorption. However, unless the use of harder carbons reduces the adsorbent losses due to attrition in the highly turbulent fluid bed contactor, the advantage is diminished. A trade-off is made between physical attrition of expensive carbon and use of reducing gas and the chemical consumption of cheaper carbon as a reducing agent. Therefore, the more successful the minimization of attrition is, the greater the advantage of the Westvaco Process over other carbon processes. Discussions with Westvaco indicated that suitably hard carbon could be made available in adequate quantities.

Sulfur plugging is a problem that any sulfur producing facility must face. Westvaco's pilot plant has only one line outside the liquid sulfur handling system where plugging can present a problem. This is the H_2S recycle line which plugged once during pilot runs. Additional steam tracing, however, solved the problem completely.

If predictions regarding carbon losses due to attrition are correct, no unusual measures other than cyclones should be needed to maintain particulate emissions below federal standards, assuming effective electrostatic precipitators prior to the SO_2 scrubbing process. On the other hand, if higher attrition rates exist, carbon fines control could become a serious problem. One possible reconfiguration of the process with good potential for improving economics would place a cyclone ahead of the adsorber instead of a precipitator and a low temperature precipitator after the adsorber. This modification would take advantage of the Westvaco Process's essentially complete removal of SO_3 in the first stage of the adsorber and the apparent ability of the fluid bed to allow fly ash to pass through without hindering the activity of the carbon toward SO_2. With the SO_3 removed, dew-point limitations are eliminated and the flue gas can be cooled to 200°F without causing equipment problems. At 200°F the efficiency of electrostatic precipitation goes up and the size of the precipitator can be reduced because the gas volume has been reduced. In this manner, savings could be made in the expense of the electrostatic precipitator, and carbon fines would be completely controlled as well. This reconfiguration presupposes that the loss of polarizing (ionization) potential due to the absence of SO_2 and SO_3 will not seriously limit the effectiveness of an electrostatic precipitator.

Pilot plant work showed that if temperatures in the sulfur generation unit reached 350°F, evolution of SO_2 began to occur. In a full scale plant the off-gas from the regeneration system would be passed to either the adsorber or the boilers. If sent to the boilers, any H_2S slippage would be managed as well.

At the present time, inert diluents of the hydrogen reducing gas such as H_2O, N_2, and CO_2 have been shown to have little effect on regeneration. CO and CH_4 are less desirable, however, as their presence can result in formation of carbonyl sulfide and carbon disulfide. Bench scale experiments have suggested that CO and CH_4 could be used directly with COS formation held down, but their use has not yet been completely proven (ST-293).

The convenience of storing the densely loaded carbon in intermediate vessels is a definite plus for the system. An important point in any design will be the volume of storage provided to decouple the adsorption and regeneration sections. This will depend on whether the boiler is used for base load or peaking power and the anticipated variation in load on the FGD system. This storage will also permit the regeneration section to be designed for the average load and run at a steady rate while the adsorption section is designed for the maximum load and run more flexibly.

Large quantities of heat are added and removed in regenerating the carbon at high temperature in the H_2S generator/sulfur stripper. Heat recovery from the carbon is technically feasible, but the economic incentive is still undetermined. In situations like this, a trade-off must be made between operating costs for energy and capital costs for equipment.

1.5 Status of Development

Westvaco has done a substantial amount of research work under contract with the EPA. The largest test unit operated was an integrated pilot plant which handled a 330 cfm slip stream from an oil-fired industrial boiler. This unit had an 18-inch SO_2 adsorber and was operated for 350 hours with one short episode of down time due to sulfur plugging. This operating time can not be considered sufficient to have completely demonstrated the process's long term reliability, but much desired information on integration was obtained.

Bench scale studies have enabled Westvaco to prepare a kinetic model of the various reactions that take place and employ the model to design the adsorber and the sulfur generator rigorously. There is, as yet, not anough data on the simultaneous generation of H_2S and thermal stripping of sulfur which occurs in the last step of regeneration to design that unit rigorously, but space velocity techniques are available. It should also be noted that the second step, conversion of H_2SO_4 to sulfur with H_2S, has not been run in a fluid bed unit under integrated pilot plant conditions; however, adequate data from individual unit testing using fluid beds is available to successfully design a large unit. The pilot plant was run using a moving bed acid converter because a fluid bed unit would have been too small for sensible construction. The fact that diluted cylinder hydrogen rather than gasifier product was used in the pilot plant also prevented complete integration, and information is still lacking on system performance under variable loads from a coal-fired boiler.

Materials of construction were not a problem in small scale operation and should not be in a full scale system. The most rigorous environments contain reducing gases, H_2S and H_2, which are commonly found in petroleum refineries. The adsorber will be made of carbon steel with stainless steel gas distributors. The regeneration equipment, which is contacted by H_2S, will be constructed of alonized carbon steel for service below 750°F and of alonized stainless for higher temperature service.

1.6 Scale-Up Considerations

Most of the scale-up considerations have already been discussed, but a brief reiteration will be made to emphasize important points. All three pieces of major equipment which must be scaled up are multistage fluidized beds. Scale-up of fluidized beds in other applications has often been difficult due to the complex interaction of factors such as bed depth, particle size, gas velocity, and bed diameter. Mechanical design of the main adsorber could be a significant problem due to the extremely large diameter equipment which is involved. One other company, Courtaulds Ltd., has had experience in designing similar types and sizes of units, but whether it will be possible to tap this experience remains in doubt. If Westvaco and Catalytic are able to come to an agreement with Courtaulds to purchase information, the design of the equipment would be substantially easier.

A similar consideration applies to the regeneration system where two more multistage fluid beds are used but to a lesser extent since the units are much smaller in diameter. In addition, a lack of good kinetic information on simultaneous formation of H_2S and thermal stripping of sulfur in the last major regeneration step has prevented any more rigorous design procedures than space velocity considerations. Detailed design data is available, however, for the adsorber and acid converter. Partial integration of the process has been demonstrated on the pilot scale but without hydrogen production and with a moving bed rather than a fluid bed acid converter.

1.7 Utility Applicability

There should be no serious limitations on applying the Westvaco process in new plant situations, although the space requirements for this process are rather large - about 25,000 square feet per 250 Mw module. Carbon supply is a vital area of concern. Each 250 Mw module requires an initial inventory of about 270 tons of carbon and an annual makeup of 370 tons. Major carbon suppliers such as Westvaco now produce around 70,000 tons (HA-402) per year of various types of activated carbon. The type necessary for the Westvaco Process is somewhat special, however, and Westvaco, as one of the nation's largest activated carbon producers, has guaranteed a sufficient supply of carbon for a minimum of 25,000 Mw installed capacity. Current carbon costs are in the range of $0.50/lb (ST-293).

Retrofit applications could be seriously hampered by the large amount of space required close to the boiler for the adsorber. The low gas velocity in the adsorber implies a large diameter unit. For a 250 Mw module, cleaning 500,000 scfm, the adsorber would be greater than 50 feet in diameter and 50 to 60 feet high.

Because of the nature of utility boilers, the load on the FGD system will not be constant and the ability of the system to operate well in the face of varying demand will be very important to its success. The turndown capabilities of the Westvaco Process are governed by the minimum fluidization velocity, which is the gas velocity necessary to maintain the solid particles in a fluidized state. The minimum fluidization velocity of the processed system is about 25 to 35 percent of the design adsorber gas velocity. A reasonable turndown rate would probably be 50 percent to preserve a margin of safety. With two modules for a 500 Mw plant, turndown to 25 percent could be accomplished by taking one module out of service. Recent information indicates that a 500 Mw installation would probably be designed with 3 modules of smaller size, and, in this case, turndown to 17 percent could be achieved by taking two modules out of service. To gain even more turndown flexibility, a clean flue gas recycle could be used to maintain adequate total gas flow through the adsorber.

In addition, the process has the advantage of simple intermediate storage. The SO_2 is stored as H_2SO_4 adsorbed on carbon at the relatively dense loading of .22 lb H_2SO_4/lb carbon, yet the carbon is still dry, free flowing, and non-corrosive. The operation of the process does not appear to be very complex, and the pilot plant demonstrated its relative insensitivity to changes in process flows. The SO_2 adsorber will be affected only slightly by load changes, and the intermediate storage will damp out fluctuations before they reach the regeneration system. The major load following problem is the adaptability of the hydrogen production plant. In any case, the intermediate storage facility should enable the regeneration system to run at a steady enough load that the need for flexibility from the hydrogen plant will not be beyond that plant's normal capabilities.

1.8 Economic Assessment

Annualized raw material and utility costs are presented in Table 1-2. The results indicate that if the initial costs of carbon and catalyst inventories are ignored, the adsorption section generates 21 percent of the annual raw material and utility cost, and the regeneration section 79 percent. The total annual operating costs, excluding capital charges, for 500 Mw base case plant is approxiamtely 8.1 million dollars, or 3.1 mills/kwhr.

TABLE 1-2

ANNUAL RAW MATERIAL UTILITY COSTS FOR WESTVACO PROCESS

Basis: 5260 hours per year at full load, 500 Mw, 3.5% S

Adsorption System		Annual Cost ($\$10^3$)	
Electric Power	13.2 Mw	1,389	
Boiler Feed Water	340 gpm	15	
Carbon Makeup	128 lb/hr	337	
		1,741	21%
Regeneration System			
L. P. Steam (150 psig)	7360 lb/hr	17	
Low Btu Gas	75.6 MM Btu/hr	1,591	
Boiler Feed Water	100 gpm	5	
Hydrogen (20%)	43,000 scfm	4,366	
Carbon Makeup	152 lb/hr	400	
Steam Production (20 psig)	49,200 lb/hr	-	
		6,379	79%
Hydrogen Production*			
Heat Recovery from Gas Heater Stack Gas	25 MM Btu/hr		
TOTAL ANNUAL RAW MATERIAL AND UTILITY COSTS		8,119	100%
UNIT RAW MATERIAL AND UTILITY COST		3.1 mills/kwhr	

* Requirements for upgrading air-blown gasifier product gas.

Table 1-3 provides a breakdown of the energy consumption for the process by both type of fuel and point of use. One simple way to assess the energy intensiveness of the process is to express the total energy consumption as a percentage of the power plant rating. For the Radian base case 500 Mw plant, the flue gas blowers use 13.2 Mw or 2.6 percent of the power plant rating. The heat requirements which could be filled by either #2 fuel oil or low Btu gas from a coal gasifier are about 75 MM Btu/hr; equivalent to 1.7 percent of the total heat rate.

The hydrogen consumption is an extremely important consideration in the process economics. Westvaco is in an intermediate position with regard to theoretical hydrogen consumption. In Westvaco's process the SO_2 is first oxidized to sulfuric acid. The overall reaction to generate sulfur is shown by Equation (1-5).

$$H_2SO_4 + 3H_2 \rightarrow 4H_2O + S \qquad (1\text{-}5)$$

Processes which do not oxidize the SO_2, such as some wet scrubbers, require only 2 moles H_2/mole SO_2 to obtain sulfur while those which oxidize to metal sulfates require 4 moles H_2/mole SO_2. The Westvaco Process actually uses 3.3 to 3.9 moles H_2/mole SO_2. The efficiency of H_2 usage, however, is good since the excess of 0.3 to 0.9 moles over stoichiometric needs is necessary to completely reactivate the carbon by reacting with chemisorbed oxygen (WE-184, BA-259).

High quality hydrogen is not essential. Dilute gas from an air blown gasifier is acceptable as long as the tars are removed and the CO is reduced to a low level by a high temperature water gas shift. The H_2S in the gas does not have to be cleaned up since the high temperature shift catalyst is able to tolerate the sulfur, and the hydrogen is used to produce H_2S anyway.

TABLE 1-3

ENERGY CONSUMPTION FOR WESTVACO PROCESS

	MM Btu/hr	%
Steam-Reheat H_2S Gas	6.4	1.3
Fuel Oil (#2)		
Reducing Gas Heat to Shift Temp.*	25.0	5.0
Gas Heater - Regeneration Feed	34.2	6.8
Gas Heater - Regeneration Reheat	35.0	7.0
Inert Gas Generator	6.4	1.3
Electric Power - Flue Gas Blowers (13.2 Mw)**	132.0	26.3
Energy Equivalent of Reducing Gas Consumption***	263.1	52.3
	502.1	100.0

* Potentially recoverable from regeneration section.

** Based on incremental fuel requirement to produce the electric power - 10,000 Btu/kwhr.

*** Based on incremental fuel requirement to produce reducing gas - 1.5 Btu/Btu H_2.

1.9 Process Summary

The Westvaco Process is a dry process which uses activated carbon to adsorb SO_2 from flue gas. A unique feature of the process is its use of multistage fluidized beds in both the adsorption and regeneration steps. Hydrogen reducing gas is used to regenerate the carbon and at the same time produce elemental sulfur. Westvaco's major problems lie in the operability of large fluid beds. Due to the low gas velocity and the need to fluidize the carbon, the main adsorber must be large, and a substantial pressure drop must be incurred. The power consumed by the flue gas blowers in overcoming this pressure drop leads to a small but significant (2.6 percent) derating of the station. The process is in a fairly early stage of development in terms of the size of the largest unit which has been demonstrated (330 cfm) and the length of the run made on it (350 hours). However, good kinetic data is available for design. An intermediate size demonstration of this process at a coal-fired boiler would seem to be the next logical step in process development in order to firm up design and scale-up data and obtain increased confidence in process operations.

2.0 SHELL/UOP - COPPER OXIDE ADSORPTION PROCESS

The Shell Flue Gas Desulfurization (SFGD) Process which is licensed by UOP's Air Correction Division is a dry metal oxide process. It is based on the ability of copper oxide to react with SO_2 in a flue gas and to be regenerated by hydrogen reducing gas. Although the Shell process is sometimes termed an adsorption process, the removal mechanism is the reaction of SO_2 with copper oxide to form copper sulfate according to Equation 2-1.

$$CuO + \frac{1}{2}O_2 + SO_2 \rightarrow CuSO_4 \qquad (2\text{-}1)$$

The process developers refer to this as acceptance and copper oxide as an acceptor. Copper is regenerated and SO_2 evolved by passing reducing gas, preferably hydrogen, over the copper sulfate. The end product of the process can be sulfur, SO_2, or sulfuric acid depending on the available markets and other economic considerations.

Although a secrecy agreement was concluded with UOP, due to problems in communicating the nature of the work being done by Radian and unfortunate delays in transmission of information, the flow sheet in Figure 2-1 is not necessarily representative of current UOP design philosophy. This flow sheet was evaluated because it is the system used by the SYS Refinery in Japan and other older UOP designs and detailed information was available on it from sources other than UOP. Current practice is more flexible in that the SO_2 recovery and concentration section can be either a water absorption/stripping, a solvent absorption/stripping, compressor/gas holder, or SO_2 liquefaction system. It should be noted that many of the problems with the water absorption/stripping system have also been considered by UOP which has led to use of different systems in recent proposals.

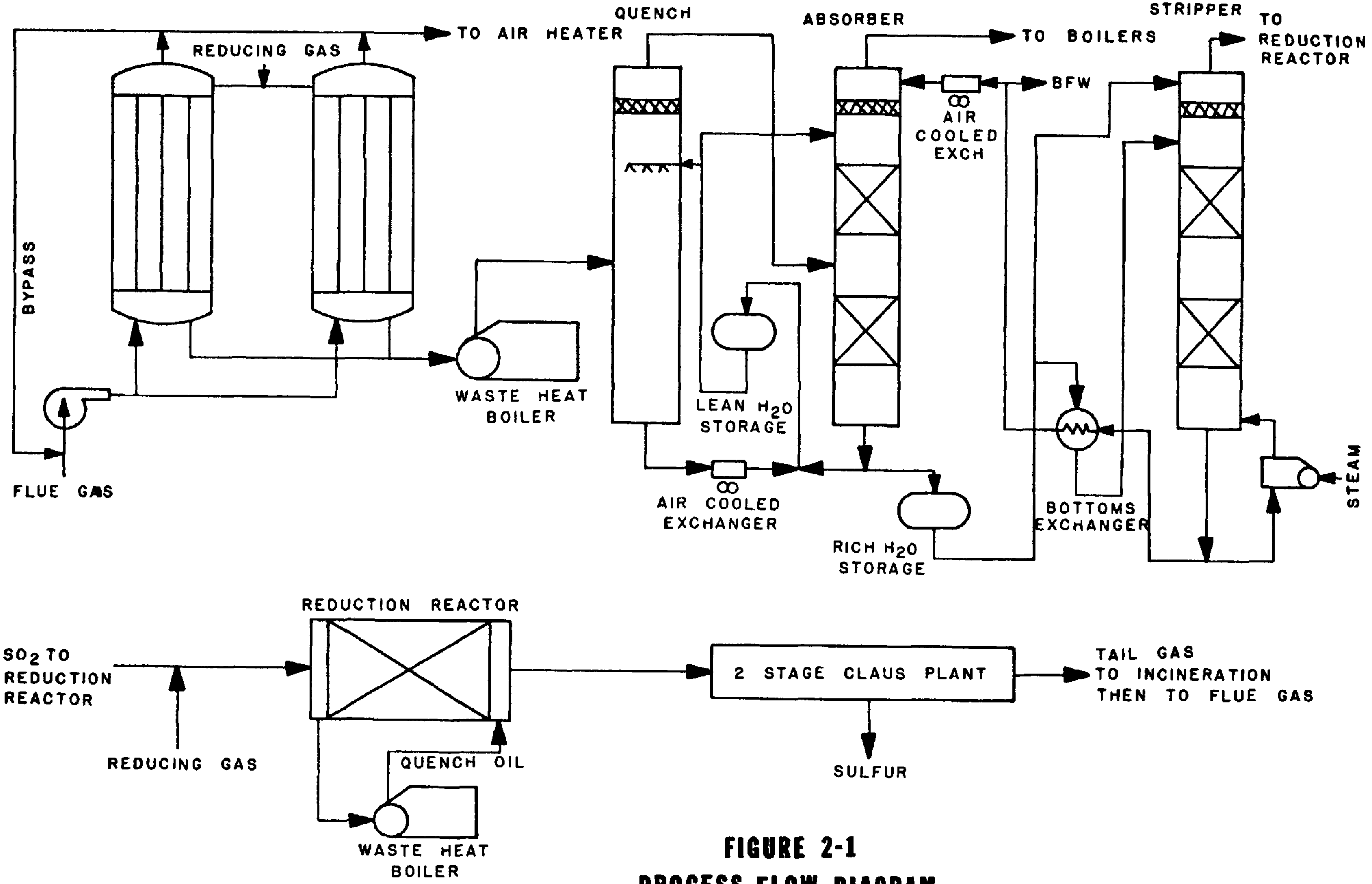

FIGURE 2-1
PROCESS FLOW DIAGRAM
SHELL/UOP
COPPER OXIDE PROCESS

2.1 Process Description

The process design evaluated for application to utility boilers contains four major processing areas which will be discussed in this section:

1) acceptance/regeneration,

2) SO_2 recovery and concentration.

3) SO_2 conversion, and

4) reducing gas production.

Figure 2-1 is a simplified process flow diagram for this process.

Acceptance/Regeneration

The unique design feature of the process is a set of specially designed, parallel passage, fixed-bed reactors which use a copper oxide on alumina acceptor for SO_2 removal. The reactor configuration was specifically designed by Shell to maintain good catalyst stability and minimize pressure drop. The reactor cross section is proportional to the gas flow while the depth of the reactor determines the removal capacity. The SFGD Process is also unique in that 90 percent removal of SO_2 is obtained irrespective of the SO_2 dilution. Because the process centers around fixed beds which of necessity must be regenerated, a swing mode of operation using multiple reactor vessels is employed.

The system operates at about 750°F in the acceptance and regeneration steps. Flue gas is routed from a hot electrostatic precipitator through the Shell/UOP system before going to the air preheater. The acceptance reaction depicted in Equation 2-1 and the regeneration reactions in Equations 2-2 and 2-3 are exothermic. Since the acceptance and regeneration occur in the same temperature range, there is no energy lost in heating or cooling the beds. The power plant will, in fact, realize an energy gain of about 65 MM Btu/hr by partially recovering the combustion value of the hydrogen reducing gas. The pressure drop of about 9 inches of water across the acceptor vessel (PO-109) is overcome by a flue gas blower. Heat is recovered from the clean gas in an air preheater before release to the atmosphere.

An open bypass between the inlet to the air preheater and the blower intake is designed to allow about 5 percent recycle of clean flue gas. This serves to protect the boilers from pressure surges. The pressure surges are a result of the changes in reactor flow configuration as acceptor vessels are valved on and off the flue gas stream. Increased recycle of gas allows very high turndown of the boiler without effecting the Shell/UOP system.

When the majority of the copper in an acceptor has been converted to copper sulfate and SO_2 breakthrough begins to occur, the acceptor vessel is valved off the flue gas stream and purged in preparation for sorbent regeneration. The spent sorbent is regenerated by passing a diluted reducing gas hydrogen through the vessel. SO_2 is re-evolved according to Equation 2-2.

$$CuSO_4 + 2H_2 \rightarrow Cu + SO_2 + 2H_2O \qquad (2\text{-}2)$$

Additional hydrogen is consumed by the following side reactions. First, any CuO which was unused during SO_2 adsorption is reduced back to copper by Reaction 2-3.

$$CuO + H_2 \rightarrow Cu + H_2O \qquad (2\text{-}3)$$

Also, another reaction can occur forming copper sulfide by Equation 2-4, but improved acceptor material has almost eliminated this problem.

$$2CuSO_4 + 6H_2 \rightarrow Cu_2S + SO_2 + 6H_2O \qquad (2\text{-}4)$$

After regeneration the acceptor is again purged and returned to flue gas service where any copper sulfide is re-oxidized to copper sulfate by oxygen in the flue gas.

$$CU_2S + \tfrac{5}{2}O_2 \rightarrow CuSO_4 + CuO \qquad (2\text{-}5)$$

Oxygen in the flue gas also oxidizes the copper back to copper oxide at the beginning of the acceptance cycle so that it is once again ready to pick up SO_2. In general, cycle times are about 40 to 80 minutes but this depends on boiler load, SO_2 concentration in the flue gas, extent of desulfurization, and height of acceptor bed.

SO_2 Recovery and Concentration

There exist several means of concentrating and preparing the SO_2-rich regeneration gases for further processing which will put the sulfur values in a useful form. Water absorption/stripping, solvent absorption, compression and condensation of water vapor, and complete liquefaction are all possibilities. Due to the lack of detailed information on these various types of systems from UOP, Radian was forced to utilize other sources. However, these sources contributed information only on the use of water absorption/stripping which is an alternative UOP proposed in the early 1970's because of its simplicity. Now it is used only when extremely low cost steam is available. Radian's flow sheet, therefore, should not be interpreted as the only system UOP can use, rather it is simply one alternative. Radian's calculations have shown it to have limitations, both from a technical and an economic standpoint. A description of the water absorption/stripping system follows.

Offgas from regeneration is sent to the SO_2 concentrator section of the process. The hot gases are initially cooled to 350°F in a waste heat boiler, before being further cooled to 150°F in a quench tower by a recirculating water spray. SO_2 in the cool gas (about 10 percent) is collected by water absorption in a packed column. SO_2-rich water from the absorber is stripped in another packed column with a steam reboiler to produce a concentrated SO_2 stream. The lean water product is recycled to the quench tower and absorber. Off-gases from the absorber, consisting mainly of inerts such as CO_2 and N_2 which were introduced with the reducing gas, are vented to the boilers where the fuel value of excess or bypassed reducing gas can be recovered.

The absorber and stripper together serve as a damping element, smoothing the flow of SO_2 to the sulfur production section somewhat. The rich water storage tank between the absorber and stripper also can function as surge capacity to prevent load fluctuations from overloading the later processing steps. Proper operation of the SO_2 conversion step, and Claus sulfur recovery unit if used, requires a stable feed gas flow and composition, which is not consistent with the cyclic nature of the swing reactor mode and expected variations in flue gas SO_2 content.

SO_2 Conversion

The SO_2 conversion section, like the SO_2 recovery and concentration section presents several options. The concentrated SO_2 stream can be processed by Allied Chemical, RESOX, or BAMAG process technology, or a variation on one of these to produce sulfur which is often selected as the product of choice. However, sulfuric acid or liquid SO_2 are options which appear, in general, to be more economical in terms of use of energy and reducing media and also to be more proven technically.

Because of the preference in many cases for an elemental sulfur product, previous designs by UOP have incorporated a catalytic SO_2 reduction reactor followed by a two stage Claus unit. This is the system presented in the flow sheet used as Radian's evaluation basis. The concentrated SO_2 stream (90 percent SO_2) from the stripper is mixed with hot reducing gas and passed through a catalytic reduction reactor at about 650°F where part of the SO_2 is reduced to sulfur and part to H_2S. A quench oil system is used to cool the reactor and transfer part of the heat of reaction to steam in a waste heat boiler. Sulfur is condensed from the gas which then enters a two-stage Claus plant where H_2S and some remaining SO_2 react to form more sulfur. About 85 percent conversion of the H_2S is obtained in the Claus plant and the Claus offgas is incinerated to prevent H_2S emissions and recycled to the acceptor vessel to recover the sulfur dioxide in the tail gas.

This arrangement is very similar to that used by Allied Chemical except that UOP employs hydrogen reducing gas while Allied employs methane as the reductant. Shell has also developed a thermal reduction reactor to replace the catalytic reactor. It is able to utilize unshifted H_2/CO reducing gas. Although sufficient information for a thorough analysis was not made available, about the same total amount of reducing gas is consumed.

In addition, either the RESOX Process using coal (under development by Foster Wheeler) or the BAMAG Process using H_2/CO (developed in Germany) could be adapted to the Shell/UOP Process to produce sulfur once they have been proven. The concentrated SO_2 stream would also be amenable to conversion of SO_2 to sulfuric acid or liquid SO_2. These options are discussed further in Section 14 of the report as they relate to the processes which can supply a concentrated SO_2 stream.

Hydrogen Production

Hydrogen production options are covered in Section 13 of this volume but it should be noted here that UOP has generally proposed steam-methane or steam-naphtha reforming as a means of supplying needed reducing gas. These systems provide fairly high concentrations of H_2 compared to air-blown coal gasification which produces a gas highly diluted by nitrogen. However, the concentrated hydrogen supply suggested by UOP is diluted in the regeneration step to a level just about equal to usual, shifted, coal gasifier product. The effects on the system of operation with this dilute, coal produced, reducing gas are discussed under material and energy balances.

2.2 Environmental Considerations

Shell has demonstrated the system's ability to control NO_x and SO_2 simultaneously in a commercial-scale installation at the SYS (Showa Yokkaichi Sekiyu) Refinery in Japan. During a two week test they were able to remove 60 to 70 percent of the flue gas NO_x by adding 100 to 150 percent of stoichiometric NH_3 which reduces the NO over the copper oxide on alumina adsorbent via Equation 2-6. Current operation at SYS achieves 40 percent reduction of NO by adding 80 percent of stoichiometric ammonia.

$$3NO + 2NH_3 \rightarrow \frac{5}{2}N_2 + 3H_2O \qquad (2\text{-}6)$$

Ammonia carryover in the flue gas was reported as 2 ppm maximum (SP-056) but there is some potential for fouling of gas heat exchangers downstream even at this low level. Shell has recommended designing for 75 percent removal.

It is not clear how only 2 ppm NH_3 escapes to the atmosphere when 150 percent of stoichiometric NH_3 is added to obtain 70 percent removal of NO_x. These values are based on data from the Japan SYS installation although no theoretical explanation has yet been verified. Other Japanese pilot units employing catalytic reduction of NO with NH_3 and which operate at 300°C versus the Shell system's 400°C, have required NH_3 decomposition catalysts after the NO_x reduction catalyst to reduce ammonia emissions to tolerable levels. One possibility is that the acceptor material in the Shell/UOP Process catalyzes both NO_x reduction and the reaction of ammonia with various oxidizing agents present such as oxygen, SO_2 and SO_3.

The acceptor cross-section is simply increased to handle larger design gas flow rates. UOP has guaranteed 90 percent SO_2 removal on the systems they design and build, but they report that increased reactor bed depth does not necessarily improve the percent removal of SO_2 although it does increase the capacity of the reactor to hold SO_2 without breakthrough.

Water is produced by the regeneration reactions and is also added to the system at various points, resulting in a fairly large quantity of excess water which is taken out by a quench in the case of a gas holder or from the stripper bottoms in the case of a water gathering system. UOP has proposed using this water as boiler feed water. Depending on the water management scheme of the power plant this should be feasible although the water will contain 30 to 50 ppm of dissolved SO_2. The amount of this water depends on the type of hydrogen supply. With steam-naphtha reforming a large amount of steam is used, so in this case, a 500 Mw plant might produce 185 gpm of this water. On the other hand, with hydrogen from coal gasification, nitrogen is a major constituent and only 120 gpm of water must be handled.

2.3 Material and Energy Balances

The performance of heat and material balance calculations on a process flow scheme based on information obtained from sources other than UOP enabled Radian to make independent estimates of raw material and utility requirements (Table 2-1). In addition, information about waste streams, equipment sizes and potential design problems can be obtained since process material and energy balances are at the center of any chemical process design. The balances performed for the Shell/UOP Process, however, were somewhat handicapped by inadvertent delays in transmission of information from the vendor.

TABLE 2-1

RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE SHELL/UOP PROCESS

Basis: 500 MW, 3.5 percent sulfur coal, water gathering system,
reducing gas from coal gasification

Processing Area	Electrical Power (Mw)	Steam (MM Btu/hr)	Ammonia (lb/hr)	#2 Fuel Oil (MM Btu/hr)	Reducing Gas (MM Btu/hr)
Acceptance/ Regeneration	5.0	10	2110	-	155
SO_2 Concentration	1.3	218	-	-	-
SO_2 Conversion	-	-	-	-	115
Reducing Gas Production	-	-	-	50	-
TOTALS	6.3	228	2110	50	270

The material and energy balances which were performed based on use of a water gathering system highlighted three major points:

1) The large quantities of water circulated through the absorber and stripper columns,
2) the large energy requirement for steam to heat the stripper reboiler, and
3) the large amount of energy consumed as H_2 reducing gas.

Some of the energy value of the reducing gas, however, is recoverable due to the exothermic nature of the reactions in this system. Balances were performed for two cases - hydrogen production by steam-naphtha reforming and by air-blown coal gasification. The reforming scheme produces a stream of about 55 percent by volume H_2 (wet basis) while the gasifier produces a stream of about 20 percent by volume H_2. The rough energy comsumption figures for both cases are given in Table 2-2 and 2-3.

Both cases are very energy intensive but the dilute hydrogen case is extremely so. The large energy requirement is mainly a result of the low concentration of SO_2 in the rich water and, consequently, the large quantities of water which must be handled. The large volumes of inerts in the regeneration gas product reduce the partial pressure of SO_2 in the gas and limit the maximum concentration of SO_2 in water to about 1 lb SO_2/100 lb water, half of what is obtainable using naphtha as a source of hydrogen. Because of the smaller amount of SO_2 in the rich water, twice as much water must be circulated through the absorber and stripper, which doubles the energy required for

TABLE 2-2

ENERGY CONSUMPTION - CASE 1*

Electric power	- Flue gas blowers	5	Mw
	- Fans for air coolers	0.7	Mw
	Total Power	5.7	Mw
Steam	- Stripper reboiler	95.0	MM Btu/hr
	- Used in regeneration	57.5	MM Btu/hr
	Total steam	152.5	MM Btu/hr
Energy Credit	- Heat recovered in air preheater due to exothermic reactions	65	MM Btu/hr

NOTE: Based on catalytic reduction of H_2 with SO_2 to H_2S.

* Case 1 - 500 Mw plant, 3.5% S, reducing gas 54% H_2.

TABLE 2-3

ENERGY CONSUMPTION - CASE 2*

Electric power	- Flue gas blowers	5 Mw
	- Fans for air coolers	1.3 Mw
	Total power	6.3 Mw
Steam	- Stripper reboiler	218 MM Btu/hr
	- Used in regeneration	10 MM Btu/hr
	Total steam	228 MM Btu/hr
Fuel Oil (#2)	- Heating reducing gas to shift temperature	50 MM Btu/hr
Heat Credit	- Energy recovered in air preheater due to exthermic reactions	65 MM Btu/hr

NOTE: (1) Based on catalytic reduction of SO_2 with H_2 to H_2S.
(2) Heating value of reducing gas consumed - 270 MM Btu/hr.

* Case 2 - 500 Mw plant, 3.5% S, reducing gas 20% H_2.

stripping. Over 5000 gpm of water must be stripped for the 500 Mw case with coal gasifier hydrogen supply. The magnified flows of inert gas and water also imply substantial increases in the size of the absorber and stripper and their auxiliaries. In addition, the use of a dilute reducing gas will require a considerable increase in the size of the Claus plant and catalytic reduction reactor if they are used.

2.4 Design Considerations

A major problem with the Shell/UOP Process is the difficulty of integrating the cyclic behavior of the fixed-bed adsorption scheme with the variable SO_2 load from the power plant and the relatively inflexible operation of the hydrogen production facility and the Claus plant, if used. The fixed-bed acceptors themselves are not affected by the variations in SO_2 loading but the problem arises rather in maintaining efficient control of a widely varying situation. Because unused copper oxide acceptor consumes H_2 during regeneration and because H_2 consumption is such an important part of operating costs, a utility will be very interested in an acceptor control mode based on SO_2 breakthrough rather than the simple time cycle used by SYS in Japan. A detailed design study of the cycle length and the number and size of acceptor vessels could lead to a configuration which would reduce fluctuations in regeneration gas flows both from the hydrogen plant and to the Claus plant.

The capability of the H_2 plant to respond to frequently varying loads will be an important point, along with its economic viability and raw material supply, in deciding what type of hydrogen production facility to use. Claus plants and other sulfur producers are rather inflexible at present. If the sulfur production plant could be modified to adapt to variable loads, system operation could possibly be improved by the elimination of the water gathering system which would result in a large savings of energy. It might also be possible to produce sulfur from SO_2 using less expensive or more readily available reductants. Acid plants are more amenable to variable feeds but good temperature control is still essential.

The long-term reliability of the process will depend on the ability of the large flue gas valves and adsorbent beds to withstand erosion or blocking by fly ash. These large valves or dampers seal off the acceptor vessels from flue gas during regeneration. The valves used on the commercial scale test unit in Japan were of a unique design manufactured in Germany, previously tested at Shell's Pernis refinery for their ability to withstand frequent cycling. However, neither the Pernis tests or subsequent operation at SYS involved high fly ash environments, although similar valves have been used satisfactorily in high dust applications (SL-062). Of course, if an electrostatic precipitator is placed upstream of the adsorption unit the dust levels should be down around the level of 0.1 grain/scf, similar to that found at the SYS installation. Currently, further testing is underway at Tampa Electric's Big Bend unit with a 0.6 Mw acceptor vessel to further evaluate these factors. The Tampa valves have sustained operation through 10,000 cycles with no significant maintenance.

One design area to be given further consideration is the water gathering system sometimes used to concentrate the SO_2 stream. This system is rather inefficient and very costly in terms of energy. The idea of running the dilute SO_2 stream directly to the SO_2 conversion steps to conserve energy has already been discussed. The feasibility of this at the present time is somewhat doubtful. There is, however, an alternative method of concentrating the SO_2 which possibly has an advantage over the water gathering system in terms of equipment size and energy requirements.

The SO_2-rich stream from regeneration could be cooled to condense out most of the water, dried with silica gel or molecular sieves, and compressed and cooled to condense SO_2. The additional energy used to condense and separate liquid SO_2 is about one-fifth that which must be added in the stripping system. Also, storage of liquid SO_2 is much more convenient than storage of dilute SO_2 in water; therefore, decoupling of adsorption and sulfur production could be complete. Liquid SO_2 is a valuable product in some areas. This alternative is more attractive for a system using a reducing gas with a high hydrogen concentration but probably has advantages over absorption/stripping in all cases.

Reductions in the amount of inlet SO_2 to the Shell FGD system will cause the utilization efficiency of the acceptors to decline. Gas velocity considerations prevent much reduction in acceptor size for low sulfur applications. In general, low sulfur applications will result in longer cycle times, a lower acceptor SO_2 loading at the end of the cycle, and a larger ratio of reactors in the acceptor mode to the regenerator mode. Overall system costs should decrease, however, since the smaller amount of SO_2 will require smaller downstream equipment and less reducing gas and utilities for processing.

Turndown evaluation is difficult on a process such as Shell where the flow criteria for acceptable reactor performance cannot be openly discussed. The information at hand indicates a minimum allowable flow through an acceptor of 60 to 70 percent of the design flow. This means that lower turndown will depend on reducing the number of reactors in the acceptance mode or increasing flue gas recycle. Because of the by-pass, boiler turndown can be almost complete without affecting the Shell/UOP system if recycle is used to maintain the flow and the cycle time were simply extended. If two active acceptors were necessary for design rates, then a minimum flow of 30 percent could be handled by taking one acceptor out of service. Currently, there is a size limitation on the acceptors, due to the upper size limits of commercially proven flue gas dampers and gas blowers. Blowers presently available can manage the gas flow from about 100 to 125 Mw. Eight-foot diameter valves have been in industrial use, and based on comparison with the SYS unit in Japan, an eight-foot valve should also be adequate for a 100 to 125 Mw capacity acceptor. Therefore, the minimum number of reactors for a 500 Mw plant might be six, four in acceptance mode and two regenerating at any one time under full load, but the number of acceptors depends on the SO_2 concentration and degree of desulfurization required. In order to smooth out the gas flows from the system to minimize H_2 consumption and adverse effects on later parts of the process, it might be possible to go to a larger number of acceptors. The economic and technical justification of this is uncertain.

One potential advantage of the Shell/UOP Process is in the area of heat recovery. In general, the lower limit on stack gas temperatures is set by the SO_3 dewpoint corrosion problem and the need to maintain plume bouyancy for good dispersion. The almost complete removal of SO_3 by the copper oxide acceptor could make it possible to recover extra heat from the flue gas leaving the acceptor without encountering the SO_3 dewpoint. UOP estimates additional heat recovery equivalent to 1.5-2.5 percent of fuel input by reducing stack temperatures from 70°F to about 200°F (PO-109).

2.5 Status of Development

Shell has gone through several phases of testing but a completely integrated unit applied to a coal-fired utility boiler has yet to be built. Extensive bench-scale testing to determine a suitable metal oxide acceptor, to select a reactor configuration, and to collect mass transfer data preceded the installation of a 400 to 600 scfm pilot unit at Shell's Pernis Refinery. The Pernis unit accumulated 20,000 hours of operating time during which various types of copper on alumina acceptors, regeneration agents, and reactor internal construction materials were examined. The flue gas used for the tests came from a high sulfur, heavy oil-fired heater. The stability of the acceptor when subjected to a flue gas environment was verified and the proposed reactor configuration was demonstrated to be successful.

Information from Pernis was used to scale up and build a commercial-scale unit which went onstream in mid 1973 at the SYS refinery in Japan. The unit there consists of two acceptors operating on flue gas from an oil-fired boiler equivalent to about 40 Mw of electric generating capacity (75,000 scfm). Only the acceptors and water gathering system were installed and tested because of refinery hydrogen and excess Claus plant capacity were available. The longest period of continuous operation has been about 2 months. The fairly successful SYS installation confirmed Shell's computer design methods for the reactor and their ability to scale up the system. Demonstration of both the viability of automatic sequencing controls and the large flue gas valves was an additional result.

The next step in Shell's development program was the testing of a reactor using coal-fired flue gas without particulate removal. This experiment took place at a Dutch utility station. The resistance of the reactor configuration to fouling by dust was examined and information was generated on erosion/corrosion tendencies of various materials of construction.

At present, actual operation of the acceptance and regeneration steps in a coal-fired flue gas environment is being tested on a 0.6 Mw unit at Tampa Electric's Big Bend Station. Results to date indicate no increase in pressure drop over time and stable catalyst activity. Dust loadings of 0.5 to 0.8 grain/scf have been experienced without noticeable effect on the acceptors. The other parts of the system, SO_2 concentration and sulfur production, are considered to be standard technology.

The availability of design information is good but more confidence could be placed in the system's overall reliability for utility applications if a fully integrated system were in operation. A fully integrated system in a utility application could answer the troubling question of process operability under varying loads.

2.6 Scale-Up Problems

Design of the acceptor vessels is somewhat complex, but computer programs based on a mathematical model of the diffusion and reaction mechanisms are available which can optimize reactor configuration. Design data for use in these programs was developed on bench-scale and pilot-scale units in the Netherlands and confirmed by successful design and operation of the SYS commercial-scale unit. Mechanical factors such as flow patterns are said to be readily scaled up.

The question of design information of the SO_2 catalytic reduction reactor is not addressed directly by any available literature but the information from design of the Shell Claus Off-gas Treating Process (SCOT) should be applicable as operations are similar. The SCOT Process uses a cobalt-molybdenum catalyst to reduce SO_2 in Claus offgas back to H_2S so it can be recovered in an amine absorption unit (NA-226). Design data for thermal reduction of SO_2 was not made available to Radian but is available from Shell or UOP.

As noted earlier, the Shell/UOP Process has been able to remove 60 to 70 percent of flue gas NO_x with only minor changes, essentially provision of a means of injecting ammonia into the flue gas. Radian was unable to ascertain the quality or quantity of design data for the ammonia addition.

2.7 Utility Applicability

The only physical drawback hindering new plant applications of the Shell process is the need for a hot electrostatic precipitator to meet the inlet dust loading criterion of 0.1 grain/scf currently placed on the flue gas by UOP. Test work at Tampa should indicate whether this criterion is really necessary. The cost differential between hot and cold ESP's is in the range of $2-$10/kw, (SC-341) which, when compared to a probable total capital cost for an FGD system in the range of $100/kw, is important but not critical.

Two factors may limit the Shell/UOP FGD system's usefulness in retrofit applications. Space requirements are fairly large because of the need for multiple vessels, some of which are out of use at any time. Flue gas in the Shell adsorbers has a superficial velocity of about 25 feet per second, but velocity in the gas channels is around 40 feet per second. Also, because of the dust criterion, flue gas will have to be taken after the cold ESP in an old plant at about 300°F and reheated to the acceptor operating temperature of 750°F. A large part of the heat can be recovered by heat exchange between the cold, dirty gas and hot, clean gas, but at least 60°F and possibly as much as 150°F of net reheat could be necessary. However, additional fuel should not be required except for start-up since the exothermic nature of the reactions in the adsorber will result in an increase in flue gas temperature across the reactor. It is conceivable that even in some new plant situations, it might be cheaper to use a cold ESP and reheat the gas to FGD system temperature rather than use a hot ESP, but it will depend on the capital cost differential of the precipitators and the heat exchangers. If the acceptor can demonstrate a capability to withstand high dust loadings, it may also be possible to put a cold precipitator after the Shell/UOP system.

The NO_x capability of the system is an extremely valuable asset but its usefulness is somewhat impaired by the problem of ammonia availability and cost. Current prices have dropped to about $200/ton but fluctuations have been large and swift. The operating costs presented in the next section are based on a price of $270/ton which was prevalent in the recent past and probably will return again due to natural gas shortages.

2.8 Economic Assessment

The Shell/UOP Process' high consumption of reducing gas and fuel is a strong liability and provides motivation to smooth out cycles, eliminate the energy intensive water gathering system, and produce sulfuric acid or liquid SO_2 instead of the more reduced form, elemental sulfur.

The utility and raw material requirements of the Shell/UOP Process, as estimated by Radian for the Figure 2-1 flow sheet, are given in Table 2-4. The energy consumption breakdown was summarized earlier in Tables 2-2 and 2-3. Major cost items will be capital charges, maintenance, ammonia, hydrogen reducing gas, electric power, and steam. Substitution of a thermal for a catalytic reduction reactor will not reduce reductant requirements but unshifted H_2/CO can be used and materials of construction problems are supposed to be lessened by this change. Table 2-5 is a summary of utility requirements provided by UOP for a plant similar to Radian's base case 500 Mw unit but with a compressor/gas holder concentration section. Radian was not provided with sufficient information to verify these figures and simply reports them for comparison.

Capital costs reported by Shell/UOP indicated that (excluding H_2 production) the acceptor vessels and ducting represent about 2/3 and the SO_2 gathering and conversion section about 1/3 of the total cost. Of course, the capital costs vary widely depending on the situation. A small unit treating very high sulfur flue gas may cost much more per kilowatt than a large unit treating flue gas with a moderate amount of SO_2.

TABLE 2-4

UTILITY AND RAW MATERIAL REQUIREMENTS FOR SHELL/UOP PROCESS

Basis: 500 Mw; 3.5 percent sulfur coal; 5.260 hours per year at full load

	Quantity	Unit Price	Annual Cost
Shell/UOP FGD System:			
Ammonia	2,110 lb/hr	\$270/ton	\$1,498,300
Hydrogen	2,050 moles H_2/hr	4.00/MM Btu	5,701,350
Electric Power	5,725 kw	.02/kwhr	602,170
Steam Consumption (L.P.)	177,400 lb/hr	.50/Mlb	466,400
Production (L.P.)	44,670 lb/hr	.50/Mlb	-(117,450)
Acceptor Replacement Allowance	-	-	1,250,000
			\$9,400,770

Unit Utility and Raw Material Cost - 3.6 mills/kwhr

Coal Gasification Hydrogen Supply Case - Additional Requirements:			
Electric Power	600 kw	\$ .02/kwhr	\$ 63,120
Steam Consumption	87,700 lb/hr	.50/Mlb	230,650
Production	32,100 lb/hr	.50/Mlb	-(84,400)
#2 Fuel Oil	50 MM Btu/hr	2.50/MM Btu	657,500
			\$ 866,870

Corrected Unit Utility and Raw Material Costs - 4.0 mills/kwhr

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Note: Based on catalytic reduction of SO_2 with H_2 to H_2S and 60 percent load factor.

TABLE 2-5

UTILITY AND RAW MATERIAL REQUIREMENTS FOR 500 Mw, 3.5% S*

Ammonia	2,110 lb/hr	$270/ton	$1,498,300
Hydrogen	2,070 lb mole/hr	$4.00/MM Btu	5,756,970
Electric Power	7,200 kw	.02/kwhr	757,440
Steam Consumption (L.P.)	83,000 lb/hr	.50/Mlb	218,290
Production (L.P.)	75,230	.50/Mlb	-(197,850)
Acceptor Replacement Allowance	-	-	1,250,000
			$9,283,150

Unit Utility and Raw Material Cost - 3.5 mills/kwhr

Excluding NO_x Reduction - 3.0 mills/kwhr $7,784,850

*Information provided by UOP for a Shell/UOP system with compressor/gas holder section.

The acceptor section expense is a function of the flue gas volume to be treated and the regeneration and SO_2 conversion section expense is a function of the amount of SO_2 recovered and the type of reducing gas supply. Because the capital costs of the FGD systems are large, the effect of changing the load factor on total annualized cost in mills/kwhr is large. Raising the load factor from 60 to 80 percent decreases the cost by about 1 mill/ kwhr.

Fans and blowers use about 1.2 percent of the power plant rating. Energy requirements in the hydrogen from naphtha reforming case are 3.4 percent of the total power plant heat rate. The corresponding figure for the hydrogen from coal gasification case is 6.2 percent. These figures do not actually represent the amount of derating of the power plant. They simply compare the energy consumed by the FGD system to the total heat rate of the boiler. However, additional heat recovery is possible due to the suppression of the acid dew point and the heat released during acceptance.

Hydrogen or other reducing agent consumed is the most important operating expense for the Shell/UOP Process. Stoichiometric hydrogen consumption would be 4 moles H_2/mole SO_2 including catalytic reduction of SO_2 but because of the factors enumerated below, the actual consumption figures will be around 5.5 to 6.2 moles H_2/mole SO_2.

1) Unreacted CuO in acceptor being reduced to Cu,

2) Side reaction to form Cu_2S discussed earlier,

3) Some excess hydrogen used in the regeneration of the copper and the reduction of SO_2 to H_2S (about 10 percent), and

4) Bypassing of H_2 around the acceptors to the concentrating section when purging and flue gas valve switching is taking place.

This large excess of valuable hydrogen is only partly offset by recovering its fuel value in the boiler. The reducing gas used by a 500 Mw plant at full load has an equivalent heating value of around 270 MM Btu/hr. About a third of this gas is not consumed by reactions in the process and is used only as fuel. The primary areas of hydrogen wastage are: (1) incomplete acceptor loading and (2) bypassing during purging and switching so the change in reduction methods will have little real effect on hydrogen efficiency.

Hydrogen quality is an important question. UOP prefers hydrogen which is low in carbon monoxide, although the original Shell research indicated CO and H_2 were almost equivalent as reducing agents. The CO tends to cause increased formation of Cu_2S which results in higher total reducing gas consumption. Hydrocarbons of higher molecular weight than methane leave coke deposits on the catalyst during regeneration, which burn off when flue gas flow is started. The temperature peaks from the coke burnoff cause thermal stresses in the adsorbent which shorten its life. Hydrogen sulfide is also undesirable as it reduces the effective life of the copper on alumina catalyst. Catalyst life under optimum conditions has been estimated at 2 years.

2.9 Process Summary

The Shell/UOP Copper Oxide Adsorption Process is based on a dry copper oxide acceptor which picks up SO_2 from hot flue gas passing over it by reacting with it to form copper sulfate. The fixed-bed acceptor is regenerated by treatment with hydrogen-rich reducing gas. The SO_2 which is re-evolved can be processed through a water gathering system, reduction reactor, and Claus plant to make sulfur. The process' primary difficulties lie in its high operating costs and the problem of integrating a swing mode adsorption/regeneration system between a varying source of SO_2 and a continuous SO_2 processing train. The acceptance/regeneration scheme has been demonstrated on a commercial scale, but only in an oil-fired application with a fairly constant SO_2 load. A fully integrated system has yet to be proven on any scale. The system has potential and has been partially demonstrated on a commercial scale. However, as a process strictly for SO_2 removal it does not look too promising economically. Its basic economic advantage is its ability to reduce NO_x emissions by 60 to 70% with only a moderate increase in operating expense of about 0.6 mills/kwhr.

3.0 BERGBAU-FORSCHUNG/FOSTER WHEELER DRY ADSORPTION PROCESS

Flue gas SO_2 is adsorbed in a moving bed of char to form H_2SO_4 in the Bergbau-Forschung/Foster Wheeler (BF/FW) system. Saturated char is then heated to yield gaseous SO_2 and regenerated char. The SO_2 stream is then reduced in the presence of anthracite coal to elemental sulfur. The adsorption and regeneration steps were developed by Bergbau-Forschung in Germany while the reduction step is proprietary technology of Foster Wheeler.

3.1 Process Description

The BF/FW dry adsorption system is comprised of three major processing steps for application as a flue gas cleanup system for utility boilers. These steps are:

(1) adsorption of SO_2 on char,

(2) regeneration of the char, producing SO_2-rich off-gas, and

(3) reduction of SO_2 to elemental sulfur.

A process flow diagram of the equipment and flows in these processing areas is presented in Figure 3-1.

Gas Cleaning

Flue gas from the boiler area passes through dust collection equipment (i.e., cyclones, electrostatic precipitator, bag house) where the bulk of the particulate matter is removed. The gas enters the adsorbers at temperatures between

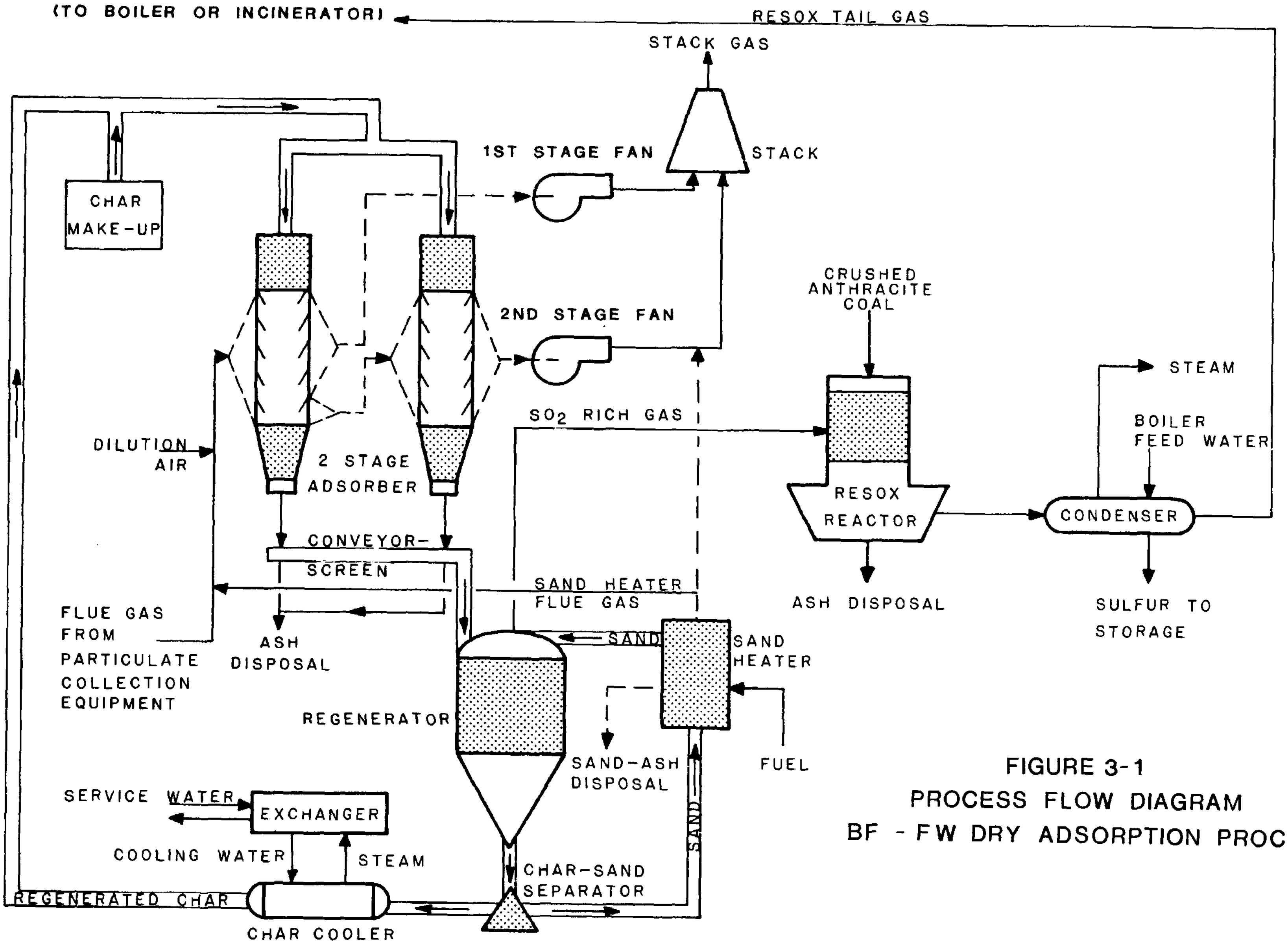


FIGURE 3-1
PROCESS FLOW DIAGRAM
BF - FW DRY ADSORPTION PROCESS

250°F and 300°F. Dilution air is added to cool the flue gas to the operating temperature of the adsorber, if needed.

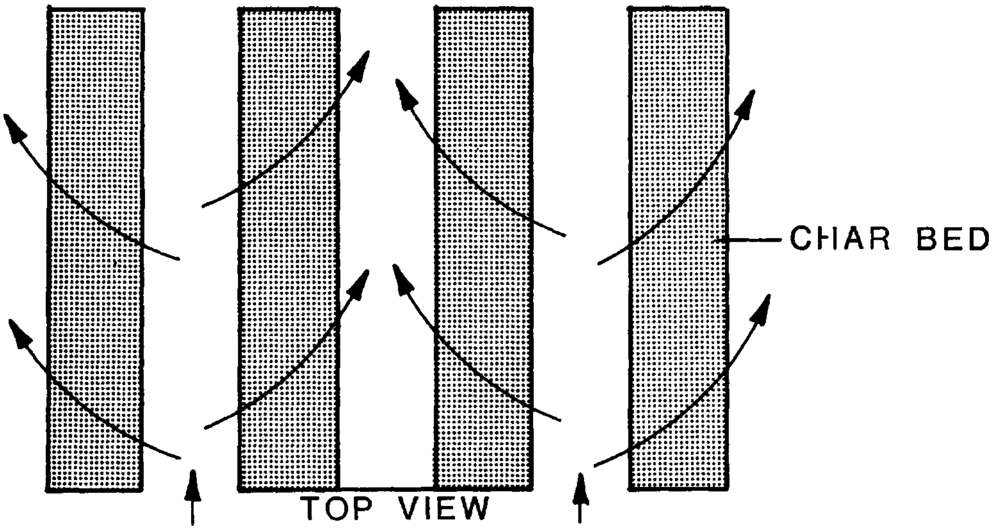
In the adsorbers, flue gas passes horizontally in cross-flow through a vertical bed of activated char which moves downward in plug flow (Figure 3-2). The approach velocity of the gas is about one foot per second while the char travels downward at one to three feet per hour. The char pellets are approximately 3/8 inch in diameter by 3/8 to 5/8 inch long.

As a result of the high sulfur coal and the SO_2 removal required, a two-stage adsorber is employed for the Radian base case. All of the flue gas passes through the first stage adsorber. A gas baffle at the first stage outlet separates those gases that have passed through the upper 50 percent of the adsorber from those that have passed through the lower 50 percent. The gas from the top section is exhausted directly by the first stage adsorber fans. The gas from the bottom section passes through a smaller second stage adsorber similar in design and operation to the first stage. This gas is then exhausted by the second stage adsorber fans. The pressure drop for the gas passing through only the first stage is about 11 inches of water while the pressure drop for the gas passing through both stages is about 17 inches of water.

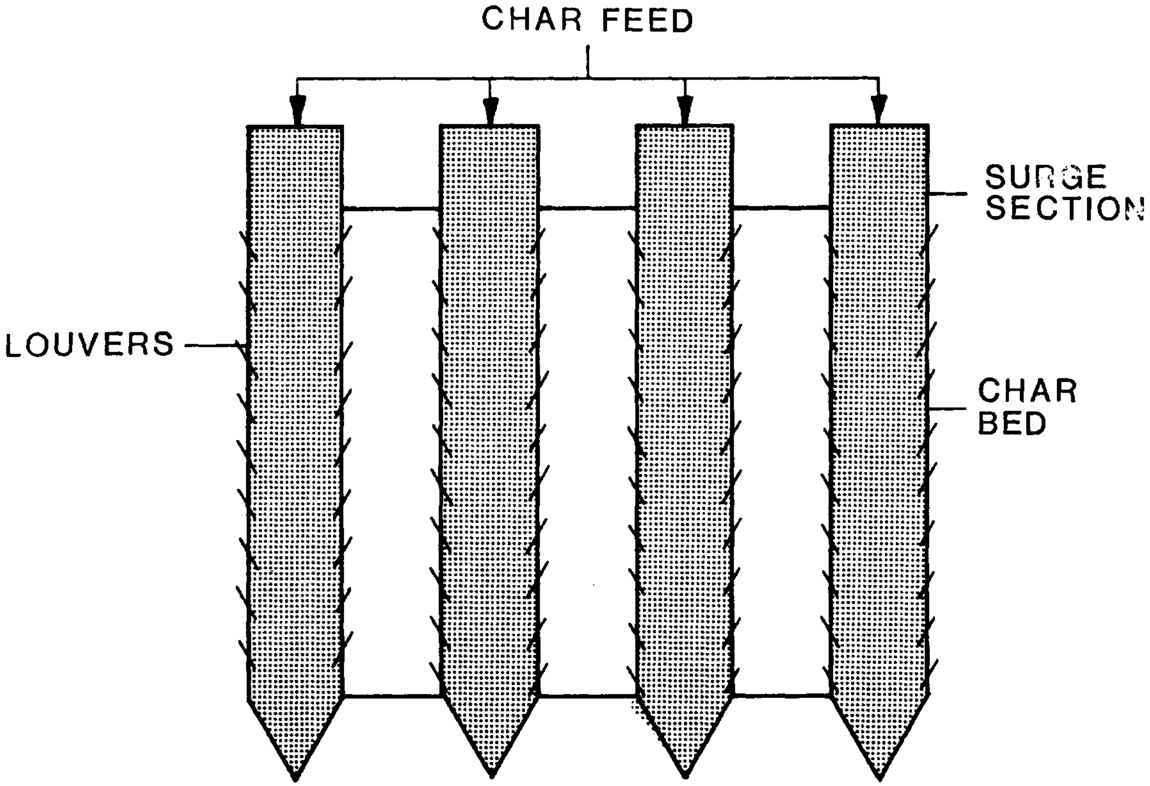
Sulfur dioxide (SO_2), sulfur trioxide (SO_3), oxygen, and water vapor are adsorbed on the char. The SO_2 in the presence of activated char reacts with O_2 to form SO_3 (Eq. 3-1) with the SO_3 subsequently reacting with H_2O vapor to form H_2SO_4 (Eq. 3-2) as shown below

$$SO_2(g) + \tfrac{1}{2}O_2(g) \xrightarrow{\text{char}} SO_3(g) \qquad (3\text{-}1)$$

$$SO_3(g) + H_2O(g) \xrightarrow{\text{char}} H_2SO_4(\ell) \qquad (3\text{-}2)$$



TOP VIEW
(ARROWS INDICATE GAS FLOW)



FRONT VIEW
(GAS FLOW PERPENDICULAR TO PLANE OF PAPER)

FIGURE 3-2
GAS FLOW IN BF/FW ADSORBER

Sulfuric acid is formed as a liquid in the pores and migrates into the interior pore system of the char pellets by capillary action. This frees pore volume near the surface of the char pellets for further gas adsorption. Almost all residual particulates are removed by entrainment and some nitrogen oxides by adsorption. Some adsorption of halogen and hydrocarbon gases may also occur but no specific data have been reported. Clean gas is vented to the stack at a temperature of 20°F to 30°F higher than the inlet temperature to the adsorber as a result of a net energy gain due primarily to the heat of reaction in the adsorber.

In the adsorber, the char flows downward within modular beds which have permanently fixed horizontal louvers arranged one above the other to form a wall of "venetian blinds" on the gas entrance and exit side of the bed. Each char bed is either four-feet or six-feet wide with a corresponding four-foot or six-foot gas passage between each bed.

The char is continuously recycled by conveyors from the regeneration section to the top of the adsorber. A conveyor distribution system at the top of the adsorber feeds the fresh char uniformly across the char bed. The char first passes through an unlouvered surge section above the adsorber and, then, moves downward in plug flow adsorbing pollutants as it travels. The char flow rate is controlled by vibro-magnetic feeders at the outlet of the adsorber. After exiting the adsorber bed, the loaded char is directed to a conveyor with a screen deck where the majority of the fly ash collected in the adsorber is separated from the char. After separation, char is transported by bucket elevator to a saturated char surge tank in the regeneration section.

Regeneration

The char, having been partially or completely saturated during the adsorption phase, must be regenerated for reuse. The char pellets are regenerated by raising their temperature to about 1200°F in an inert atmosphere. At this temperature and in the presence of carbon, the reverse of the adsorption reactions will occur, given sufficient residence time. The H_2SO_4 will concentrate, vaporize, and disassociate to H_2O and SO_3 (Eq. 3-3). The SO_3 will be reduced to SO_2 while the carbon is oxidized to CO_2 (Eq. 3-4).

$$H_2SO_4(\ell) \rightarrow H_2SO_4(g) \qquad (3\text{-}3a)$$

$$H_2SO_4(g) \xrightarrow{1200°F} H_2O(g) + SO_3(g) \qquad (3\text{-}3b)$$

$$2SO_3(g) + C(s) \xrightarrow{1200°F} CO_2(g) + 2SO_2(g) \qquad (3\text{-}4)$$

Likewise, any captured NO_x will probably be reduced to N_2. Halogen gases or hydrocarbons that might be adsorbed should also be liberated.

Physically the regeneration occurs in a vessel in which char at the flue gas temperature is mixed with hot sand at about 1500°F. The sand merely serves as an inert heat transfer medium. Movement of the char and sand through the regenerator is by gravity flow. The exiting char-sand mixture, at a temperature of about 1200°F, passes through a char-sand separator and feeder. The char pellets are sent to the char cooler. The sand and char fines are recycled to the sand heater. The regenerated char is quenched to a temperature of about 250°F and transported by bucket elevator to the adsorber. Steam generated in the char cooler exchanges heat with service water in a heat exchanger, is condensed, and recycled to the char cooler.

Make-up char to compensate for losses is combined with the regenerated char prior to being fed to the adsorber. Sand out of the regenerator is recycled by bucket elevator to a fluid bed sand heater where differential heat is added to bring the temperature of the sand to about 1500°F. Flue gas from the sand heater is either sent to the stack or the adsorber. A periodic bleed of sand-ash may be taken. The quantity depends on the amount of ash entering the sand loop as a result of ash carried by the char and combustion of fossil fuels in the sand heater.

The off-gas from the regenerator contains approximately 20 volume percent SO_2, 50-60 volume percent steam, a very small amount of N_2, and the remainder CO_2. This gas is fed to the RESOX unit for reduction of sulfur dioxide to elemental sulfur. The regenerator off-gas could also be fed to an Allied Chemical, Bamag, IFP, or other sulfur production unit as well as to an acid plant.

Reduction

The RESOX system is a proprietary process for the production of elemental sulfur from gaseous sulfur dioxide. Crushed anthracite coal moves slowly downward by gravity while the SO_2 stream from the regenerator moves upward in this countercurrent reactor. The overall reduction, which is synergistic in the presence of water, is:

$$C(s) + SO_2(g) \xrightarrow[H_2O(g)]{1100\text{-}1500°F} S(g) + CO_2(g) \qquad (3\text{-}5)$$

The maximum reaction temperatures range from about 1100-1500°F depending on the coal used and the composition of the gas fed. This maximum temperature occurs only in the zone of the coal bed near the gas inlet with the temperature decreasing as the gas flows up through the bed. Air or steam may be injected into the SO_2 gas stream to aid in control of this reaction temperature; air burns some of the coal while steam dilutes the reactants. The reactions occur at atmospheric pressure.

Ash and unreacted or unburned coal leave via the bottom of the reactor. They are cooled and discarded. About 90 percent of the inlet SO_2 is reduced to vapor phase elemental sulfur. Other gases going overhead from the RESOX unit are steam, unreacted SO_2, CO_2, and N_2. Small amounts of hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), perhaps some hydrogen (H_2), and, possibly some carbon monoxide (CO) would be present in the off-gas depending on process parameters. The RESOX product gas then passes to an inclined shell-and-tube condenser similar to those used in Claus sulfur-recovery units. Boiler feedwater is converted to steam on the shell side. The gaseous elemental sulfur condenses at about 320°F on the tube side. The molten sulfur is collected and can be stored in insulation tanks at about 270°F or sent to pits to solidify. A portion of the 50 psig steam generated on the shell side of the condenser can be used to heat trace molten sulfur lines and to maintain the temperature in the liquid sulfur tanks, if applicable. The remaining steam is available for other uses.

The condenser off-gas could contain unreacted SO_2, hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2) and, therefore, is not suitable for venting. This gas stream would be routed to an incinerator or to the boiler to oxidize the various sulfur compounds. The gas out of the incinerator would be combined with the flue gas. Thus, the resulting sulfur dioxide would be in the flue going to the adsorber.

3.2 Environmental Considerations

Although the Bergbau Forschung/Foster Wheeler Process was designed to remove SO_2 from flue gas, Radian's evaluation must include some consideration of the total environmental effect of the process in addition to the effectiveness of the process for removal of SO_2. The BF/FW Dry Adsorption Process has been reported to have some type of removal capability for SO_2, SO_3, particulates, and NO_x. It seems likely that some halogens and hydrocarbons may also be adsorbed by the char pellets.

The BF/FW Process was proven capable of removing up to 97 percent of the inlet SO_2 in pilot plant testing. However, FW reports that the process is not economically feasible above a 95 percent removal design for the inlet SO_2 concentrations specified in this study. A process advantage, however, is the relatively small impact resulting in an incremental change in the design basis from 90 percent to 95 percent SO_2 removal. Due to the modular design of the adsorber and since the kinetics of SO_2 adsorption on carbon are less than first order relative to SO_2 concentration (BA-254), the system can be designed to effect 95 percent SO_2 removal with only about a 10 percent increase in char throughput and a negligible increase in pressure drop relative to a system designed for 90 percent removal. The carbon loading (lb SO_2/lb carbon) would be decreased by approximately 4 percent, the dwell time of the carbon in the adsorber would be decreased by about 12 percent, and the gas residence time would remain the same.

The increase in char throughput is accomplished by the decrease in the dwell time of the char in the adsorber. A unique feature of this system is its capability to remove varying amounts of SO_2 by adjusting the char dwell time. The same increase in char throughput would result if the char dwell time for the 90 percent design were maintained and 10 percent more modules were added to the adsorber. The carbon loading would again be decreased by approximately 4 percent, but the flue gas residence time would be greater and the pressure drop would decrease for the 95 percent design since the gas would flow through a greater area of char bed.

As a consequence of increasing the design removal efficiency from 90 percent to 95 percent, char fed to regeneration would increase about 10 percent while adsorbed H_2SO_4 on the char to the regenerator and SO_2 to RESOX would increase approximately 5 to 6 percent. Solids handling equipment can be readily adapted to the increased load. The heat duty for the regenerator would be increased by roughly 9 percent due to the greater char throughput and the greater quantity of adsorbed H_2SO_4. The RESOX unit would then have to process the additional 5 to 6 percent SO_2 in the regenerator off-gas.

Treatment of the sand heater flue gas must be discussed separately. FW reports that EPA views the sand heater as a process heater that does not require SO_2 controls. However, some state regulations will require that the sand heater flue gas be routed through the adsorber to remove SO_2. Cycling this gas containing about 1,100 lb/hr of SO_2 through the BF/FW system will add about 5 percent to the total raw material and utility costs for the process. No technical or operational problems should result from this treatment of the gas.

Another environmental consideration of primary interest is the effect of the system on particulate emissions. In pilot plant testing by BF, adsorption of SO_2 was not affected by the presence of fly ash in the flue gas while the adsorber was found to be effective in reducing the dust content of the flue gas.

With a range of inlet loadings from 0.2 gr/scf to 1.3 gr/scf, the particulate removal efficiencies were 93 to 96 percent. Furthermore, capability for fine particulate matter removal was also demonstrated in one test, whereby the adsorber removed 67 percent of the fines when the inlet loading was 0.061 gr/scf.

As would be expected, increased grain loading produced a correspondingly greater pressure drop across the adsorber bed. However, by increasing the downward movement of the bed, the flow of char would also increase and carry away any buildup of fly ash. The pressure drop was thereby reported to be controllable within normal limits under the worst dust loading tested (1.3 gr/scf).

Improved particulate removal might be anticipated for proposed commercial units for the following reasons:

1) Char dwell time was 20 hours in the pilot plant while char in commercial units would serve as a filter media for roughly 30 hours. The longer dwell time means that more particulate matter will be deposited in the bed giving rise to a higher pressure drop.

2) The depth of the char bed in the test unit was 3.28 feet (one meter), whereas the depth in a commercial installation would be six feet. The result is nearly twice the thickness of char for the gas to contact in the first stage adsorber.

3) Finally, about 50 percent of the flue gas will pass through a second six-foot depth of char providing further cleaning.

The potential of the adsorber to act as the primary particulate control equipment in addition to SO_2 removal has not be adequately examined. FW states that if the system is offered primarily for SO_2 control, there is a limit up to which particulate loading will be accepted without affecting SO_2 removal performance. However, FW also reports that the system can be designed for particulate removal on flue gas out of a 90 to 95 percent efficient electrostatic precipitator. Trade-offs involving parameters such as increased char throughput, increased pressure drop, removal efficiency of the char, and placement of the electrostatic precipitator or perhaps even no precipitator must be evaluated. Using the adsorber to take over the loading of the electrostatic precipitator may not be technically or economically feasible but this possibility certainly warrants examination. More data will be available after operation of the units at Lunen and Scholz.

A third area of primary interest is the ability of the char pellets to simultaneously remove NO_x. The process vendor predicts anywhere from 40 to 75 percent removal of the NO_x entering the BF/FW Process. Although NO_x removal was not a primary concern, a 70 percent reduction of incoming NO_x was recorded at the Bergbau-Forschung pilot plant at Welheim, West Germany. It has been recently reported that tests conducted at the BF facility at Lunen, West Germany by an independent testing organization retained by the West German government indicated that NO_x was not removed from the flue gas. The lack of confirmation of results of the Welheim pilot plan data was not clearly understood. Discussions with the parties involved resulted in the following statements (SL-073).

1) NO_x removal does not occur at 250 to 300°F, but will take place at about 575°F. Bergbau is said to be able to support this with laboratory data.

2) The NO_x analytical technique in the BF pilot plant work at Welheim was not accurate.

3) NO_x is removed at temperatures below 175°F or with ammonia addition, above 575°F.

4) The pilot plant work by BF at Welheim was at a temperature below 175°F, at which level NO_x removal is attainable.

The evaluation of NO_x removal at the FW facility at Scholz was planned but data is not available. At this time, the potential of the BF/FW Process for NO_x removal has not been conclusively determined. Some definitive data on the NO_x removal question is desirable.

From Radian's experience in NO_x removal technology and analytical techniques, the basis for any reported NO_x removal must be carefully evaluated. The solubility of NO_x in H_2SO_4 is a function of the partial pressure of O_2, H_2O, and SO_2, acid concentration, temperature, and total pressure. Evaluation of the Welheim results was not attempted by Radian for the following several reasons. Determination of NO_x concentration in flue gas is not a routine analysis particularly in the presence of SO_2, CO, and H_2O. Problems with data reproducibility are not uncommon. Also, since the oxidation state of NO_x is difficult to determine, confirmation of any proposed mechanism is extremely difficult. Finally, since the purpose of the tests was to investigate SO_2 adsorption on BF char, corroboration of these results in tests emphasizing NO_x adsorption would be desirable.

Hydrocarbon adsorption is also predicted by Foster Wheeler. Any hydrocarbons captured are expected to burn off either during char regeneration or RESOX reduction. Hydrochloric acid (HCℓ) present in the flue gas might also be expected to adsorb in water on the char. Whether its volatility would result in its desorption in the adsorber or whether it would desorb in the regenerator is unknown. At the adsorber temperature of 250 to 300°F, the HCℓ in solution will probably desorb and be exhausted through the stack. At the BF Lunen facility, a 40 percent reduction in chlorides and fluorides is reported.

FW states that attrition of the char pellets in the adsorber to produce carbon fines that might be entrained in the cleaned gas to the stack should be negligible. Since the char flows at about two ft/hr, very little agitation occurs in the adsorber bed. Also, the louvers are designed to prevent char particles from departing with the flue gas. A recent report by A. J. Slack (SL-073) has indicated, however, that there was a significant concentration of carbon fines in the gas leaving the adsorber at Scholz, based on the color of the plume. This would be quite undesirable environmentally since the fines are loaded with sulfuric acid in the pores.

Response of the BF/FW Process to surges above the design SO_2 concentration by adjusting the char flow rate is very slow. A more rapid response results from increasing the dilution air to lower the flue gas temperature and increase the rate of adsorption of SO_2 on the char. Extreme care must be taken, however, not to cool the gas to the sulfuric acid dew point.

The by-products of the BF/FW Process, other than elemental sulfur, are relatively small quantities of coal ash. Fly ash streams from the adsorber (about 400 lb/hr) and the cyclone on the sand heater flue gas (about 1,000 lb/hr) should be compatible with boiler fly ash and could be sent to the utility ash disposal systems. A purge of sand and/or ash from the sand heater loop (about 800 lb/hr), if necessary, should also be compatible with boiler fly ash and could be treated as above. The final ash stream is the RESOX ash which contains significant quantities of unburned coal and, thus, might be sent to the boiler. If combustion is not desirable or practical, this ash could also be sent to the utility ash disposal system. A purge from the char cooler water loop might also be necessary if the water stream from the condenser is not completely evaporated in quenching the hot char since soluble salts could build up in water out of the char cooler.

3.3 Material and Energy Balances

The material and energy balances prepared by Radian for the 500 Mw base case are an integral part of this evaluation. These calculations provide a basis for an independent determination of energy and raw material requirements and the magnitude and nature of waste streams. Also, the approximate sizes of equipment for a commercial system and the degree and difficulty of scale-up of operating units were estimated.

Foster Wheeler supplied material and energy balances for a 650 Mw and a 500 Mw system. Each had a design basis that differed from the Radian base case. Foster Wheeler also provided operating costs, capital costs, plot requirements, byproducts produced, and raw material and energy requirements specifically for the 500 Mw Radian base case. This information also included data for a 95 percent SO_2-removal efficiency system.

The raw material and energy requirements resulting from Radian's calculations are presented in Table 3-1. These requirements are presented for the primary processing areas. Radian assumed that the sand heater flue gas was cycled to the adsorber for these calculations. If this gas is exhausted to

TABLE 3-1

RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE BF/FW PROCESS

Basis: 500 Mw; 3.5% (wt.) S coal

Process Section	Sand (lb/hr)	Char (lb/hr)	Coal (plant) (MM Btu/hr)	Coal (anthracite) (MM Btu/hr)	Boiler Feedwater* (M gal/hr)	Electric Power (Mw)
Adsorption	-	-	-	-	-	6.4
Regeneration	800	3,000	210	-	-	1.3
Reduction	-	-	-	160	3	0.1
TOTAL	800	3,000	210	160	3	7.8

* Recycled

the stack as in the FW basis, the raw material and utility requirements will be reduced about five percent.

Generally, Radian balances were in good agreement with those of Foster Wheeler. Any differences were all reconcilable by adjusting the bases for calculations.

3.4 Design Considerations

The key design features for each processing area will be discussed in this section. Possible alternative processing methods or sequences and the ability of the system to overcome potential problems will also be examined.

Adsorption

A system for dry adsorption of SO_2 must be based on and designed for an activated char or coke with certain characteristics. Bergbau-Forschung reports the development of a patented process for manufacture of char pellets that exhibit:

1) improved adsorption efficiency,

2) high compressive strength and abrasion resistance, and

3) high ignition temperature.

Another requirement, reduced pressure drop across the filter bed, was realized by optimizing the size and shape of the char pellets.

The adsorber in the BF/FW Process is a unique gas-solid contacting device. The adsorber must be designed for gas flow as well as char flow. It is very important that both materials flow with even distributions and velocities throughout the adsorber. The louvers perform several functions that influence the distribution and velocity of the gas and the char. As a result, the most important aspect of the adsorber is the louver design. The area of the louver face is set by the volume and the approach velocity of the gas. For the Radian base case and an approach velocity of 1 fps, the required louver area is about 17,000 ft^2. However, a velocity of 1 fps is not maintained throughout the adsorber. Entering the channels between the char beds, a maximum gas velocity of 15-25 fps is attained.

The sulfur content of the coal and the SO_2 removal efficiency required determine whether a one-stage or a two-stage adsorber is used. As a general guide, FW suggested 2 to 2.5 percent S coal and 60 to 70 percent removal efficiency as the maximum conditions under which a one-stage adsorber is optimum. For a higher sulfur coal or removal efficiency, a two-stage adsorber is probably optimum.

The primary design criteria for the louvers are the angle of inclination at the gas inlet and outlet, the vertical spacing between the louvers, and the width of the louver measured in the direction of gas flow. These criteria have a direct bearing on gas side pressure drop, load distribution of the char weight to the structural support columns, the uniform downward flow of char to insure plug flow in the beds, the mixing action of fly ash with the char to prevent buildup at the inlet face of the char bed, and the minimization of entrainment of fines in the exit gas.

Design considerations for the char beds are the char depth, the number of modules placed in series to form a bed, and the number of beds in parallel. These criteria influence the degree of SO_2 removal, gas side pressure drop, and gas residence time. The char beds have been modularized for commercial application. The modules are either 4 ft by 4 ft or 6 ft by 6 ft. The depth of the char bed is then set by the module choice. The number of modules in a bed and the number of parallel beds is determined by the SO_2 concentration in the flue gas and the removal efficiency desired. The modules in a bed are not separated by partitions and, therefore, are more conceptual than real. Consequently, the char can undergo horizontal movement (cross flow) with a possible increase in estimated char attrition.

Gas distribution across the bed is aided by the inlet and exit louvers but is maintained primarily by pressure drop across the beds. FW reports that proper distribution is insured due to the self-compensating effect of fly ash in the gas stream. If the gas flow becomes unbalanced, higher quantities of fly ash will be deposited in the area of the adsorber with the higher gas flow. The resultant increase in pressure drop in that area will tend to rebalance the gas distribution. Gas flow also helps to dissipate heat from the char pellets. The potential for "hot spots" would increase in areas where gas flow was prevented or very limited.

The potential for combustion of char pellets in the adsorber must be minimized. The primary factors that effect char combustion are inleakage of air to the adsorber, and the adsorber operating temperature. Air inleakage occurs mainly through the char exit hoppers at the bottom of the adsorber. A negative pressure is created at these hoppers as a result of the induced draft fans pulling the flue gas through the adsorber beds. FW reported that creation of a back pressure downstream of the adsorber to lessen the negative pressure on the hoppers may be necessary. An alternative might be to put the fan ahead of the adsorber and operate with a positive pressure, which would reduce inleakage and increase adsorption efficiency somewhat. This possibly could cause a fugitive dust problem, however, in which case, a balanced draft arrangement would be more desirable. Air can also enter through the top of the adsorber if a seal is not maintained by an adequate level of char pellets in the surge section.

The operating temperature of the adsorber is primarily a function of the flue gas temperature and the temperature of the recycled char pellets from the regeneration section. The design operating temperature of the adsorber is approximately 280°F. Dilution air is used to cool the flue gas to this operating temperature. The char out of the regenerator must be adequately and uniformly cooled by a water quench prior to recycle to the absorber. FW experience relating to char hot spots at the Scholz pilot plant is discussed in Section 3.5, Status of Development.

Solids handling and control is another important consideration in the BF/FW adsorption section. Regenerated char must be uniformly distributed over an entire adsorber bed in a full-scale design. Solids handling equipment must be designed for the operating temperatures of the adsorption section.

The specified operating temperature of the adsorber is 250 to 300°F. The absorption reactions would benefit from lower temperatures. At Lunen, for a fixed bed depth and gas velocity, SO_2 removal was about 65 percent at 300°F and 80 percent at 265°F. Therefore, operating at a lower temperature would reduce the depth of number of adsorber beds. The acid corrosion problem associated with operation near the acid dew point might be overcome by constructing the metal parts of the gas inlet side of stainless steel without greatly increasing capital cost (SI-073). FW indicated that 250°F at full load is the minimum practical application. Temperatures above 300°F could also be incorporated into the design, but removal efficiency begins to fall off above 300°F.

The char becomes more and more saturated with pollutants as it travels downward in the beds. Since adsorption is a function of saturation, the upper part of the bed will be more efficient than the lower part. Two-stage adsorbers, as described in Section 3.1, are designed on this basis. The two-stage adsorber increases the loading on the char (lb SO_2 per lb char) by increasing the saturation of the char.

Char replacement and activity also influence adsorber design. The char residence time in the adsorber is on the order of 30 hours due to the 1 to 2 ft per hour flow rate. BF reports that char rates of this magnitude insure low make-up requirements due to reduced abrasion in the adsorber. The activity of the char has been found to increase until a stable level is reached after about three months of use. The lifetime of a char pellet is about 6 months or 120 cycles.

Control of the adsorber is accomplished by adjusting the char flow rate, the first and second stage adsorber loads, and the amount of dilution air added to the flue gas. The char flow rate is not critical as long as enough char is fed to the adsorber to achieve the required degree of removal. Addition of dilution air should be carefully controlled to keep the flue gas temperature above the acid dew point. Also, a water quench might be an alternative cooling method for a commercial installation.

There are no design considerations specifically related to NO_x removal. However, BF reports that NO_x removal increases with SO_2 removal. Therefore, features of the system that enchance SO_2 removal would also enhance NO_x removal.

An alternate processing sequence for the adsorption section that is similar to the method used by Westvaco might be to first contact the flue gas with a bed designed to remove the SO_3. This bed would operate at 250-300°F due to dew point considerations. After the SO_3 is removed, the flue gas would be cooled by a water quench to the 175 to 200°F operating temperature of the main adsorbers. The adsorption reactions occur more rapidly at the lower temperatures. The minimum exit gas temperature of 175°F would also be maintained.

Regeneration

Design considerations in the regeneration section focus on the thermal regeneration of the char pellets. The method of transferring heat to the char in a reducing atmosphere is the primary concern.

The regeneration reactor design is based on a Bergbau-Forschung unit that has been in operation over five years. The primary design factors are complete mixing, residence time, and a noncombustible atmosphere. Conductive heat transfer using sand at about 1500°F as an inert heat transfer medium occurs to raise the char temperature to about 1200°F. The flow of the char and sand through the regenerator is of a simple gravity nature. Char out of the adsorption section is transported by bucket elevator to a surge tank above the reactor to supply the necessary head to flow through the regeneration section. The fluid bed sand heater is likewise elevated to provide a head for gravity flow of the sand. The fluidized level is maintained by sand leaving through a refractory lined overflow pipe which empties into the regenerator.

Complete and uniform mixing of the char and sand is very important. The mixing of two hot solids of widely differing particle size is difficult. Operating problems were reported at Welheim, but BF has since improved the regenerator design. BF reports that the proper design of entrance tubes for the char and the sand and the use of mixing rings inside the vessel insure proper mixing. The volume of the regenerator determines the residence time of the char-sand. The residence time of the char in the regeneration reactor is 12 to 20 minutes. No excess oxygen should be permitted to enter the vessel as this would increase the char consumption above that necessary for the chemistry of the regeneration process. For this reason, a reducing atmosphere with a slightly positive pressure is maintained in the vessel. Minimum resistance to upward flow of the evolved gases is also necessary. A means for the gas to move upward without having to find its way through the char-sand mixture may be required. Otherwise, evolution of gas may continue until after the char leaves the regenerator, resulting in "burps" in the char-sand separator.

Char is consumed in the regeneration reactor via the reaction given by Equation 3-4. Approximately 90 percent of the char make-up requirement is reportedly due to this chemical consumption. The remaining 10 percent is a consequence of mechanical or abrasive losses. At Welheim, BF found that char consumption was less than the stoichiometric amount indicated by Equation 3-4. Based on these data, BF asserts that a portion of the SO_2 is simply adsorbed in the char pores and never oxidized. The SO_2 would then be released in the regenerator without undergoing any chemical reaction.

Fluidized bed sand heaters have been operated on a commercial scale using oil and gas as the heat source. FW reports that a vendor is now prepared to offer 100 percent coal firing in their fluidized bed sand heater equipment. Coal firing has not been tested by BF or FW any any of their facilities.

Coal firing would be very desirable, but this procedure may introduce operating problems as a result of increased ash loading and sulfur and trace constituents in the coal.

Operation of the regeneration section is dependent on six variables:

1) char flow rate,
2) char inlet temperature,
3) sand flow rate,
4) residence time of char-sand mixture,
5) char-sand mixture temperature, and
6) sand inlet temperature.

The char flow rate and inlet temperature is set by conditions in the adsorber. The sand flow rate and mixture residence time are kept relatively constant. The mixture temperature at the outlet is determined by the regenerative properties of the char. Therefore, the remaining parameter, the sand inlet temperature, is used for control. The fuel to the sand heater is adjusted to control the temperature of the sand and, thus, the temperature in the regenerator. Optimization of the sand to char temperature differential and the sand to char weight ratio has not been completed. Higher temperature differentials and lower sand to char weight ratios would be more cost effective.

Handling materials at 1200°F could result in major operating problems in the regeneration section. Oscillating equipment (char-sand separator, horizontal sand conveyor, and char cooler) and the sand bucket elevator must be designed for this high temperature service. The availability of the regeneration section will depend on the reliability of this mechanical equipment.

The char cooler must quench the char pellets uniformly to prevent localized concentrations of hot char being recycled to the adsorber. The exit temperature of the char from the cooler should also be low enough so as not to initiate hot spots in the adsorber. The water quench of the hot char also must not produce thermal strains that result in breakage of the char pellets. BF feels that the char is strong enough to resist thermal stresses satisfactorily as long as air leakage into the unit is prevented.

Reduction

Design considerations in the RESOX process for reduction of SO_2 are primarily concerned with the reaction of SO_2 gas with anthracite coal to produce elemental sulfur. Some factors that might influence this reaction are feed gas composition, pressure, temperature, residence time, gas distribution, and stoichiometry of carbon to SO_2.

Foster Wheeler reports that the pressure and gas distribution are not critical design considerations. The operating pressure is atmospheric. Proper gas distribution is accomplished by injection of the SO_2 rich gas at various ports around the lower vessel circumference. The stoichiometry of carbon to SO_2 is likewise not a sensitive parameter as long as an excess of carbon is present. Presently FW uses a carbon to SO_2 stoichiometry of about 2:1. About half of the RESOX coal feed leaves the bottom of the reactor as part of the RESOX ash stream. An economic incentive may exist to recover the heating value of the RESOX ash by burning it in the boiler.

Due to kinetic considerations, the temperature and the residence time are considered to be the most important parameters in RESOX design. The temperature is 1100°F to 1500°F. The gas residence time is 3 to 8 seconds, and the coal residence time is 12 to 20 hours.

Radian performed equilibrium calculations for the pressure (one atmosphere) and temperature range (1100-1500°F) specified. These calculations were first done using the regenerator off-gas composition and an average analysis of anthracite coal. The carbon to SO_2 stoichiometry was input at 1:1 and 2:1. At equilibrium over 90 percent of the sulfur was present as H_2S for each set of conditions examined. Water vapor in the feed gas and H_2 in the coal are the sources of hydrogen. Almost no elemental sulfur resulted. The gas feed was then changed to pure SO_2 and the solid feed to carbon. With these new feeds and a carbon to SO_2 stoichiometry of 1:1, over 95 percent of the sulfur was present as elemental sulfur. However, at a stoichiometry of 2:1, the major equilibrium sulfur species were COS and CS_2 with only small quantities of elemental sulfur.

The results of these equilibrium calculations were discussed with Foster Wheeler. They agreed that the equilibrium products were reasonable. However, with a gas residence time of 3 to 8 seconds, FW reports the kinetics favor sulfur as the product rather than H_2S, COS, or CS_2. Also, the reaction zone is localized so that only a portion of the carbon is available at any given time and, then, only at the surface of the coal particles. The presence of SO_2 and H_2O copromotes the reactions of SO_2 with C and H_2O with C. The reaction between either SO_2

or steam and coal is not very fast at the operating temperatures of RESOX. With the promotion of both reactions in RESOX, the SO_2 is reduced at a lower temperature.

Based on their experience with RESOX, FW concludes that about as much steam exits the process as enters. Only small amounts of H_2S are produced. Carbon is the primary reducing agent but CO and/or H_2 may be an intermediary at the surface of the crushed coal particles. Hydrogen could be formed by the reaction of coal with steam, and when SO_2 is contacted, the H_2 would reduce the SO_2 and go back to water. After the SO_2 is reduced to elemental sulfur or other species, the reaction of H_2O with C does not proceed rapidly at the operating conditions of the RESOX unit.

Published thermodynamic data indicate that in the absence of a catalyst, neither H_2 nor CO react to an appreciable extent with SO_2 below about 1450°F. It therefore appears as if the anthracite coal must have some catalytic effect that determines the course of the reaction. Great care should be taken in testing coals for use in the RESOX unit for their catalytic properties.

The crushed anthracite coal flows through the reactor by gravity. There are no internals for the reactor. Anthracite is specified due to its low volatile matter content. FW has tested a number of coals for use in RESOX. All were acceptable chemically but some were less sutiable due to characteristics such as caking or volatile content. Bituminous coals higher in volatility result in hydrocarbons being condensed with the sulfur in the RESOX condenser. If a utility desires to stockpile only one coal type, a devolatilizer can first prepare the coal for use in RESOX. FW is also examining accommodation of caking coals by means of moving internals in the reactor.

Control of SO_2 reduction is accomplished by the addition of air or steam to the gas feed. Air burns some of the coal and thus raises the temperature. The increase in temperature causes more SO_2 to react. Steam retards the reduction by acting as a dilutant and lowering the temperature.

The composition of the regenerator off-gas varies within rather narrow limits. As a result, design of the RESOX unit is based more on the quantity of SO_2 in the regenerator off-gas rather than the composition of this gas.

3.5 Status of Development

Design data for the BF/FW Dry Adsorption Process comes from both pilot-scale and prototype plant operation. Testing at the pilot level was completed in the late 1960's, while the prototype systems have only recently begun operation. The important design factors and operating histories of these facilities are summarized in Table 3-2.

In 1963, Bergbau-Forschung began a research and development program in West Germany to improve and expand the known technology of SO_2 adsorption via activated carbon. A potential process for the manufacture of char pellets was the outcome of this program. The char was first evaluated on a 20 scfm bench scale system that included the adsorption and regeneration steps. The char was developed concurrently in a facility which could produce approximately 5,000 tons per year.

The results of the bench scale work led to the installation of a pilot unit at the Welheim Power Plant in West Germany in 1968. This facility operated on a 1,750 scfm slip stream of flue gas from a 35 Mw pulverized coal-fired boiler. The inlet SO_2 concentration varied between 1,000 and 3,000 ppm and the

TABLE 3-2

STATUS OF DEVELOPMENT - BF/FW FLUE GAS DESULFURIZATION PROCESS

Unit	Bergwerksverband	Kellerman Power Plant	Gulf Power Scholz Station
Location	Welheim, W. Germany	Lunen, W. Germany	Chattahoochee, Florida
Gas Source	Coal-fired	Coal-fired	Coal-fired
Gas Flow Rate	1100 - 1800 scfm	88,000 scfm	104,000 acfm (design)
Particulate Loading			
Inlet gas	.2 to 1.3 gr/scf	.05 gr/scf	After 99.7% ESP
Outlet gas	.014 to .09 gr/scf	.012 gr/scf	-
Inlet SO_2 Concentration	3000 ppm	1000 - 2000 ppm	900 - 2100 ppm
SO_2 Removal Efficiency	Up to 95	Up to 99	Up to 99
Period of Operation	May, '68 - April, '70	July, '74 - Present	March 15 - April 4, '76
Longest Continuous Run	6000 hr	1000 hr	500 hr
Operations Included*	1,2	1,2	1,2,3

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* 1 - SO_2 adsorption
2 - regeneration
3 - RESOX

inlet flue gas temperature from 212°F to 284°F. The grain loading also varied from 0.064 grains/scf to 1.3 grains/scf. The Welheim facility was operated for two years. The adsorber/ thermal regeneration unit operated on a continuous basis for over 6,000 hours. Removal of up to 95 percent of the SO_2 in the flue gas with an inlet SO_2 concentration of 3,000 ppm was accomplished. BF also reported 40 to 60 percent removal of the inlet NO_x. The system exhibited 90 to 95 percent particulate removal for the flue gas after a precipitator.

Based on the success of the pilot plants, a prototype 45 Mw unit was installed by BF in the summer of 1974 at the Kellerman Power Plant in Lunen, West Germany. The adsorption and regeneration sections operate on a 88,000 scfm slip stream from a 350 Mw coal-fired peaking service boiler. The SO_2 inlet concentrations are 1000 to 2000 ppm. Off-gas from the regenerator is treated in a modified Claus unit to produce sulfur. The facility was started up in late 1974. As of December 1975, approximately 1,500 hours of operation have been logged by the adsorption section and about 3,000 hours by the regeneration section. The longest continuous run has been 1000 hours. Preliminary data indicates a 95 percent SO_2 removal.

The char consumption at Lunen, based on early tests, was 0.12 pounds per pound of SO_2 fed to the adsorber. However, recent tests covering a longer period of operation and including unexplained losses indicated a total consumption of 0.18 pound. Since this higher figure probably includes some losses that could be prevented or reduced in a commercial installation, BF states that char make-up should be somewhere between the two values. Also, stronger char which is now available should reduce make-up requirements (SL-073).

The first fully integrated application of the BF/FW Process is being demonstrated by FW on a 47.5 Mw coal-fired boiler at Gulf Power's Scholz Steam Plant. The unit consists of a 20 Mw adsorption section and 47.5 Mw regeneration and RESOX sections. This is the first facility that employs a two-stage adsorber. The adsorption and regeneration section underwent shakedown runs for ten days in August, 1975. The RESOX unit was operated for five days in October, 1975 including start-up and shutdown. During this time regenerator off-gas was treated for about 14 hours.

Several problems were identified during the August and October shakedown runs at the FW Scholz demonstration unit. The operational problems were attributed primarily to mechanical problems or failures. Distribution of char in the upper adsorber area was not satisfactory. As a result, the flow of char in some modules had to be stopped to allow the levels to equalize across the bed. Hot spots then developed in the hoppers at the bottom of the adsorber where flue gas did not flow through the char. FW is modifying the char distribution system. They are also including the capability to pass gas through the char in the hoppers to help dissipate heat and prevent hot spots.

The star valve that feeds char to the regenerator caused numerous short interruptions in the operation of the regeneration section. This valve is a feeding device and a locking device to prevent leakage from the regenerator. Another mechanical problem resulted when the heat shields on the hot sand bucket elevator caused interferences due to the close tolerances. After the shields were removed, the equipment operated satisfactorily. During the shakedown runs, the char-sand separator performed adequately from a process point of view, but mechanical failures caused considerable downtime.

The RESOX unit treated regenerator off-gas for about 14 hours. The off-gas was produced using char that was set aside during shakedown runs of the adsorption section. FW reports that they were able to stabilize the operating temperature in RESOX during this run. Elemental sulfur was not recovered in the sulfur condenser, but neither was SO_2 detected in the gas out of RESOX. After subsequent heating of the RESOX unit to about 1000°F, some sulfur was found at the entrance to the condenser. FW suggested that the elemental sulfur produced in RESOX condensed in the reactor since the reactor was operated at only about 30 percent of design capacity. The percent conversion of SO_2 to S is not known. Also, the composition of the off-gas from RESOX was not determined.

Some of the positive outcomes of the shakedown runs were better removal of SO_2 and a smaller pressure drop across the beds than expected. FW concluded that operational problems in the adsorption and regeneration sections resulted solely from mechanical problems.

Information on the potential for char combustion, which has been a concern in carbon adsorption processes, was gained during subsequent operation of the unit in the spring of 1976. Inleakage of oxygen to the adsorber and inadequate quenching of char recycled to the adsorber were identified as the primary factors contributing to hot spots in the char beds.

A negative pressure exists at the adsorber outlet hoppers due to the action of induced draft fans pulling flue gas through the adsorber beds. As the quantity of flue gas passing through the beds increases, the negative pressure at the hoppers also increases. A greater tendency to draw oxygen in through the hoppers results. A positive backpressure was created downstream of the adsorber to reduce the negative pressure at the hoppers and reduce oxygen inleakage.

The temperature of the recycled char out of the char cooler (200°F) was found to be too hot for feed to the adsorber. The control was reset to about 240°F so that after additional heat loss in the char surge tank, the char entered the adsorber at 140 to 170°F.

FW also discovered that gas flow through the first and second stage adsorbers was not balanced. Flow through the second stage was not adequate to prevent heating of the char above desirable limits. The gas flow was modified to provide cooling of char in the second stage.

According to a recent report by Slack (SL-073), the non-chemical losses of char at Scholz have been so high as to be unacceptable. This is attributed to several factors in the design of the system including:

1) Susceptibility to char cross-flow in the adsorber,

2) A potential grinding effect due to the long stroke of oscillating conveyors,

3) Tendency of char pellets to bounce out of bucket elevators,

4) Char dumping into chutes with breakage on impact,

5) The long stroke and excessive movement of vibrating screens, and

6) Air leakage into hot char in the char-sand separator.

Modifications of the sulfur condenser have also been required. The dust in the exit gas from the RESOX reactor has resulted in plugging of the condenser. Furthermore, the product sulfur has contained impurities that would presumably have to be removed (SL-073).

The materials of construction used in the system are primarily carbon steel. The adsorber is totally carbon steel. The regenerator, sand heater, and RESOX reactor are all refractory lined carbon steel. The high temperature material handling equipment is 304 stainless. The other conveying equipment is mild steel. No exotic metals or lined equipment (other than refractory lined) is required or used in the system.

3.6 Scale-up Considerations

Uncertainties of scale-up exist in the adsorption, regeneration, and RESOX process steps. Most of the considerations that affect scale-up have already been presented under design considerations. Process areas that are currently under development will be emphasized with scale-up factors for a 500 Mw installation presented where appropriate.

Adsorption

The adsorber is a unique piece of equipment designed and tested specifcially for the BF/FW Process. Adsorber design and particularly louver design have undergone considerable testing and development. Since the adsorber is based on a modular design, scale-up to large units will mostly entail the addition of sufficient modules. The char distribution system at the top of the adsorber may present a scale-up problem. Uniform distribution has been difficult to obtain on demonstration units and should be even more difficult on larger adsorber beds. Prevention of hot spots in commercial units may also be more difficult. The materials handling equipment should not present any unsolvable problems. Assuming that adequate information is gained from the 20 Mw adsorption section of the Scholz facility, scale-up to a 250 Mw capacity would be about 12:1 on a Mw basis. Foster Wheeler has specified two two-stage adsorbers for the 500 Mw Radian base case.

Regeneration

The regeneration reactor is based on a BF process step for calcining char that has been employed at their char making facilities since the late 1960's. The regeneration reactor has been operated at the pilot plant level and is now being tested on demonstration units. The complete and uniform mixing of the sand and char appears to be the only aspect of the process that may be difficult to scale-up. The 45 Mw Lunen unit and the 47.5 Mw unit at Scholz should present an adequate scale-up basis. FW anticipates 150 Mw regeneration modules which would entail a scale-up of about three to one.

The fluidized bed sand heater is a commercial equipment item. Coal firing remains to be demonstrated, however. A process vendor is ready to offer 100 percent coal firing. Scale-up should not be difficult.

Handling of hot materials in the regeneration section could be a scale-up problem. Larger quantities of material will result in equipment subjected to a greater heat sink. The effect of these high temperatures on equipment has not been adequately examined. Uniform and adequate quenching of the char recycled to the adsorption section may also be a problem with a commercial installation.

Reduction

Data for the RESOX process has been generated with a 2 ft^3 volume bed. An adequate basis for design or scale-up does not exist at this time. If design information can be acquired at the Scholz RESOX unit, RESOX could be in a reasonable position for scale-up. At this time the capability of the RESOX unit at Scholz is unknown. Scale-up of RESOX is the least certain of any of the process steps.

The Scholz demonstration plant is fully integrated. The BF Lunen facility is also fully integrated but a modified Claus unit is used for reduction of SO_2 rather than RESOX. The Scholz Station has the only integrated BF/FW Process.

3.7 Utility Applicability

The BF/FW Dry Adsorption Process is generally suitable to both new and retrofit applications on fossil fuel-fired utility boilers. Unless extensive conveying systems are employed, it will be necessary to locate both the adsorption and regeneration sections near the stack. The RESOX unit can, however, be located at a position more remote from the stack. The amount of boiler area ground space for this equipment is reduced by the fact that some of the vessels are elevated and can be effectively "stacked" atop one another. FW reports that about 38,000 ft^2 will be required for a 500 Mw system.

Bergbau-Forschung could presently produce approximately 5,000 tons per year of char in West Germany. This is less than the yearly consumption for the 500 Mw Radian base case. The availability of adsorbent char in the United States is one possible limiting factor in the application of the BF/FW Process.

BF asserts that the lag time associated with construction of a utility would enable them to license their technology to U.S. companies and have production underway in time to meet the needs of the utility. The current price of char FOB East Coast is estimated to be $390 per ton.

Anthracite coal is presently specified for RESOX. Approximately 167 x 10^6 MM Btu of anthracite was produced in 1975 (US-335). Assuming 13,500 Btu per pound, the production by weight was about 6.2 x 10^6 tons. This production is sufficient for RESOX units on roughly 100,000 Mw of generating capacity burning 3.5 percent sulfur and specifying 90 percent removal of SO_2 (Radian base case parameters). However, some of this production may be captive and therefore not available to a utility. Also, production decreased 6 percent in 1975 over 1974. If the decline continued, providing anthracite coal for RESOX could become a problem. Since almost all anthracite is mined in Pennsylvania, shipping costs could be very significant. Petroleum coke or devolatilized bituminous coal are potential alternatives that are yet to be evaluated.

Turndown of the adsorber to about 15 percent of full load is reported by FW. The char flow rate is simply decreased. However, it is very important to keep the char flow well ahead of the gas flow due to the slow reponse of the system. FW specified four Regeneration-RESOX modules; each designed to handle 30 percent of the total char flow. When maintenance is required on one module, operation at 90 percent of full load can still be maintained. With these modules, turndown of the regeneration and RESOX process sections to 15 percent of full load should be readily attainable by operating only one module at 50 percent of design. Procedures for start-up and shutdown of the RESOX unit may be particularly important, however, since temperature control is important for the RESOX reaction.

The BF/FW Process also has the potential for relatively simple decoupling of process areas. Insulated storage tanks can be provided, but decoupling is not cost effective according to Foster Wheeler. Nevertheless, prolonged decoupling is possible and can be carried out if required.

3.8 Economic Assessment

A detailed economic evaluation of the BF/FW Process is beyond the scope of this project. Raw material and utility costs based on energy and material balance calculations will be presented. Also, the relative contribution of each section of the process to these costs will be identified.

The raw material and utility requirements and costs are shown in Table 3-3. The basis for these results is the energy and material balance calculations performed by Radian for this evaluation. The total annual raw material and utility costs are $5,889,000 or 2.25 mills per kwhr. The relative breakdown by process section is as follows:

Adsorption	11%
Regeneration	74%
Reduction	15%

The impact of char make-up requirements is very evident since it represents about 52 percent of the cost. The sand heater coal (19 percent), the RESOX coal (14 percent), and power (14 percent) are the other primary considerations in the cost analysis.

TABLE 3-3

RAW MATERIAL AND UTILITY COSTS FOR THE BF/FW PROCESS

Basis: 500 Mw; 3.5 (wt.) % S Coal;
5,260 hr/yr at full load

		Annual Cost (10 dollars)
Adsorption		
Electric Power: 6,400 kw		673
	Subtotal	673
Regeneration		
Electric Power: 1,300 kw		137
Sand Heater Coal (Plant): 210 MM Btu/hr		1,105
Sand Make-up: 800 lb/hr		40
Char Make-up: 3,000 lb/hr		3,077
	Subtotal	4,359
Reduction		
Electric Power: 110 kw		12
RESOX Coal (Anthracite): 160 MM Btu/hr		842
Boiler Feedwater: 3,300 gph (recycled)		3
	Subtotal	857
	ANNUAL RAW MATERIAL AND UTILITY COSTS	5,889
	UNIT RAW MATERIAL AND UTILITY COST	2.25 mills/kwhr

3.9 Process Summary

The Bergbau-Forschung/Foster Wheeler Process is a dry adsorption process which uses activated char pellets to adsorb SO_2 from flue gas. The char is thermally regenerated, and the SO_2 in the off-gas is reduced in the presence of anthracite coal to elemental sulfur in RESOX. The unique features of the process are the louvered wall design of the adsorber and the RESOX unit. The louvers influence the distribution and velocity of the flue gas and the char. RESOX is a proprietary process for the reduction of gaseous SO_2 to elemental sulfur. The major problems lie in the mechanical reliability of equipment and the availability of design and operating data for the RESOX unit. Char combustion, which has been a problem with other carbon adsorption processes, must also be considered in the design and operation of a unit. The BF demonstration plant at Lunen, West Germany, and the FW facility at the Scholz Station could be sources of design and scale-up data. Successful operation at these prototype units should prepare the vendor to scale-up the process to a commercial application.

4.0 ATOMICS INTERNATIONAL AQUEOUS CARBONATE PROCESS

The Aqueous Carbonate Process (ACP) as developed by Atomics International utilizes an aqueous sodium carbonate (Na_2CO_3) solution to sorb sulfur dioxide (SO_2) from power plant flue gas. The dry scrubber product is treated to regenerate the scrubbing solution and to produce elemental sulfur. Two design features unique to this process are:

1) the use of a spray dryer as an SO_2 scrubber, thus producing a dry, granular salt mixture suitable for regeneration, and

2) reduction of the sodium salts in a molten pool.

The technology for the regeneration and sulfur production steps is based principally upon established practice in the pulp and paper and chemical industries.

4.1 Process Description

The ACP can be logically divided into the following five processing areas as shown in the process flow diagram illustrated in Figure 4-1:

1) Gas cleaning - Flue gas is scrubbed with NA_2CO_3 solution in a spray dryer to remove SO_2 and particulates,

2) Reduction - Dry scrubber product is reduced to NA_2S in a molten salt pool,

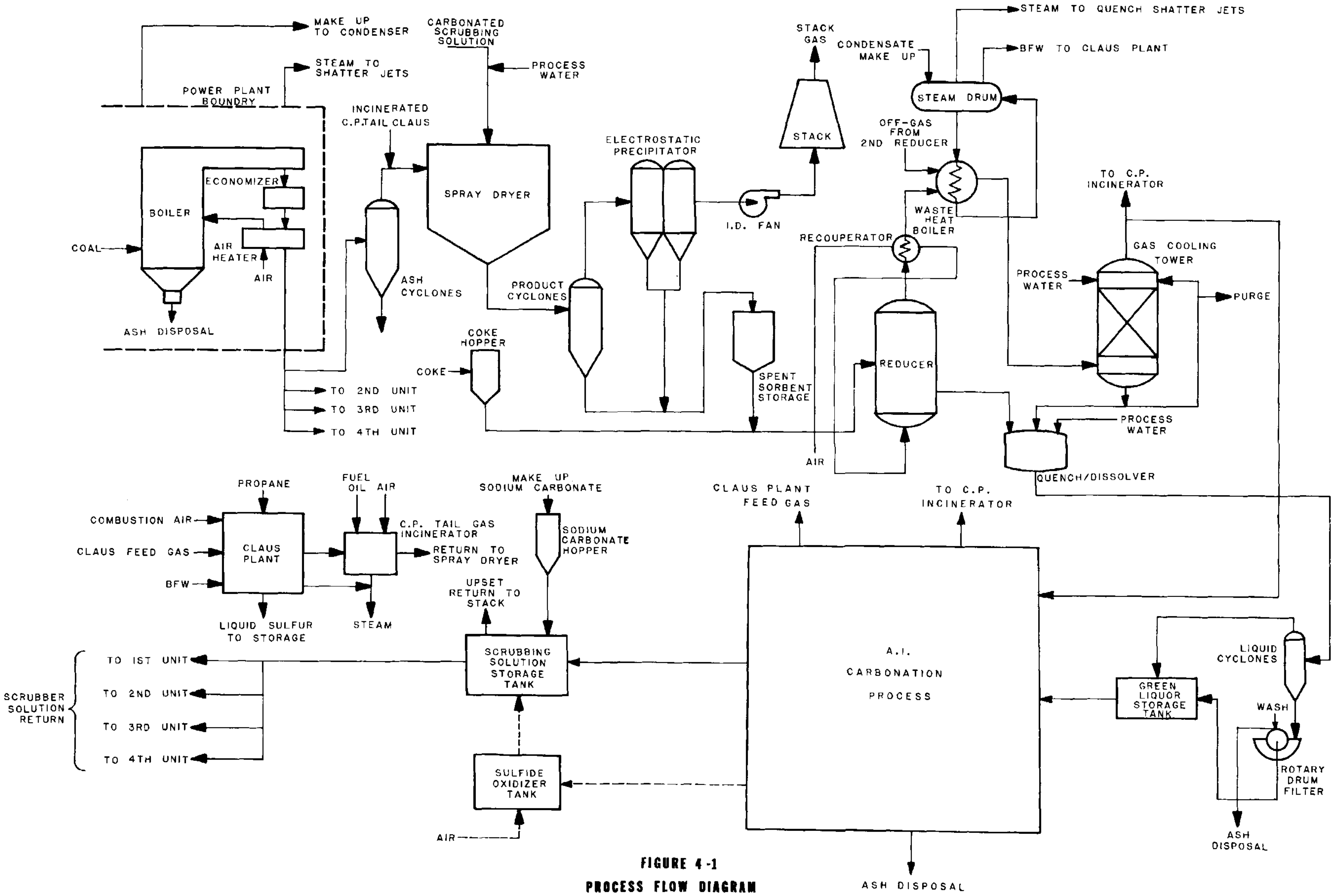

FIGURE 4-1

PROCESS FLOW DIAGRAM
ATOMICS INTERNATIONAL
AQUEOUS CARBONATE PROCESS

3) Quenching and filtration - Steam and cooling water are used to quench and dissolve the reducer melt. Fly ash is filtered from the solution and washed to recover sodium values,

4) Carbonation - CO_2-rich gas contacts the Na_2S solution to regenerate the Na_2CO_3 scrubbing solution and evolve H_2S, and

5) Sulfur production - H_2S is converted to elemental sulfur in a Claus plant.

Each of these process concepts will be discussed below with particular emphasis placed on processing equipment and unique design features.

Gas Cleaning

The SO_2 scrubbing and product collection equipment are combined in the gas cleaning subsystem. The gas cleaning subsystem, diagrammed in Figure 4-1, employs a spray dryer for SO_2 scrubbing and a bank of cyclones, in series with an electrostatic precipitator, for product collection and final particulate removal from the gas stream.

Before reaching the gas cleaning subsystem, the ash content of the flue gas must be lowered to 1.0 gr/scf or less in order to limit the size of the ash removal equipment in the regeneration section. This may be accomplished with existing particulate removal equipment, if available, (i.e., electrostatic precipitators, cyclones, etc.) or by installing a bank of cyclones between the air heater and spray dryer.

After ash removal, flue gas enters the spray dryer scrubber at temperatures typically between 250 and 350°F. Care must be taken to insure the gas remains above the dewpoint temperature to prevent condensation. Here the gas is contacted with atomized droplets of Na_2CO_3 solution. These droplets are typically generated by high speed centrifugal atomizers and driven outward, in crossflow to the flue gas.

In the scrubber, gaseous SO_2 is sorbed into the liquor where it reacts with Na_2CO_3 to form sodium sulfite, (Na_2SO_3) as indicated in Equation (4-1).

$$SO_2(g) + Na_2CO_3(aq) \rightarrow Na_2SO_3(aq) + CO_2(g) \qquad (4\text{-}1)$$

In addition to this primary reaction the following reactions produce sodium sulfate (Na_2SO_4):

$$Na_2SO_3(aq{+}s) + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4(aq{+}s) \qquad (4\text{-}2)$$

$$SO_3(g) + Na_2CO_3(s) \rightarrow Na_2SO_4(s) + CO_2(g) \qquad (4\text{-}3)$$

The product mixture formed by these reactions is usually about 60 percent sulfite, 20 percent sulfate, and 20 percent unreacted carbonate, by weight.

Typical liquid-to-gas (L/G) ratios for this operation are near 0.3 gal/1,000 scf. Because of the low liquid rate, insufficient water is present in the scrubber to saturate the gas, so that the spent reactant is entrained as dry particles. Gas exit temperatures are in the 150 to 250°F range, which can result in the need for reheat before rejection to the atmosphere.

For the base case design conditions (flue gas temperature of 300°F), the spray dryer can operate to achieve 90 percent

SO_2 removal and produce an exit gas with a temperature of greater than 175°F. If the inlet gas temperature, or flue gas temperature, drops much below 300°F, the system will probably require stack gas reheat to maintain a 175°F exit temperature. Some cushion is allowed as the system can cut back the water content of the scrubber feed solution and at the same time increase the degree of atomization to maintain constant SO_2 removal without lowering the exit gas temperature. The concentration of salts in the scrubber feed would, of course, increase as the dilution water is reduced.

Sulfur dioxide-clean flue gas exits the spray dryer and is routed to a bank of product collection cyclones, where the majority of the dry particles are removed. Final particulate removal is accomplished in high efficiency electrostatic precipitators in which particulate emissions are limited to 0.01 grain/scf or less. Spent reactants from both the cyclones and precipitator are collected and sent to the reduction section.

Reduction

The dry product collected in the gas cleaning system is stored in a silo and then conveyed pneumatically to the reducer vessel. This vessel contains a pool of molten salts at temperatures between 1700 and 1900°F. Carbon is injected in the form of petroleum coke (or coal). Combustion air is bubbled through the melt from injection nozzles in the vessel walls.

In the molten salt pool, the following reactions are known to take place:

$$Na_2SO_3(\ell) + 3/2C(s) \rightarrow Na_2S(\ell) + 3/2CO_2(g) \qquad (4\text{-}4)$$

$$Na_2SO_4(\ell) + 2C(s) \rightarrow Na_2S(\ell) + 2CO_2(g) \qquad (4\text{-}5)$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad (4\text{-}6)$$

Reactions (4-4) and (4-5) are endothermic. Reaction (4-6) is exothermic, however, and provides heat for both the endothermic reactions and system heat losses. The mechanism for reaction (4-6) is complex, involving sequential oxidation-reduction of the sulfur-containing salts as well as direct oxidation of carbon.

The CO_2-rich off gas from the reducer is sent to the carbonation section after passing through a recuperator, waste heat boiler, and gas cooling tower. Reducer melt is continously withdrawn and directed to the quench/dissolver vessel.

Quenching and Filtration

The sodium sulfide melt from the reducer is dispersed into fine droplets by steam shatter jets and dissolved in solution (green liquor) near its boiling point. Insoluble material, mostly fly ash and unreacted coke, is filtered out at this point using a rotary drum vacuum filter. Sodium is recovered from the ash filter cake using a simple washing technique. Both the quench and filtration operations are considered proven technology in the pulp and paper industry.

Carbonation

After the quench-filtration step, green liquor is contacted with CO_2-rich reducer off-gas in a series of carbonation towers. The technology for this process step has been developed in the pulp and paper industry and proven processes are available. AI is currently developing their own carbonation scheme by modifying existing technology. The details of the AI carbonation process are proprietary. The process reacts the CO_2-rich reducer off gas and the green liquor from the ash filter, and produces a concentrated Na_2CO_3 solution for recycle to the gas cleaning subsystem plus an H_2S-rich Claus plant feed gas. A vent gas stream is also produced and sent to the Claus plant incinerator, and some additional ash is removed and sent to disposal.

Sulfur Production

The H_2S produced in the carbonation section is directed to a Claus plant for conversion to elemental sulfur. Claus technology is commercially available but has not been tested for specific application with this desulfurization process. The Claus plant tail gas and precarbonator off-gas are combusted and returned to the spray dryer for treatment. AI proposes the use of an incinerator to combust these gases, however, they may be returned to the boiler for combustion.

4.2 Environmental Considerations

Although the ACP has been developed primarily for SO_2 pollution control, the system also reduces the emissions of SO_3, particulates, and halogen gases. The waste materials leaving the system consist of a damp filter cake containing mostly fuel ash and a chloride purge stream discharged with the spent cooling water.

The ACP can be designed to remove 90 to 95 percent of the SO_2 from inlet flue gases from a coal-fired power plant under normal operating conditions. The remaining sulfur is emitted with the stack gas as a combination of SO_2 and sulfur-containing particulates. Effective removal of flue gas SO_3 is accomplished by reaction with dry Na_2CO_3 powder in the spray dryer and electtostatic precipitator.

AI specifies the use of cyclones in conjunction with high efficiency electrostatic precipitators to reduce particulate emissions to 0.01 grain/scf or less on the exit gas from their product collection equipment. This low particulate emission is readily achievable due to the unusually good removal of fine fly ash particles. The fine fly ash particles entering the spray dryer tend to agglomerate with the atomized droplets and can be removed along with the spent absorbent.

Other environmental considerations regarding the ACP involve the disposal of wet filter cake and the discharge of chlorides with spent cooling water. According to material balance calculations, almost 12,000 lb/hr of wet filter cake (mostly fuel ash) will be generated by an ACP installed on a 500 Mw power plant which does not have an ash precipitator (see Section 4.3 for details). AI proposes to add this cake to the normal fly ash disposal system used by the power plant. No significant environmental impact is expected since the leachable fraction of these solids is less than that of fly ash.

A chloride blowdown stream is required to prevent the buildup of unacceptable chloride levels in the process liquor. These chlorides, along with possible trace contaminents, which are adsorbed in the spray dryer, will be purged with the gas cooling tower water in the reduction section. It is estimated that this purge stream will raise the concentration of total dissolved solids in the effluent cooling water by about 250 ppm. A potential use for this purge water stream is to sluice ash.

4.3 Material and Energy Balances

Material and energy balance calculations have been performed around the major equipment pieces in the ACP. Information for these calculations is taken from an AI statement of qualifications submitted to EPA in January, 1975 for a 500 Mw installation, and from portions of a proposal for a 125 Mw demonstration plant, in addition to personal communication with AI engineering personnel.

The Statement of Qualification submitted by AI to EPA (RO-158) contained material and energy balance information for a 500 Mw installation using the identical basis outlined by Radian earlier in this report. For this reason it was sufficient to review these figures for consistency and completeness. Using the information supplied in the qualification statement and composition data furnished by AI engineering personnel, it was found that material and energy balances around major pieces processing equipment closed in all cases to within 2 to 3 percent.

The only major discrepancy between the figures quoted in this report and those presented in the EPA qualification statement concerns the Na_2CO_3 make-up requirement. The sodium salts which are lost with the chloride purge stream represent the largest single requirement for make-up Na_2CO_3. AI does not include this stream in its design for a 500 Mw ACP installation as presented in the EPA qualification statement. Consequently, the AI estimate for Na_2CO_3 make-up with no purge is lower than Radian's estimate for a system with a chloride purge stream.

While a detailed, stream-by-stream review of these balances is not in order here, the calculations provided information as to major sources of raw material consumption, utility requirements, sulfur production, and quantities of influent and effluent streams. These figures will be highlighted for each of the major processing sections.

Gas Cleaning Subsystem

The basic performance of the gas cleaning subsystem is illustrated by comparing sulfur and particulate concentrations in the influent and effluent streams. Flue gas from the boiler area is divided into four streams and directed to four identical gas cleaning systems. The spray dryer feed stream contains 95.5 lb mole/hr sulfur as SO_2 and 1686 lb/hr of fly ash. After cleaning, the gas contains 8.1 lb mole/hr SO_2 and 0.16 lb mole/hr sulfur in the particulates. The total particulate emission rate is 25 lb/hr. Thus, the net reduction of sulfur and particulate emissions is 91.5 percent and 98.5 percent, respectively. If the ash cyclones, which are located before the spray dryer, are included in the gas cleaning subsystem, the overall reduction of particulate emissions becomes 99.7 percent.

The particulates leaving the system with the stack gas are equivalent to a total of 0.80 lb mole/hr Na_2CO_3. This corresponds to a Na_2CO_3 make-up requirement of approximately 85 lb/hr.

In addition to SO_2, $HC\ell$ is absorbed in the spray dryers at a rate of 10.0 lb mole/hr to form $NaC\ell$. This rate assumes 0.1 wt percent chloride in the coal and 95 percent absorption efficiency.

Reduction and Associated Equipment

Spent absorbent is collected from the four gas cleaning modules and sent to a storage hopper. Two equipment trains are required for reduction of the 370.2 lb mole/hr of sulfur as Na_2SO_3 and Na_2SO_4. A steady-state reduction rate of 95 percent is obtained by using 1.2 lb of coke per lb of sulfur ultimately produced in the Claus plant. This corresponds to a coke usage rate of 13,060 lb/hr total. Approximately 50 percent of this coke is consumed chemically, the other 50 percent satisfies heat balance requirements.

The reducer off-gas, containing approximately 35 vol. percent CO_2, is routed through a gas-to-gas recuperator, waste heat boiler, and gas cooling tower for heat recovery. Approximately 14,000 lb/hr of 50 psig steam is produced in the reducer waste heat boiler. This steam, along with additional steam from the boiler area, is used in two redundant sets of steam shatter jets to quench the reducer melt. The net steam requirement in the reduction section is nearly 3,500 lb/hr. A small amount (12 gpm maximum) of condensate make-up water is also required from the boiler area.

Particulates with high chloride concentration will be conveyed in the reducer off-gas and collected in the gas cooling tower. A chloride-rich purge stream is discharged with cooling water at a rate of approximately 500 gpm. This stream contains 580 lb/hr $NaC\ell$ and 64 lb/hr Na_2CO_3. Make-up requirements for Na_2CO_3 associated with this purge amounts to 585 lb/hr. These figures are very sensitive to the chloride content of the coal, which in this case is set at 0.1 wt percent.

Before being sent to the carbonation section, the green liquor is filtered to remove unreacted coke and ash. Wet filter cake is produced at a rate of 11,950 lb/hr. The sodium salt concentration of this cake, after washing, corresponds to approximately 200 lb/hr of make-up Na_2CO_3.

Carbonation

The material and energy balance calculations around the equipment in the carbonation cycle are dictated by the performance criteria of the equipment. The major flows in this area include 36,500 lb/hr of 50 psig steam (from the Claus plant boiler) and approximately 870 lb/hr Na_2CO_3 added to the scrubbing solution storage tank to make-up for sodium losses elsewhere in the system. The Claus plant feed gas contains approximately 35 vol. percent H_2S and 10 vol. percent CO_2. This gas is sent to the Claus plant for sulfur production.

Material and energy balance data for the Tampella Recovery Process (TRP) were supplied to Radian by Babcock and Wilcox. If the TRP is used for carbonation of the green liquor in place of the AI process, the steam requirement of this subsection increases by a factor of 3.5 to 4.0 while the electrical consumption is multiplied by more than 6.0. The feed gas to the Claus plant, however, contains more than 80 percent H_2S by volume while the carbonation off-gas carries less than 1 percent CO_2.

Sulfur Production

Liquid sulfur is produced in the Claus plant at a rate of nearly 10,900 lb/hr. Claus tail gas, residual reducer off-gas and pre-carbonator off-gas are incinerated and returned to the gas cleaning subsection in a 28,000 scfm stream containing approximately 26 lb mole/hr sulfur as SO_2. The Claus plant requires 210 gallon/hr of No. 6 fuel oil but produces 40,000 lb/hr low pressure steam for use elsewhere in the system. The net steam requirement of the ACP is therefore very low--2000 to 3000 lb/hr of low pressure boiler steam required by the redundant steam shatter jets.

Raw Material and Utility Requirements

The raw material and utility requirements for each subsection have been tabulated in Table 4-1. These figures are based on projections made by AI personnel in their statement of qualifications to EPA (RO-158). Where possible, checks have been made by the Radian author using material and energy balances to verify the accuracy of the numbers.

4.4 Design Considerations

There are a number of key design features that govern equipment size and operation in each of the processing areas of the ACP. In this section, these features will be reviewed with respect to their impact on system performance, control strategy, and the ability of the system to overcome potential problems.

Gas Cleaning Subsystem

The gas cleaning subsystem performs the dual role of removing SO_2 and particulates from flue gas and collecting the dried product formed in the spray dryer. Pilot scale tests of the spray dryer showed 90 to 95 percent SO_2 removal at flue gas temperatures and SO_2 concentrations typical of coal-fired boilers with an L/G of 0.3 gpm/1,000 scfm. Tests also showed that approximately 2 pounds of Na_2CO_3 are required for every pound of SO_2 removed to assure good scrubbing efficiency. This corresponds to a stoichiometry of approximately 120 percent based on SO_2 removal rates.

Process control of the spray dryer feed solution is basically simple and straightforward. However, the scrubbing solution must be carefully controlled as too much will result in condensation in downstream equipment and not enough will

TABLE 4-1

RAW MATERIAL AND UTILITY REQUIREMENTS FOR ACP

Basis: 500 Mw, 3.5 Percent Sulfur Coal

Subsystem	Power (kw)	Process Water (gpm)	Treated Water (gpm)	Cooling Water (gpm)	Coke (lb/hr)	Na_2CO_3 (lb/hr)	No. 6 Oil (gph)	Steam (lb/hr)
Gas Cleaning	8,100	1	24	0	0	85	0	0
Reduction, Quench, Filtration	930	320	35	2,100	13,000	780	0	+ 3,500
Carbonation	910	32	0	2,300	0	0	0	+36,500
Sulfur Production	620	0	0	0	0	0	210	-40,000
Net	10,600	350	60	4,300	13,000	870	210	0*

+: Utility required

-: Utility produced

*: Does not include boiler steam to redundant shatter jets

prevent attaining the required SO_2 removal efficiency. The concentration of Na_2CO_3 in the scrubbing solution is determined by the molar removal rate of flue gas SO_2 and the allowable temperature drop across the scrubber. Regenerated Na_2CO_3 is fed in concentrated solution to the spray dryer in sufficient quantity to effect the desired SO_2 removal. Dilution water is added to this stream just prior to entry into the scrubber. A maximum amount of dilution water is added since higher scrubbing efficiencies are possible with more dilute carbonate solutions. This is due to the fact that higher feed rates result in more spray droplets and hence better gas-liquid contact area. An upper limit is set on the amount of dilution, however, by the need to keep the total amount of water evaporated in the scrubber below that which will saturate the gas. The scrubber feed rate, then, is set by the inlet temperature of the gas and the allowable temperature drop across the scrubber such that the outlet gas temperature remains at least 20°F above the dewpoint, even during upsets. This procedure also assures a dry product suitable for collection.

AI reports that they can operate the spray drier in a mode in which stack gas reheat is unnecessary (exit gas temperature of 175°F or greater). Radian heat balance calculations agree with their claim for flue gas temperatures of 300°F or greater. If the flue gas temperature drops much below 300°F, the exit gas will probably require some reheat to exit at a temperature of 175°F. AI can, of course, cut back the amount of dilution water being added to the scrubber solution in order to maintain the 175°F exit temperature. This practice should work for small temperature variations but may result in reduced SO_2 removal.

The key to reliable operation of the spray dryer is efficient atomization of scrubbing solution. In its design for a 500 Mw installation, AI calls for three atomizers in each of its spray dryers, plus one spare. These are high speed centrifugal atomizers driven at a rate of around 18,000 rpm by a frequency converter and capable of producing droplets in the 100 to 150μ size range. Since the energy for atomization comes from a spinning disc and not from nozzle constriction, erosion problems are minimized.

Another key design feature concerning the performance of a spray dryer as an SO_2 absorption device is gas residence time. Enough residence time must be provided in the dryer for SO_2 to absorb into the scrubbing solution and react, and for water to evaporate to leave a dry product. Based on data and figures in the qualification statement (RO-158), a gas residence time on the order of 10 seconds was calculated. This figure can be compared with the 5 seconds residence time obtained in the pilot test unit. Increased residence time is reasonable, however, since large spray dryers are generally designed for greater residence times than small dryers.

The AI design for a 500 Mw plant requires four spray dryers of 42 ft diameter. These large dryers operate with superficial gas velocities around 4 ft/sec. Pilot scale tests were carried out with a much smaller spray dryer, 7 ft in diameter, and at gas velocities between 2.1 and 2.7 ft/sec. Although superficial gas velocity is not typically used as a basis for spray dryer sizing, it is not certain at this time what effects gas velocities above 3 ft/sec will have on performance. In any event, scale-up of the spray dryer has been based on results obtained with the 7 ft diameter dryer, the standard scale-up tool used by Bowen Engineering, Inc., a leading U.S. manufacturer of spray drying equipment. Bowen has designed and built spray dryers up to 44 ft in diameter, although this is the first application of the dryer as an SO_2 absorption device.

The design of cyclones and precipitator in the particulate collection system is considered standard industrial practice and should present no major problems when applied to the ACP. It can be noted, however, that the use of cyclones in series with a precipitator has generally been abandoned by utilities in collecting fly ash. AI prefers this scheme as a safety measure to assure that particulate losses to the atmosphere will be less than 0.01 grain scf.

For new, coal-fired plants, AI proposes to use cyclones for bulk dust removal (about 80 percent) before the spray dryer and the cyclone-precipitator combination for product collection after the absorber. This scheme avoids the need for two precipitators but increases the amount of ash filter cake produced in the regeneration section and thereby increases sodium losses with the cake.

The total pressure drop across the gas cleaning system is on the order of 20 inches H_2O. This includes a total of 12 inches H_2O drop across both the ash removal and product collection cyclones (6 inches for each), 3 inches H_2O across the scrubber, and 0.5 inches H_2O across the electrostatic precipitator. The remaining pressure drop is ascribed to ducting and an adequate safety margin.

Turndown of both the spray dryer and product collection equipment is said to be simple and quite high. As gas rate decreases, the scrubber feed rate is decreased in direct proportion. SO_2 removal efficiency is maintained at lower flow rates due to increased atomization efficiency. Turndown ratios as high as 4 to 1 have been demonstrated with a single scrubber without loss of removal efficiency. For a large installation with four scrubbing modules, dampers could be arranged to allow system turndown of as much as 16 to 1.

Turndown of the product collection equipment is also straightforward. Isolation dampers are provided on each bank of cyclones to maintain the optimum gas velocity and collection efficiency at reduced gas flow. As gas flow decreases, the collection efficiency of the precipitator increases due to longer residence times. Thus, the turndown capability of the product collection equipment is compatible with that of the scrubber.

The gas cleaning subsystem does not involve any inherent maintenance requirements other than periodic inspection and maintenance of the centrifugal atomizers. Plugging and scaling of equipment internals should not be problems.

Reduction

Sodium sulfite, sulfate, and unreacted carbonate are collected and sent to the spent absorbent storage hopper which is sized to accommodate materials for approximately two days operation. This is done in an attempt to decouple the operations of the gas cleaning and regeneration processing areas. Five to ten days of coke storage is also provided.

Operation of the molten salt reactor is the key design feature for this process. From a preliminary engineering viewpoint the design basis appears sound, as AI has identified potential problem areas associated with this reactor and have taken appropriate control measures. Historically, however, the operation of molten salt beds under reducing atmospheres has been particularly difficult to control, and it is likely that any unanticipated process problems will occur in this area.

Spent reactant, coke, and air are fed to the reducer to accomplish the reduction of sulfite and sulfate to sodium sulfide. Pilot plant data indicate that a steady-state reduction of 95 percent can be achieved with about 4 wt percent excess coke maintained in the reducer melt. Approximately one-half of the carbon in the coke is consumed chemically by the reduction reactions. The other one-half is burned to supply the heat needed for endothermic reduction to Na_2S, to melt the incoming salts, and to offset thermal losses and preserve the 1700 to 1900°F operating temperature. Typical reducer off-gas contains less than 1 percent O_2 and 35 percent carbon oxides with a CO_2:CO ratio of 10 to 1 or higher. Heat is recovered from the off-gas in a recuperator and waste heat boiler before the gas is cooled for use in the carbonation step.

Two reducers are called for in the 500 Mw design, each of which is a carbon steel vessel lined with 8-inch thick Monofrax, a refractory brick. This brick is a high density alumina which is resistant to the corrosive effects of the melt. The inside diameter of the reducer is set at 19 feet to accommodate superficial gas velocities of about 1 ft/sec. This gas velocity is considerably less than those used with the pilot reducer. Pilot data showed that gas velocities of 2.0 and 2.5 ft/sec could be tolerated before the level of salt carryover with the off-gas became unacceptable. This lower gas velocity of the full-scale reducer reflects the conservative nature of AI's design for an initial demonstration unit. Presumably, with the acquisition of more experience and data, the reducer gas velocity can be increased and the size of the vessel decreased.

The expanded depth of the melt is approximately 6 feet, and 15 to 16 feet of freeboard height is allowed to minimize carryover. The total flange-to-flange height of the reducer, then, is approximately 25 feet. Mist eliminators have been used in bench scale testing but have been deemed unnecessary. Any carryover will be captured in the gas cooling tower.

Combustion air is introduced to the reducer through downward sloping injection nozzles located in the vessel walls. The coke and spent sorbent material are conveyed with reducer off-gas and introduced with 3 solids feeders, 8 inches in diameter. This arrangement minimizes hot spots in the reducer and assures uniform melt composition.

In the current conception, petroleum coke is utilized as the carbon source in the reducer. The use of coal as a carbon source would be desirable in some locations because of coal's low cost and availability. Other design problems may arise, however, due to the increased amounts of fly ash, chloride, and trace contaminants. Preliminary tests have been made using coal as a reducing agent with encouraging results. A more thorough test program is planned for Fall, 1975.

The reducer can be continuously run at rated capacity or can be turned down to standby condition corresponding to 5 percent of the design feed rate. To compensate for vessel heat losses and maintain operating temperature during standby operation, approximately 400 lb/hr of carbon is required in excess of the normal absorbent to carbon ratio. It will be important to avoid wide swings in melt temperature since appreciable spalling of refractory lining was noted in pilot tests under these conditions. For typical boiler load cycles or downtime, the preferred operating mode for the reducer is either 100 percent capacity or standby.

Because of its volatility, $NaC\ell$ will be the predominant salt in the reducer off-gas. It is likely that some of these salts will condense on the heat exchange surfaces of the recuperator and waste heat boiler and result in serious corrosion problems. AI has noted such deposits in pilot scale tests but claims, however, that the material can be easily removed with periodic washing or soot blowers. Most of the NaCℓ-rich particulates will be scrubbed from the gas in the gas cooling tower. A portion of the recirculating cooling tower liquid stream will be used as a chloride purge for the ACP.

Quenching and Filtration

The technology for quench and filtration of the reducer melt is considered standard practice in the pulp and paper industry. The design of equipment in this processing area borrows heavily from this technology.

The quench/dissolver is a thick-walled carbon steel vessel similar to those used in the paper industry. Some corrosion of the carbon steel is expected but the walls will be 5/8 inch thick to allow for it. Carbon steel is the preferred construction material for this application because it minimizes the possibility of embrittlement and cracking at the quench operating temperatures (around 200°F).

Two factors that are key to avoiding explosive conditions in the quench/dissolver are:

1) the melt must be broken up and dispersed into fine droplets, and

2) the green liquor should be maintained at or near its boiling temperature to avoid pressure excursions.

To assure operation in this mode, AI has specified that two completely redundant steam shatter systems be provided. One will use process steam generated in the waste heat boiler and the other will use low pressure steam generated in the boiler.

Also, all pumps in the circulating liquor loop will be spared to insure an adequate water supply to the quench tank.

In recent tests, AI has shown that solidified reducer melt will rapidly dissolve in water. Results of these tests may lead to a process modification whereby the quenching operation can be eliminated. AI is currently investigating this area.

Filtration of fly ash and other solids from process liquor has caused problems in other alkali scrubbing systems. This situation is complicated in the ACP by the effect of high temperature reduction on the filtering characteristics of ash and unreacted coke in green liquor. Tests at AI's Molten Salt Test Reactor facility have shown that the fly ash and fuel ash present in the melt do not dissolve but do interact with other melt constitutents to significantly alter their physical and chemical properties upon quenching. Laboratory tests have shown that it is possible to filter the ash and coke from simulated green liquor and concentrate the solids to a 40-60 wt percent solids filter cake. A prototype test loop is also being prepared to demonstrate the rotary drum filter and other pieces of green liquor handling equipment.

Carbonation

Like the quench and filtration steps, the technology for carbonation is well developed by virtue of its use in the pulp and paper industry. Several commercial carbonation processes are available and can be applied to the ACP regeneration scheme. Most of these processes feature high energy and steam consumption, however, which has led AI to develop their own proprietary carbonation process. This process uses a series of sieve-tray columns to react the CO_2 from the reducer off-gas with the sodium sulfide in the green liquor from the quench step. The diameters of the columns are set by the superficial velocity of the carbonation gas, in this case between 1 and 2 ft/sec. The heights of the columns are dictated by the mass transfer characteristics of the sieve trays. The key design criteria are H_2S and CO_2 uptake. AI's design values for both of these performance criteria are conservative with respect to pilot data.

The off-gas from the carbonation process is sent as the feed stream to the Claus plant. This gas contains approximately 36 percent H_2S and not more than 10-11 percent CO_2. All of the above criteria have been demonstrated at the pilot level except the CO_2 content of the off-gas. Space limitations on the height of the test carbonation tower resulted in CO_2 levels around 15 percent. Modifications are being made to the tower to allow demonstration of all performance criteria.

The regenerated carbonate solution is sent to a leaf filter to remove any residual ash, coke, or precipitated contaminants, and then pumped to the scrubbing solution storage tank. A sulfide acidizer tank is also provided as an upset precaution against high NaHS concentrations in the regenerated scrubbing liquor and subsequent evolution of H_2S in the spray dryer.

The columns in the carbonation section are constructed with 316 stainless steel. The liquor circulating through the columns will contain chlorides and other trace contaminants, but AI does not feel these will present a problem. Corrosion tests at AI laboratories indicate that chloride attack of 316 stainless steel is negligible for the low temperature and pressure ranges specified in the carbonation loop. No embrittlement or cracking was observed using chloride concentrations as high as 5000 ppm with corrosion rates less than 10 mils/year at 170°F. Typical temperatures in the carbonation towers will be in the 120 - 140°F range so that even lower corrosion rates can be expected. The laboratory results generated by AI support the operating experiences reported in the pulp and paper industry, specifically by B&W with the Tampella Recovery Process.

Turndown of the carbonation equipment is compatible with the rest of the regeneration scheme. Two days of green liquor storage is provided to damp out swings in boiler load and SO_2 concentration. Like the reducer, preferred operation is near 100 percent capacity. Operation of the carbonation equipment is contingent, however, on reducer operation for a supply of CO_2- rich gas.

Sulfur Production

Production of elemental sulfur from the H_2S in the crystallizer off-gas is standard Claus technology. Because of the low H_2S concentration (30-35 percent) of this stream, however, a three-stage Claus plant is required for 97 percent sulfur recovery. Other carbonation schemes produce a more concentrated feed stream and thus require a smaller Claus plant, but AI claims the overall economics favor their process concept. Calculations indicated that H_2S concentrations as high as 37 vol. percent may be possible, in which case a two-stage Claus plant may be sufficient. This performance has not been demonstrated on a continuous, full-scale basis yet, but, if feasible, would result in considerable capital savings for a 500 Mw ACP installation.

General

Experience with similar equipment in the pulp and paper industry indicates that the ACP regeneration system will require 2 to 3 shutdowns per year for maintenance. Presumably this work can be accomplished during scheduled boiler outages or during off-peak load periods.

Since an entire ACP system has not been operated in integrated fashion even on a pilot scale, it is possible that contaminants from one processing area may present operational problems in another area. Of particular concern are the impurities introduced with fly ash, coke, or coal in the gas cleaning and reduction areas that might recrystallize in downstream equipment and cause plugging.

4.5 Status of Development

All of the process steps in the ACP system have been tested on a 1000 scfm scale or are considered proven technology by Atomics International. This section presents a concise history of the developmental work to date as well as plans for additional testing in the near future.

The spray dryer has been tested on pilot units at Bowen Engineering's North Branch, New Jersey facility and at Southern California Edison's Mohave Station. Preliminary tests at Bowen were made with a 7 ft ID scrubber using simulated flue gas at 1,000-1,8000 scfm and 400-2,200 ppm SO_2. The scrubber demonstrated greater than 95 percent SO_2 removal with centrifugal atomization of sodium carbonate slurry.

The Mohave tests were made with a 5 ft ID spray dryer using a slip stream of power plant flue gas. The scrubber removed greater than 90 percent of the 400-1500 ppm SO_2 in the inlet gas flowing at rates up to 1375 scfm. Parametric studies at the Mohave plant also fixed the optimum L/G at 0.3 gal/1000 scf and the optimum carbonate stoichiometry at 2.0 lb carbonate added per lb SO_2 removed. The cyclone also demonstrated 95 percent to 99 percent collection efficiency under conditions similar to those expected for coal-fired applications (4-6 grain/scf inlet). Tests indicated the NO_x removal capability of the ACP spray dryer is limited to less than 5 percent.

A final series of tests at Bowen facility on simulated flue gas extended the data base to flow rates of 4,000 scfm, SO_2 concentrations of 7,300 ppm, and higher gas temperatures. These tests generally confirmed the results obtained at the Mohave station, although it was determined that higher gas temperatures (400°F-500°F) are required for SO_2 concentrations above 4000 ppm to insure a dry product.

In October, 1975, tests were run on a spray drier with three centrifugal atomizers in place of the single atomizer. These tests indicated that the three atomizer configurations would achieve the same removal efficiencies as the single large atomizer with one-third of the scrubbing liquor going to each of the atomizers. During these same tests, one atomizer was shut off and the scrubbing liquor was distributed equally between the remaining two atomizers to examine the effect of an atomizer failure. When operating with only two atomizers, an equivalent SO_2 removal efficiency was achieved which tends to indicate that excess atomization capacity may be included in the AI design. It is important to note that these tests were conducted in the 7-foot Bowen scrubber and may not represent the operations of a large 40-foot spray drier. The test results do, however, lend confidence in the use of multiple atomizers in the spray drier.

The molten salt regeneration unit is a backmix reactor that has been operated at feed rates equivalent to a 1.25 Mw plant. Reducer development has proceeded from bench-scale to pilot-scale at AI test laboratories. Early bench-scale work was performed in 1973 to establish reaction conditions, determine off-gas characteristics, and obtain kinetic data. Based on encouraging results from this equipment, two series of pilot-scale tests were conducted using a 3 ft ID and 12 ft high refractory-lined reducer. Actual spent sorbent was fed to the reducer at rates up to 150 lb/hr (equivalent to 1.25 Mw for 3.5 percent S coal). These tests confirmed earlier bench-scale results and provided adequate design data for scale-up. Specifically, these tests demonstrated the following:

1) Optimum reaction temperatures are in the range of 1700°F-1900°F to effect the reduction reaction and maximize CO_2/CO ratio in the off-gas,

2) At optimum conditions, CO_2/CO ratios were typically in the range of 10 to 15 to 1, well above design requirements,

3) Steady-state reduction of 90 percent to 95 percent of the incoming sodium salts can be achieved with approximately 4 wt percent excess coke, and

4) CO_2 content of the off-gas was only 25 percent as compared to design basis of 35 percent due to high relative heat losses from bench-scale reducer. Larger reducers should achieve 35 percent CO_2 in the off-gas without any difficulty.

The pilot-scale reducer tests described above were performed in semibatch mode since it was not possible to operate with continuous withdrawal and quenching of the melt. Recently, modifications have been made to the reducer to allow continuous melt withdrawal. Tests are planned for Fall, 1975 to demonstrate operation in this mode. The modified reducer will also feature four downward sloping air inlet ports designed to improve bed mixing and product uniformity.

Bench scale tests are currently underway to investigate the feasibility of using coal as the carbon source in the ACP reducer. These tests have indicated the use of coal as the source of carbon reductant is technically feasible. The coal ash, however, is difficult to filter from the green liquor in downstream process operations. Minor modifications are planned to the rotary vacuum drum filter for applications using coal as the ACP reductant.

In a related development, AI has identified and investigated the use of the molten salt reactor as a coal gasifier. Pilot-scale tests have been successful and plans are being made to install a 5 ton/hr gasifier plant at the Norwalk Harbor Generating Station of Connecticut Light and Power Company by 1977. Because of the similar processing concepts involved in gasifying coal in a molten salt mixture and molten salt reduction, results from the gasification work will help to define problems and solutions involved in using coal as the reducing agent in ACP.

Laboratory tests were performed during 1974 to study the physical and chemical aspect of melt quenching. Up to 1200 lb/hr of melt was quenched and dissolved in a 14 ft^3 tank. The key to reliable quenching was found to be dispersion of the melt into fine droplets and maintaining the bulk dissolving liquor at or near its boiling point.

Laboratory tests have been performed to establish the filtering characteristics of fly ash suspended in green liquor. Results from these tests have been used to specify design parameters for the filter equipment. It was also found that a simple washing technique can reduce the sodium losses associated with the filter cake to less than 1% of the cake weight, thereby reducing carbonate makeup.

To investigate this processing area in both the ACP and the coal gasification process, AI is currently constructing a spent salt regeneration test loop. The test loop will circulate green liquor formed by the dissolution of reducer melt in water at rates up to 25 gpm (35 Mw equivalent). A number of equipment pieces will be piped into the loop including three different types of pumps, a rotary vacuum filter, liquid cyclone, solids settler, shell-and-tube heat exchanger, and various valves and piping materials. The equipment should be ready for testing by Fall, 1975.

Pilot-scale tests have been performed at AI laboratories to determine optimum operating conditions and column configurations for the three processing steps in the AI carbonation scheme. Four-inch ID glass columns were designed to handle gas and liquid flow rates equivalent to about 0.5 Mw. As indicated in Section 4.4, all of the key design criteria were met during pilot operation, save complete demonstration of the CO_2 absorption reactions due to equipment limitations (i.e., number of trays). The carbonation equipment is currently undergoing modifications to include expanded liquid and gas throughputs (about 1 Mw equivalent), modified tray design and more trays, and automated instrumentation and controls. Further testing will begin in September to optimize column performance and obtain additional scale-up and design information.

The Tampella Recovery Process (TRP), now licensed in the U.S. by Babcock & Wilcox, was identified as the best commercially available carbonation process for ACP application. A preliminary engineering study by B&W showed that TRP technology is suitable for use as the ACP carbonation step. A 50 Mw equivalent test of a TRP stripper carried out at Alizay, France confirmed the technical feasibility of this application.

Commercially available Claus plants will be used to convert the H_2S produced in the ACP to elemental sulfur. No developmental work has been deemed necessary to investigate this specific application. Primary design responsibility for the Claus plant will vest with the supplier.

4.6 Scale-Up Considerations

Scale-up of the ACP equipment will be based on pilot test data and vendor specifications and/or guarantees. Scale-up factors for the major equipment pieces associated with a 500 Mw installation are summarized in Table 4-2.

Each of the four spray dryers in the 500 Mw design will be six times larger than the pilot test dryer and handle almost 70 times the gas volume. As mentioned earlier, superficial gas velocities in the full-scale unit will be on the order of 4 ft/sec while those in the pilot unit were only 2.5 ft/sec. The gas residence time in the larger dryer (10 seconds) will be nearly twice that of the test dryer (5 seconds).

There is a question here as to the reliability of spray dryer scale-up when such key design parameters as gas

TABLE 4-2

SCALE-UP FACTORS FOR 500 MW ACP INSTALLATION

Equipment Piece	Size Tested	Throughput	Size for 500 Mw System (Number Required)	Throughput per Piece	Scale-up Factor
Spray dryer	7 ft ϕ	4000 scfm	42 ft ϕ (4)	273,000 scfm	6
Cyclones	2.75 ft ϕ	4000 scfm	6 ft ϕ (64)	17,875 scfm	2
Electrostatic Precipitator	-	355,000 acfm	-	366,000 acfm	1
Reducer	3 ft ID	400 lb/hr	19 ft ID (2)	33,500 lb/hr	6
Rotary Filter	1 ft x 2 ft	0.5 gpm	6 ft x 8 ft (1)	30 gpm	25
Precarbonator	4 in. ϕ	0.5 gpm	9½ ft ϕ (1)	320 gpm	29
Carbonator	4 in. ϕ	0.5 gpm	12 ft ϕ (2)	280 gpm	36
Crystallizer	4 in. ϕ	0.5 gpm	17 ft ϕ (2)	350 gpm	51
Decomposer	-	-	12 ft ϕ (1)	320 gpm	-
Claus plant	Standard Practice		Skid Mounted, 3-Stage Unit	130 ton/day	1

velocity and residence time differ by as much as a factor of two. In addition, it has been Radian's experience that gas and liquid distribution can be serious problems in large-scale gas scrubbers and could significantly affect SO_2 absorption efficiency. However, the residence time increase should be a positive factor, and AI (and Bowen) claim that superficial gas velocity is not critical to spray dryer performance.

The reducers for the 500 Mw unit will be 19 ft in diameter and handle 33,500 lb/hr as compared to the 3.0 ft ID pilot vessel processing 400 lb/hr. More importantly, the superficial gas velocity for the full-scale reducers is about 1 ft/sec as compared to 2.0 to 2.5 ft/sec for the test reactor. This specification leads to a reducer scale-up factor of over 6 to 1 which appears somewhat high in light of the novelty of this technology.

The full-scale ACP installation includes a 6 ft diameter by 8 ft long rotary vacuum drum filter as compared to the 1 ft by 2 ft rotary filter installed in the spent salt regeneration test loop. Neither of these filters is considered large for equipment of this type and scale-up should not be a problem providing the solids in the green liquor prove filterable. Recent tests have shown, however, that filtering coal ash is difficult. Modifications to the rotary vacuum drum filter are planned for coal filtering applications.

The largest scale-up factors for the full-scale ACP system are associated with the carbonation equipment. These will be 29, 36, and 51 for the precarbonator, carbonator, and crystallizer tower, respectively. Liquid throughputs will be over 700 times that of the pilot columns although gas velocities will be approximately equal. On the positive side, however, is the fact that carbonation technology is already in a high state of development due to extensive work in the pulp and paper industry. Presumably, AI will be able to apply some of this technical expertise to the design and scale-up of its own equipment. The Tampella Recovery Process has already been applied as the carbonation step for a similar application on an equivalent 50 Mw basis so that scale-up to a full-size unit (500 Mw) will involve an overall factor of 10.

The Claus plant required for the ACP regeneration scheme will process almost 130 ton/day of molten sulfur. Claus plants of this capacity are already in operation so that no scale-up problems are anticipated in this area.

Although not directly related to equipment scale-up, the extent of integration of process components is an important consideration in assessing any system's potential for successful application. Unfortunately, in the case of AI's ACP, this integration has yet to be demonstrated. Extensive developmental work has been performed for each of the major processing areas but little effort has been made to date to link the steps together. It is not possible to tell whether contaminants from one area will present operational problems in another. This is a particularly important consideration with respect to the reduction and carbonation equipment. AI recognizes this to be a disadvantage for their system, and is planning to demonstrate the integrated process in a smaller, single-train plant (30 to 100 Mw) before building a full-scale plant.

4.7 Utility Applicability

The Aqueous Carbonate Process is well suited for application to new power plants but, due to the space requirements, may experience some difficulties when retrofitted to an existing plant. Because of the low gas velocities maintained in the spray dryers, these vessels will be rather large, on the order of 42 ft in diameter. Based on plot plans included in the EPA Qualifications Statement, all of the equipment in the gas cleaning subsection can be placed in a plot with approximate dimensions of 200 ft by 200 ft, or 40,000 ft^2. If the ash cyclones ahead of the spray dryers are excluded, as might be expected in a retrofit application, the plot reduces to approximately 200 ft by 160 ft, or 32,000 ft^2.

Ground space requirements for the regeneration section are less critical for retrofit applications since this equipment could be located in a peripheral plant area, or completely off-site, if desirable. To do this, spent sorbent could be conveyed either pneumatically or mechanically to the regeneration site and regenerated scrubbing solution pumped back to the gas cleaning area. The exact equipment arrangement will vary according to the specific requirements of the power plant. The regeneration section ground space requirements for a 500 Mw installation are estimated as 250 ft by 200 ft, or 50,000 ft^2. This requirement includes approximately 14,400 ft^2 for the Claus plant. The total ground space requirement for a new 500 Mw installation, then, is approximately 90,000 ft^2.

Other than ground space requirements, there are no technical factors that would limit the successful application of the ACP to either new or existing coal-fired power plants. Installation of the ACP equipment will have a minimal impact on boiler area operations since the only demands the system makes are for small quantities of condensate make-up and low-pressure steam.

The two major raw materials required by the ACP are Na_2CO_3 and petroleum coke. Soda ash (or Na_2CO_3) is currently produced at a rate near 7,000,000 ton/yr and sells for nearly

$52/ton. Overall availability is considered high. Based on current production rates, enough petroleum coke is produced in this country to supply over 200,000 Mw of ACP installations (US-064). Petroleum coke availability is regarded as high by AI, especially on the East or West Coast or any area of high refinery operations concentration. The alternative of using coal would obviously be attractive if delivered coke costs were excessively high.

4.8 Economic Assessment

Raw material and utility costs have been estimated for AI's Aqueous Carbonate Process installed on a new 500 Mw coal-fired boiler subject to the basis reviewed earlier. These costs are based primarily on the figures presented in AI's proposal to the EPA (RO-158), but have been reviewed for consistency and modified somewhat to reflect Radian's cost basis.

Capital cost estimates for this system which were prepared by AI indicate that over half of the capital costs (almost 54 percent) are associated with the gas cleaning section, most due to equipment costs. The remainder of the costs are almost evenly distributed between the reduction (14 percent), carbonation (11 percent), and sulfur production (12 percent) areas. A small amount (10 percent) is allotted for construction, facility services, and utilities. These figures are taken directly from the EPA Qualifications Statement.

The annual raw material and utility cost estimates for a new, 500 Mw ACP installation are summarized in Table 4-3. The revisions made to the AI estimate include (1) a Na_2CO_3

TABLE 4-3

RAW MATERIAL AND UTILITY COSTS FOR THE AQUEOUS CARBONATE PROCESS

Basis: 500 Mw; 3.5 Percent Sulfur Coal; 5,260 Hours
Per Year of Full Load

Processing Area	Chemical & Energy Consumption		Cost (10^3 $ per year)
Gas Cleaning	Power:	8,100 kw	851.9
	Process Water:	1,440 GPH	0.6
	Sodium Carbonate:	870 lb/hr	118.9
		SUBTOTAL	$971.4
Reduction, Quenching & Filtration	Power:	930 kw	97.6
	Process Water:	21,000 GPH	8.8
	Cooling Water:	124,000 GPH	19.6
	Petroleum Coke:	13,000 lb/hr	1,545.6
		SUBTOTAL	$1,671.6
Carbonation	Power:	910 kw	95.7
	Process Water:	1,900 GPH	0.8
	Cooling Water:	136,000 GPH	21.4
		SUBTOTAL	$117.9
Sulfur Production	Power:	620 kw	65.2
	Fuel Oil:	210 gal/hr (31.7 MM Btu/hr)	383.5
		SUBTOTAL	$448.7
	TOTAL RAW MATERIAL & UTILITY COSTS		$3,209.6

UNIT RAW MATERIAL AND UTILITY COST 1.2 mills/kwh make-up rate of 2288 ton/yr; and (2) $45/ton charge for coke.* These costs result in estimated raw material and utility cost per unit of energy produced of 1.2 mills/kwhr.

4.9 Process Summary

The Atomics International Aqueous Carbonate Process utilizes an aqueous sodium carbonate (Na_2CO_3) solution to sorb sulfur dioxide from flue gas and produce a dry scrubber product which is subsequently treated to regenerate the scrubbing solution and produce sulfur. Design features unique to this process are the use of a spray dryer as an SO_2 scrubber and the use of a high temperature (1700-1900°F) pool of molten salts to completely reduce the sodium salts formed in the spray dryer to sodium sulfide. Process sections have been independently demonstrated but have not been integrated into a complete system to determine what effects, if any, one process section may have on another.

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* Delivered price based on price-controlled oil; production cost ∿ $7/ton, and delivered price of ∿ $25/ton is probable in near future.

5.0 CATALYTIC/IFP AMMONIA SCRUBBING PROCESS

The Catalytic/IFP flue gas desulfurization process is a regenerable process which removes SO_2 from flue gases by absorption in an aqueous ammonium sulfite and bisulfite solution and converts the sulfur values to elemental sulfur. Basically, the process is Catalytic's ammonia wet scrubbing operation combined with a regeneration scheme developed by Institut Francais du Petrole (IFP).

Catalytic Inc. is a multi-faceted corporation providing a wide range of engineering, construction, and maintenance services. IFP is a French research organization which works on problems of the petroleum industry including removal of H_2S from process streams. IFP has developed a "Liquid Claus" process in which an H_2S-SO_2 stream is reacted at relatively low temperature in an organic solvent to produce molten elemental sulfur.

5.1 Process Description

The Catalytic/IFP Process can logically be divided into the following processing areas as illustrated in the process flow diagram shown in Figure 5-1.

1) SO_2 Absorption

2) Spent Brine Reduction

3) Sulfur Production

4) Ammonia Separation and Recycle

Each of these processing areas will be discussed in this section.

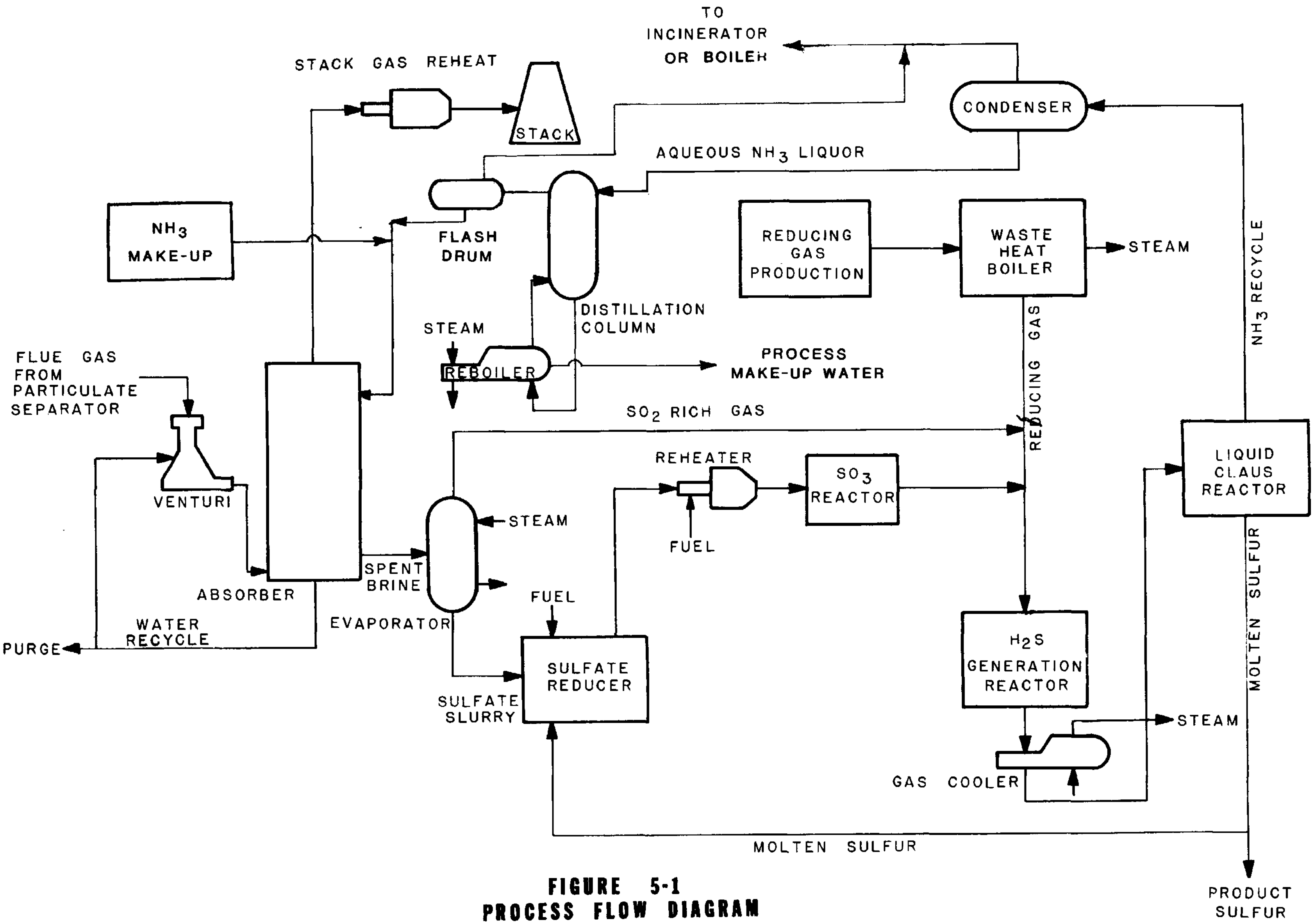

FIGURE 5-1
PROCESS FLOW DIAGRAM
CATALYTIC/IFP
AMMONIA SCRUBBING PROCESS

SO_2 Absorption

The Catalytic/IFP Process utilizes a venturi humidifier/cooler to prepare the hot flue gas for contact with the aqueous ammonia scrubbing liquor. The flue gas is adiabatically saturated with water and $HC\ell$ is removed. The venturi operates with its own water loop, independently of the absorber section. A 25 gpm chloride and fly ash purge stream amounting to about 10% of the recycle liquid is continually removed, neutralized with lime, and sent to the ash pond for disposal.

Catalytic employs a staged absorber similar to that shown in Figure 5-2 utilizing mist eliminators before and after each stage. The staged operation of the absorber is required to produce a liquor with a high sulfur concentration for regeneration while maintaining low salt concentrations on the final stage to reduce ammonia losses and the potential for plume formation.

The primary reactions occurring in the absorber are shown by the following equations:

$$SO_2 + (NH_4)_2SO_3 + H_2O \rightarrow 2NH_2HSO_3 \qquad (5\text{-}1)$$

$$SO_3 + (NH_4)_2SO_3 \rightarrow (NH_4)_2SO_4 + SO_2 \qquad (5\text{-}2)$$

$$O_2 + 2(NH_4)_2SO_3 \rightarrow 2(NH_4)_2SO_4 \qquad (5\text{-}3)$$

Flue gas from the venturi enters the first of three or four absorption stages at a flow rate of approximately 500,000 scfm and a temperature of 125°F (250 Mw modules). The scrubbing liquor, an ammonia salt solution, passes countercurrently to the gas at a rate of 17 gallons/1,000 scf flue gas.

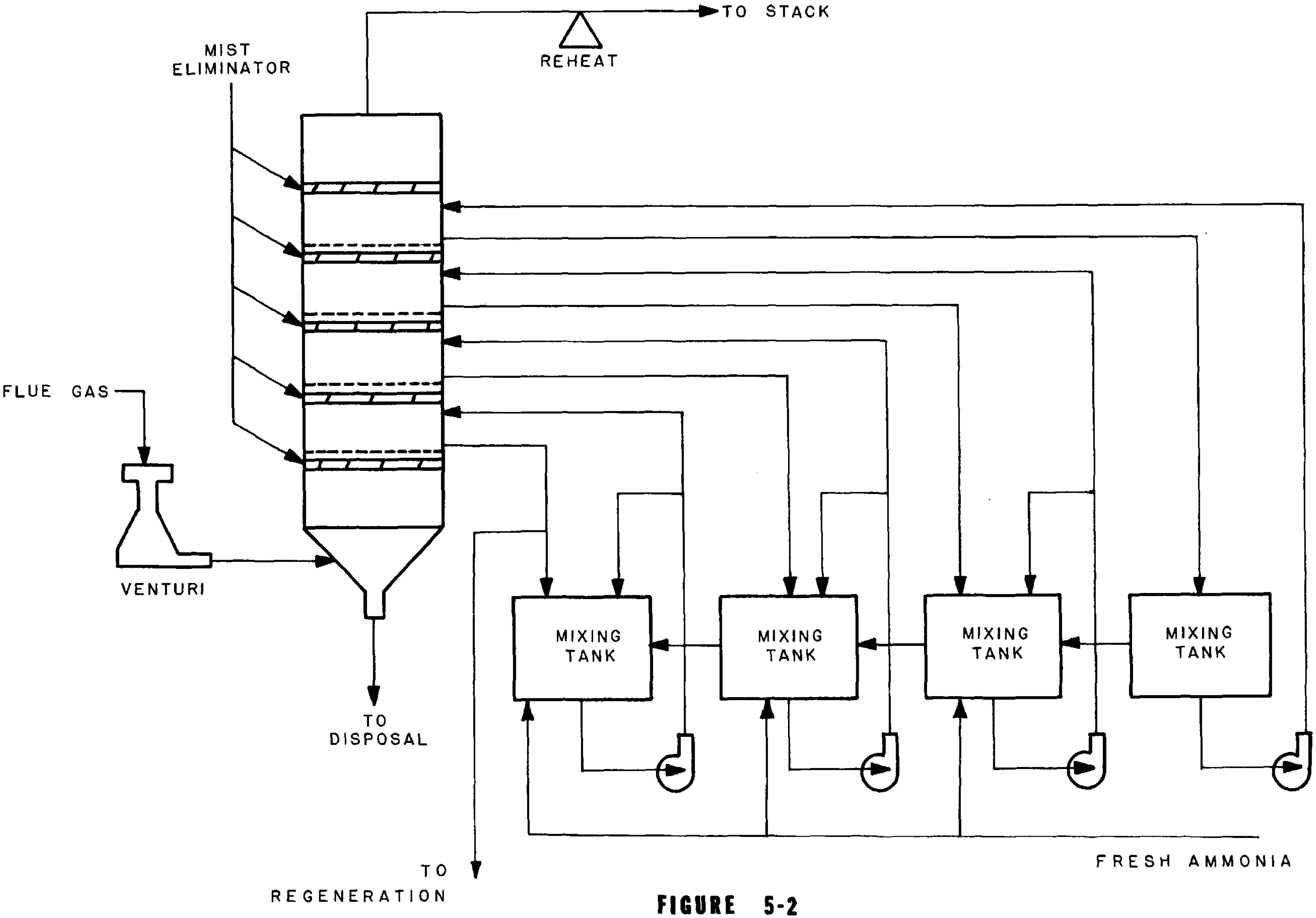

FIGURE 5-2
PROCESS FLOW DIAGRAM
ABSORPTION SECTION
CATALYTIC/IFP PROCESS

The concentration of ammonia salts in the liquor decreases going up the absorber. Clean gas from the absorber is reheated with distillate oil, steam, or low Btu gas to 175°F before release to the atmosphere.

Each absorber stage has a separate liquid feed and effluent stream as shown in Figure 5-2. A portion of the liquid effluent stream from each stage is fed to the next lowest stage through a series of mixing tanks. Concentrated liquor from the bottom stage mixing tank is drawn off for regeneration.

Ammonia returning from the regeneration section is introduced primarily to the first and second stage mixing tanks. Scrubber feed liquor from these tanks is used to remove most of the SO_2 in the first and second stages of the absorber. The third stage also provides some SO_2 removal capability due to the ammonia salts present in the liquor. The upper stage is operated with no direct addition of ammonia. Process make-up water is primarily introduced to the fourth and final stage to reduce the concentration of dissolved ammonia and sulfur due to fuming considerations. No SO_2 is removed by the top stage in the absorber.

Interstage tankage equivalent to two weeks of absorber output at design capacity (about 15×10^6 gallons) separates the absorption and regeneration process areas. This tankage allows the regeneration section to operate with a more constant throughput.

Spent Brine Reduction

The spent brine solution from the absorption system enters a steam-heated plate-type forced-circulation evaporator operating at 300°F to evaporate the volatiles, thus reducing the load on the sulfate reducer. A portion of the feed is evaporated and thermally decomposed to form a vapor overhead of primarily H_2O, NH_3, and SO_2 by the following reactions:

$$(NH_4)_2SO_3 \rightarrow 2NH_3 + H_2O + SO_2 \qquad (5\text{-}4)$$

$$NH_4HSO_3 \rightarrow NH_3 + H_2O + SO_2 \qquad (5\text{-}5)$$

The thermal decomposition of ammonium sulfites also forms elemental sulfur, thiosulfates, thionates, and other non-volatile sulfur compounds by disproportionation in addition to the primary products indicated above. This vapor mixture is ultimately combined with the output of the sulfate reducer and fed to the H_2S generation reactor. Steam equivalent to the amount used in the evaporator is generated elsewhere in the process.

The salt slurry from the evaporator bottoms contains the sulfates present in the brine from the absorber since the sulfates do not decompose at the operating conditions of the evaporator. This concentrated sulfate slurry continues to the sulfate reducer where under the conditions of high temperature (600-700°F), a reducing atmosphere, and in the presence of sulfur or a sulfur compound acting as a reducing agent a vapor overhead of SO_2, NH_3, and H_2O is formed as shown below:

$$(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3 \qquad (5\text{-}6)$$

$$2NH_4HSO_4 + S \rightarrow 3SO_2 + 2H_2O + 2NH_3 \qquad (5\text{-}7)$$

Reaction heat is provided by an oxygen-starved submerged combustor which bubbles hot gases up through the melt. The combustion zone is above the sulfate reducer with the hot gases exhausted directly to the melt through a submerged entry tube.

A small amount of SO_3 is also formed during decomposition of the ammonium sulfate as follows:

$$(NH_4)_2SO_4 \rightarrow 2NH_3 + H_2O + SO_3 \qquad (5\text{-}8)$$

Vapor overhead from the sulfate reducer passes through a reheater to heat the gas to the SO_3 decomposition temperature and proceeds to a catalyzed SO_3 reduction reactor where the SO is converted to SO_2 in the presence of a reducing gas by the following reactions:

$$SO_3 + CO \rightarrow SO_2 + CO_2 \qquad (5\text{-}9)$$

$$SO_3 + H_2 \rightarrow SO_2 + H_2O \qquad (5\text{-}10)$$

Feed to the H_2S generation reactor is made up from a gasification product reducing gas stream, the overhead vapor from the forced circulation evaporator, the gas out of the SO_3 reduction reactor and combustion products from a heater that burns low Btu gas to provide heat for the reactions. H_2S is generated from these streams according to the following reactions:

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O \qquad (5\text{-}11)$$

$$SO_2 + 3CO + H_2O \rightarrow H_2S + 3CO_2 \qquad (5\text{-}12)$$

These are catalytic reactions which occur at about 900°F.

Product gas from H_2S generation is cooled in a waste heat boiler before being fed to the "Liquid Claus" sulfur production unit. A ratio of H_2S to SO_2 slightly greater than 2:1 must be maintained in this sulfur production stream for successful conversion to elemental sulfur. The steam generation in the waste heat boiler is of the same magnitude as the steam consumption in the evaporator.

Sulfur Production

H_2S-SO_2 feed to the sulfur production unit is reacted at a relatively low temperature (300°F) in a catalyzed organic solvent to produce elemental sulfur:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \tag{5-13}$$

Product sulfur is drawn from the bottom of the reactor for ultimate disposition to either sales or storage. A small quantity of this molten sulfur, about 25 moles/hr or 7 percent of the SO_2 sorbed, may be required as a reducing agent in the sulfate reducer.

Ammonia Separation and Recycle

The purpose of this section is to produce high quality process water and to separate ammonia from the noncondensables contained in the overhead stream from the Liquid Claus unit. Water with amines present should not be used on the top stage of the absorber as the partial pressure of ammonia in the water would contribute to ammonia emissions. Also, the water used to adiabaticably saturate the flue gas in the venturi must have a low ammonia content due to fuming considerations. In addition, overhead gas from the Liquid Claus unit contains H_2S and COS that must be separated from the NH_3 before the NH_3 is recycled to the absorption section.

The overhead stream from the Liquid Claus unit is sent to a condenser for initial separation of NH_3 and water from the noncondensables. The noncondensable gases which include H_2S and COS are burned in an incinerator or the boiler. The aqueous condensate which still contains small amounts of H_2S, COS, and CO_2 is routed to a distillation column where an essentially pure water stream is taken off the reboiler and gas composed of H_2O, NH_3, COS, H_2S, and CO_2 goes overhead and is sent to a flash drum. The bottom of the flash drum is an aqueous ammonia stream that is recycled to the absorber. The flash drum overhead is routed through a tail gas scrubber and combusted in the boiler or an incinerator.

5.2 Environmental Considerations

The primary environmental consideration of a flue gas desulfurization process is, of course, SO_2 removal efficiency. Nevertheless, attention must be directed to the overall environmental effect of the process for any evaluation to be meaningful.

The Catalytic/IFP aqueous ammonia process can be designed for up to 99 percent removal of SO_2. To achieve this removal, more stages with associated liquor loops would be added to the absorber between the third and fourth stages of the base case design as shown in Figure 502. These additional stages would result in about 10 percent more ammonia passing through the system than in the design for 90 percent removal and in an increase of roughly 8-10 percent in the raw material and utility costs.

Temporary surges in SO_2 concentration in the flue gas might be handled in several ways. The system could utilize the

15 percent excess absorber capacity specified in the Catalytic design approach and rely on interstage tankage to buffer the regeneration section from the temporarily increased load. A capital cost is associated with the excess capacity so that a tradeoff exists between flexibility and costs. Longer term alternatives would be:

1) increase the IFP regeneration capacity,

2) install additional tankage as necessary and try to market the spent brine to the fertilizer industry, or

3) neutralize the spent brine with lime, recover the ammonia, and dispose of the sludge.

The solution chosen would depend on the particular circumstances.

Most of the particulate matter in the flue gas from the electrostatic precipitator should be removed in the Catalytic/IFP Process. The brine out of the absorber is filtered upstream of the regeneration section to remove most of the particulates scrubbed out of the flue gas in the absorber with the remaining particulates probably concentrating in the sulfate reducer. A small purge is specified in the Catalytic flow sheet, but the quantity of solids or the long term impact of any solids buildup in the sulfate reducer is uncertain.

The effect of the Catalytic/IFP Process on NO_x emissions is unkown. It is assumed to be negligible although this capability has not yet been examined by Catalytic.

Chlorides from the coal are expected to be present in the flue gas as gaseous HCl and as very fine chloride salt particulates. Greater than 90 percent removal of chlorides with a venturi is reported by Catalytic and Ametek, a venturi equipment vendor (NA-248, HA-353). The chlorides build up in the venturi water loop, which is independent of the closed ammonia absorber loop. A purge stream of approximately 25 gpm, is taken off the venturi recycle, neutralized with lime, and sent to the ash pond to control chloride build-up in the venturi water. Catalytic reports that chlorides not removed in the venturi pass through the process to the NH_3-CO_2-H_2O stripper where they are taken off the bottom of the column as an aqueous stream containing an estimated 75 lb/hr of $NH_4C\ell$. This purge would be treated within the battery limits of the Catalytic/IFP Process.

One environmental consideration unique to ammonia scrubbing is the formation of an ammonium salt plume. Formation of such a plume, especially one that eventually oxidizes to very fine (0.2 micron) ammonium sulfate particles, would be a serious process handicap.

Catalytic has developed a patented "fumeless" technology for operation of the absorber including control strategy and process instrumentation. This technology has been applied to a four-inch diameter bench-scale absorber at the Catalytic laboratory and to the TVA Colbert Station 1.2 Mw pilot plant during EPA-TVA-Catalytic cooperative runs. Catalytic reports they have successfully operated the bench scale unit in a "fumeless" mode and can predict the onset of fuming. Test program constraints at the Colbert pilot plant prevented any clear demonstration that a fume did not form in the scrubber. The potential for formation of a plume will be discussed further in the Sections 5.4 and 5.5 dealing with Design Considerations and Status of Development.

There are very few purge streams from the Catalytic/IFP ammonia scrubbing, and all of them are small. For a typical 500 Mw installation, the purge from the venturi recycle has a flow of roughly 25 gpm and contains primarily calcium salts and fly ash. An estimated 2 gpm stream containing fly ash and a very small quantity of ammonium salts will result from the brine particulate filter in the regeneration section. The purge from the venturi and the filter will probably be sent to the ash pond. These waste streams should not present serious disposal problems due both to the species and the quantities present.

If the sulfate reducer is not included in the design, a sulfate purge stream would be necessary. Commercial ammonium sulfate crystallizers are in use in the fertilizer and steel industry. However, the impurities in the spent brine are different from those usually present, and, therefore, it is not known what difficulties might be encountered in crystallization. Ammonium sulfate as a by-product does have a potential advantage over other sulfate by-products because a market for it may exist in the fertilizer industry.

5.3 Material and Energy Balances

An integral part of this process evaluation was the performance of material and energy balance calculations. The results of these calculations were used to estimate the process raw material and energy requirements plus the size and seriousness of waste streams and approximate sizes of equipment.

Catalytic prepared an energy and material balance including stream compositions specifically for the 500 Mw Radian base case. Radian calculations were compared with those supplied by the process vendor. In general, close agreement was found with Catalytic results with the exception of a 13 MM Btu/hr increase in steam consumption in the IFP regeneration section for the 500 Mw base case installation. This change results in a zero net steam consumption for the process rather than a reported steam credit of 13 MM Btu/hr (SL-063, AI-020).

Detailed stream-by-stream compositions for the process will not be reported due to secrecy agreement limitations. Process raw material and utility requirements are, however, summarized for each section of the process in Table 5-1.

5.4 Design Considerations

The key design features for each processing area will be discussed in this section. Possible alternate processing methods or sequences and the ability of the system to overcome potential problems will also be examined.

SO_2 Absorption

The basic design problem associated with an ammonia absorber is elimination of the ammonia plume. To prevent fuming, HCℓ should be removed from the flue gas before it contacts the ammonia, and the partial pressures of NH_3, SO_2, and H_2O must be maintained at such levels that ammonium salts do not form in the gas phase.

The venturi humidifier/cooler cools the flue gas, removes some particulates, and removes more than 90 percent of the chlorides. The pressure drop on the water side is about 80 psi with a near zero pressure drop on the gas side (NA-248). The materials of construction must withstand erosion and corrosion at a pH as low as 1. Catalytic has proposed lining a

TABLE 5-1

ESTIMATED UTILITY AND RAW MATERIAL CONSUMPTION FOR CATALYTIC/IFP PROCESS

Basis: 500 Mw; 3.5% (wt.)

Process Section	Ammonia (lb/hr)	Lime (lb/hr)	Low Btu Gas (MM Btu/hr)	H_2O (M gal/hr)	High Pressure Steam (MM Btu/hr)	Reducing Gas (MM Btu/hr)	Electricity (Mw)
SO_2 Absorption	160	560	-	24	77	-	7.2
Spent Brine Reduction	-	-	50	11	-	103	1.4
Sulfur Production	-	-	-	1	-	-	0.2
Ammonia Separation and Recycle	-	-	20	-	-	-	0.2
Total	160	560	70	36	77	103	9.0

mild-steel venturi with acid/abrasion resistant tile over FRP. A water quench is not acceptable because adequate chloride removal would not be obtained.

The absorption tower is designed to remove SO_2 from the flue gas in the lower stages and ammonia and other volatiles from the cleaned gas in the upper stages. A minimum of weepage and entrainment and semi-independent operation of each stage is required to avoid ammonia fuming. Should a fume appear, the stage-to-stage material and energy balances must be adjusted to eliminate this condition and thus bring the process into fumeless operation.

A sulfuric acid injection system could be installed on the top stage of the absorber to control any excess ammonia emissions that might occur. This acid wash would be for emergency situations such as an upset in the system. However, if the ammonia emissions cannot be satisfactorily controlled by adjustment of material and energy balances, the acid wash may be desirable as a standard operating procedure.

Oxidation in the absorber is important, not as a potential for production of a sulfate purge stream but due to the impact on the sulfate reducer. Increased oxidation generates more sulfates and, therefore, a greater energy requirement for the sulfate reducer. Sulfates are important from the standpoint of energy consumption rather than as a result of environmental considerations or raw materials consumption.

The IFP regeneration unit is designed to process 80 percent of the designed output of the absorber. Interstage tankage between absorption and regeneration acts as surge capacity, and, as a result, the liquor can be fed to the regeneration section at a more constant rate. The backend could operate for about 70 days with the absorber (and the boiler) at 100 percent load. In the event of an overload on the system, the problem would probably be approached similarly to a SO_2 surge as discussed in Section 5.2. Catalytic feels that the regeneration section will not be overloaded as a consequence of the above design basis, however, since the boiler load will probably be cycling up and down rather than maintained at design capacity.

Spent Brine Reduction

Problems with the forced circulation evaporator may result from its handling of salt slurry mixtures. Due to potential fouling problems, Catalytic has spared this evaporator in their design.

It is important that the transport system which conveys evaporator bottoms to the sulfate reducer be designed to provide a steady flow rate so that a relatively constant heat rate can be maintained in the sulfate reducer. An auger type slurry pump is consequently used to maintain an extremely constant flow of slurry feed and facilitate steady state operation.

The sulfate reducer operates at a temperature of 600-700°F in a reducing atmosphere to thermally decompose sulfates and other volatile components in the spent brine while recovering the ammonia for ultimate recycle.* The load on the sulfate reducer is a function of oxidation of absorbed SO_2 to $SO_4^=$ in the system. Catalytic's material balance indicates about 10

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*Ammonia does not decompose at this temperature due to the inert reducing atmosphere present.

percent oxidation of absorbed SO_2. This calculation is based on data from their bench scale absorber and from the TVA pilot plant. If oxidation should prove to be greater at a commercial installation, an increase in energy requirements for the sulfate reducer would result. If the unit should not operate satisfactorily as designed, an electric induction furnace would be substituted for the submerged combustor. The induction unit would be more expensive to operate and, therefore, not as desirable.

If elemental sulfur is used as a reducing agent, only a small recycle of product molten sulfur (approximately 25 lb-moles/hr, or about 7 percent of the SO_2 sorbed) would be necessary. Recycle of sulfur to the sulfate reducer may not be necessary, however. Part of the NH_4HSO_4 will decompose to NH_3 and SO_3 at these high temperatures. More significantly, H_2S gas leaving the "Liquid Claus" unit could serve as a reducing agent if it is scrubbed out by contact with a side stream of scrubber solution. The H_2S reacts with $(NH_4)_2SO_3$ to form $(NH_4)_2S_2O_3$ (ammonium thiosulfate) which can reduce $(NH_4)_2SO_4$. The reducing materials formed by disproportionation in the evaporator, as previously discussed, also act as reducing agents in the sulfate reducer.

The compatibility of the SO_3 reduction catalyst with reducing gas produced from coal gasification is not known. The effects of halides and particulates which may be present in gasification product gas on the catalyst should be investigated. The catalyst must also be selective so that it will not decompose ammonia at the operating temperature of 900°F.

The H_2S generator must be designed and controlled to produce a 2:1 ratio of H_2S to SO_2 in the feed gas to the Claus reactor. The reducing gas which has been cooled during cleanup, and the streams from the SO_3 reactor and forced circulation evaporator require addition of heat to maintain the reaction temperature. The heat for H_2S generation is supplied by combustion of low Btu gas in a heater with the combustion gases subsequently fed to the H_2S generator with the other feed streams. The reaction temperature in the H_2S generation reactor is controlled below the decomposition point (over 1200°F) of ammonia in a reducing atmosphere. A water quench for emergency temperature control is provided. Any effect of a CO/H_2 reducing gas produced from coal on the catalyst is unknown, but reducing gas entering the reactor must be halide and particulate free. Interfacing this unit with a reducing gas production system is a potential problem.

Sulfur Production

The IFP "Liquid Claus" reactor also operates below the decomposition temperature of ammonia. An organic solvent serves as a medium for heat and mass transfer. The tail gas is routed through a water quench to prevent loss of sulfur and the organic solvent from the Claus unit. Claus plant sulfur production technology is well established and should not present design problems.

Ammonia Separation and Recycle

Standard technology is used for ammonia separation and recycle processing steps. A condenser and NH_3-CO_2-H_2O stripper are used for ammonia separation and recycle. Emissions of non-condensable gases from the ammonia condenser could present a problem as they would contain H_2S and COS. The potential problem is readily averted, however, by combusting the non-condensables in either the boiler or a tail gas incinerator.

5.5 Status of Development

The primary contribution of Catalytic, Inc. to ammoniacal scrubbing of SO_2 laden flue gases is their patented "fumeless" technology for operation of an ammonia system without formation of fine particulates and the associated visible plume. Developmental work for SO_2 removal by ammonia scrubbing has been done primarily by the Tennessee Valley Authority which has operated a 1.2 Mw pilot plant on a coal fired boiler since 1970. Some of the conclusions drawn from the TVA work (TE-188) are as follows:

1) Absorption efficiency is 90 percent or greater over a wide range of operating conditions.

2) The removal efficiency for given operating conditions can be reliably predicted.

3) Fly ash has a negligible effect on SO_2 removal.

4) Stainless steel is a satisfactory material of construction in the absorber loop.

5) Plume formation while producing a concentrated spent brine ($C_A>12$)* is controllable by proper operation of the scrubber.

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* C_A is the moles of ammonium as sulfite and bisulfite (active ammonia) per 100 moles of water.

Catalytic has operated their own bench-scale unit in their laboratory. They had a four-inch diameter four-stage absorber from which they gained operating data and reported the ability to turn the plume on and off. A 4,000 ACFM engineering Optimization Unit on a coal-fired industrial boiler was started up in the Spring of 1976, and operated for about four months. Catalytic reports greater than 80 percent removal of SO_2 with the pilot unit. A mechanical collector was present in the original system, but modifications including the addition of an electrostatic precipitator are planned. Catalytic reported that the opacity of the gas out of the pilot unit was less than the opacity of the feed to the pilot unit. Adequate cleanup of the feed gas must be accomplished before fumeless operation can be demonstrated.

IFP currently has three ammoniacal brine recovery process installations that are integrated to varying degrees. Information on these units is presented in Table 5-2. None of these installations is integrated with a Catalytic absorber, but the composition of spent brine which is processed is basically the same. The only fully integrated unit is located at the Champagne EDF power plant where the IFP regeneration unit has operated successfully for over a month. The Maruzen installation is also expected to start-up in the near future.

After one month's continuous run, the system at Fuji was inspected and minor modifications were performed. Since the Fuji unit is located at a refinery with fuel gas and H_2S available, the capability to operate using coal gasification product gas has not been demonstrated. The sulfate reducer was found to be intact with no signs of corrosion and the lining of the sulfate reducer entry tube showed no ill effects from the thermal shock associated with high-temperature gas.

The vaporization of spent brine in the forced-circulation evaporator was shown to follow laboratory work. Previous problems with introducing the sulfate slurry to the sulfate reducer at a slow but very constant rate were overcome.

IFP's "Liquid Claus" reactor is considered proven technology as more than 20 of these units exist at commercial installations. The only unit operation not tested at Fuji was reducing gas/H_2S generation. However, at the EDF plant in France, preliminary operation of the H_2S generation reactor has not indicated any chemistry or equipment problems when integrated with a methane produced reducing gas.

TABLE 5-2

IFP AMMONIACAL BRINE RECOVERY INSTALLATIONS

	Feed Gas		
Owner	Source	Flow (scfm)	SO_2 (ppm)
Maruzen	FCC purge gas and Claus incinerated gas	16,000	2,600
Fuji	Claus incinerated gas	6,000	10,800
EDF	Oil-fired utility boiler	50,000	1,800

The fully integrated system at the EDF utility will be a good source of confirmation for the results at Fuji, and since it is an integrated 25 Mw unit, will constitute a small demonstation size facility. Scale-up based on this plant would be much more desirable than from the 6,000 scfm installation at Fuji.

5.6 Scale-Up Considerations

Process areas which are currently under development will be examined on an individual basis initially with a discussion of the degree of integration following. Scale-up factors necessary to construct a 500 Mw FGD system will also be presented where appropriate.

Absorption

Catalytic has not constructed and operated an absorber employing their fumeless design technology other than a four-inch diameter laboratory model. They are proposing 250 Mw absorber modules which would require absorber tower diameters to be on the order of 40 feet to maintain an 8 ft/sec superficial gas velocity. The absorber modules would have to be scaled-up from Catalytic's laboratory scale absorber (four-inch diameter) until data from the 2 Mw Calvert City pilot facility is obtained.

Although the scale-up factor is large, scale-up of the absorber of SO_2 removal should not present a major process limitation as commercial ammonia scrubbing units are operating and are available today. On the other hand, scale-up of Catalytic's "fumeless" operating technology remains to be demonstrated as all operating ammonia scrubbing processes suffer from fuming problems.

Spent Brine Reduction

A totally integrated 25 Mw IFP regeneration process is located at the EDF Champagne power plant. To date, this system has operated in a totally integrated mode for about one month. The forced-circulation evaporator, sulfate reducer, and sulfur trioxide reducer were all demonstrated at Fuji, but the H_2S generation facility was not tested, due to available H_2S at the Fuji site.

The EDF installation after undergoing preliminary unit testing has operated for one month. Results from this demonstration size operation should provide first-hand data on the probability of success in scaling up this system to a full-size module. The scale-up factor of EDF data will be about 17:1 for 500 Mw capacity.

Sulfur Production and Ammonia Separation and Recycle

Technology to be employed for sulfur production ("Liquid Claus Process") and ammonia separation (condensers, NH_3-CO_2-H_2O strippers) are commercially available and should present no scale-up problems. Compatibility with the reduction section when processing H_2S produced from coal based reducing gas remains to be demonstrated.

5.7 Utility Applicability

Limitations on applicability of the Catalytic/IFP Process to a new facility should not be serious. The rather large space requirement of about 65,000 square feet for the absorption section of a 500 Mw installation reported by Catalytic (AI-020) could hinder the ability to retrofit the process. There would be two absorbers for 500 Mw of capacity, each about 40 feet in diameter and about 70 feet tall. The regeneration section and ancillary space requirements are about 150,000 square feet but could be located anywhere on the plot and should not be a major process limitation.

Air Products and Chemicals, parent company of Catalytic, is a producer of ammonia and will guarantee raw material availability. The current ammonia price is less than \$300 per ton. The cost of ammonia is not a large operating expense due to the small amount of make-up required.

A 500 Mw facility is expected to require about 103 MM Btu/hr of reducing gas for the H_2S generator. Low Btu gas requirements for the sulfate recuver (about 50 MM Btu/hr) were included as fuel rather than reducing gas under utility requirements in the evaluation criteria table.

Catalytic's approach to design of a system includes the capability to operate from boiler idle up to full load plus 15 percent. Using valve trays in the absorption tower and two towers for 500 Mw capacity, the turndown capability of the absorption section is reported to be 20 percent of full load. This turndown is obtained by operating one absorber at 40 percent capacity.

Tankage capacity for two weeks operation is also specified between the absorption and reduction processing areas. This tankage will act as a buffer zone and allow adjustments in the back end as necessary to follow the front end load fluctuations. Likewise, the tankage allows the front end to return to full load rapidly by having fresh brine already stored. This would overcome the time lag associated with regeneration.

5.8 Economic Assessment

A detailed economic analysis of the Catalytic/IFP Process will not be attempted as it is beyond the scope of this project. Detailed raw material and utility costs based on energy and material balance calculations will be presented. Also, the relative contribution of each section of the process to these costs will be discussed.

The capital costs for a Catalytic/IFP regenerable flue gas desulfurization process on a 500 Mw boiler burning coal with 3.5 percent sulfur by weight were supplied to Radian by Catalytic, Inc., specifically for this evaluation. The contribution of each process area (excluding reducing gas production) to these costs is as follows:

Processing Area	Percent
Ammonia Scrubbing	46
Claus Gas Preparation	33
Claus Reaction and Ammonia Stripping	21

Raw material and utility costs were determined based on energy, fuel, water, and raw material consumption for each process area based on the energy and material balances (Table 5-3). Relative operating costs of each processing area, excluding capital charges, are as follows:

Processing Area	Percent
Ammonia Scrubbing	26
Claus Gas Preparation	65
Claus Reaction and Ammonia Stripping	9

5.9 Process Summary

The Catalytic/IFP Process is a wet process that employs an ammonium sulfite liquor to absorb SO_2 from flue gas

TABLE 5-3

RAW MATERIAL AND UTILITY COSTS FOR CATALYTIC/IFP FLUE GAS DESULFURIZATION PROCESS

Basis: 500 Mw, 3.5% Sulfur Coal (Wt.),
5,260 hours per year at full load

Process Area	Chemical & Energy Consumption		Annual Cost (10^3 $)
Ammonia Scrubbing	Power: 7,200 kw		757
	Steam: 77 MM Btu/hr		416
	Process Water: 23,700 GPH		10
	Raw Materials:		
	Ammonia 160 lb/hr		114
	Lime 560 lb/hr		32
		SUBTOTAL	1,329
Claus Gas Preparation	Power: 1,400 kw		147
	Fuel (low Btu gas): 50 MM Btu/hr		1,052
	Reducing Gas: 103 MM Btu/hr		2,167
	Boiler Feed Water: 11,300 GPH		9
	Raw Materials: -		-
		SUBTOTAL	3,375
Claus Reaction and Ammonia Stripping	Power: 400 kw		42
	Fuel (low Btu gas): 20 MM Btu/hr		421
	Process Water: 1,000 GPH		Neg
	Raw Materials:		
	Organic Solvent 16 lb/hr		26
		SUBTOTAL	489
	TOTAL ANNUAL RAW MATERIAL AND UTILITY COSTS		5,193
	UNIT RAW MATERIAL AND UTILITY COST		2.0 mills/kwhr

streams. The unique features of the process are the staged absorber, the sulfate reducer, and the "Liquid Claus" reactor. A H_2/CO rich low Btu gas produced from coal is utilized to reduce ammonium sulfate and sulfur trioxide, to produce hydrogen sulfide for the Claus reaction, and to incinerate the tail gas. Major problems associated with this process are formation of a "blue plume" and availability of design and operating data for the sulfate reducer and H_2S generator. Ammonia scrubbing and the IFP regeneration are considered developed processes. Also, Catalytic has developed a fumeless technology for operation of the absorber, but has not yet constructed and operated an absorber for a system. Operation of the 2 Mw pilot plant at Calvert City could be a source of scale-up data for Catalytic. Economics for the Catalytic/IFP Process seem to have a reasonable basis and indicate the competiveness of the raw material and utility costs. With the advent of the 25 Mw IFP unit on an EDF boiler in France and the 2 Mw Catalytic installation at Calvert City, the process has the potential to be in a very good position to scale up to a commercial application.

6.0 CITRATE/PHOSPHATE BUFFERED ABSORPTION PROCESS

The Citrate/Phosphate flue gas desulfurization process is a regenerable process which removes SO_2 from flue gases by absorption in an aqueous sodium citrate or sodium phosphate solution. Sulfur values are converted to elemental sulfur in subsequent processing steps. The U.S. Bureau of Mines pioneered the development of the Citrate Process with developmental work also being done by Arthur G. McKee and Company, Peabody Engineering, and Pfizer, Inc. Stauffer Chemical Company offers the Phosphate Process which is licensed to Chemical Construction Corporation (CHEMICO).

6.1 Process Description

The Citrate/Phosphate Process can be systematically divided into the following four processing areas as illustrated in the process flow diagram in Figure 6-1.

1) SO_2 Absorption

2) Regeneration and Sulfur Separation

3) Sulfate Purge

4) H_2S Generation

Each of these processing areas will be discussed in this section.

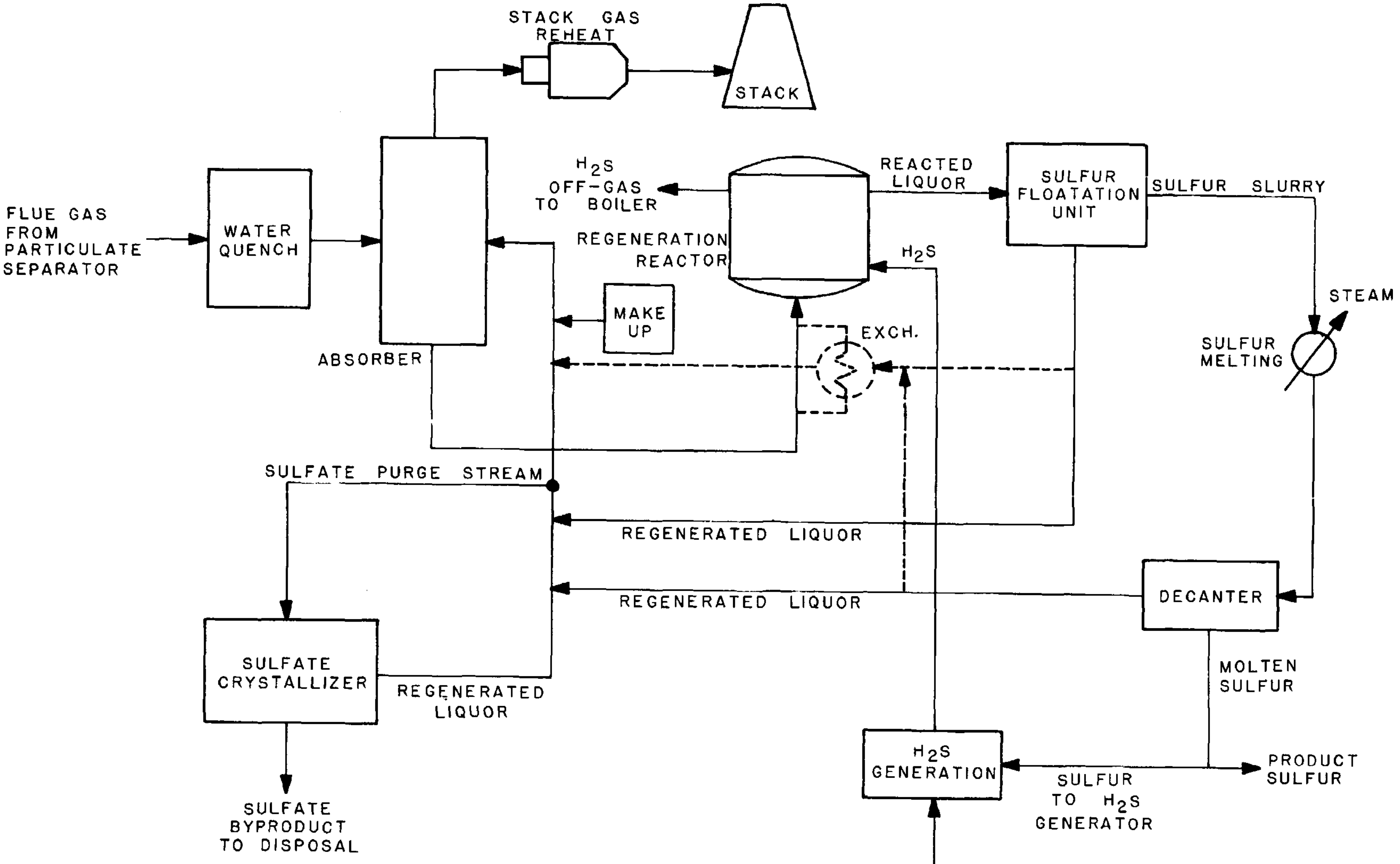

FIGURE 6-1
PROCESS FLOW DIAGRAM
CITRATE/PHOSPHATE PROCESS

SO_2 Absorption

The Citrate/Phosphate Process employs a water quench to cool the flue gas before it enters the absorber. One process developer uses deionized water to cool the flue gas to a temperature slightly above its adiabatic saturation temperature while not contributing to the build-up of chlorides in the system. The gas is further cooled to its adiabatic saturation temperature by evaporating some of the water from the absorber solution in the base of the absorber. Other vendors adiabatically saturate the flue gas with an independent process water loop in the quencher. For the 500 Mw Radian base case, a 210 gpm purge stream from the quencher recycle water is continuously drawn off and sent to the client's treatment facility for neutralization and disposal. A demister after the quencher prevents carryover of entrained water to the absorber. Deionized water is specified as it has lower chloride concentrations than process water, and, therefore, would not contribute as greatly to chloride buildup in the closed-loop system.

Impingement tray or packed bed absorbers are used for SO_2 removal depending upon the process developer. The scrubbing solution is composed mainly of sodium citrate or sodium phosphate, plus a small quantity of sodium sulfate which builds up in the absorber loop.

The primary reactions occurring in the absorber are given in the equations below:

$$SO_2 + H_2O \rightarrow HSO_3^- + H^+ \qquad (6\text{-}1)$$

$$HCit^= \text{ or } HPO_4^= + H^+ \rightarrow H_2Cit^- \text{ or } H_2PO_4^- \qquad (6\text{-}2)$$

Flue gas from the quencher enters the absorber at a flow rate of approximately 250,000 scfm and a temperature of 125-130°F (125 Mw modules). The saturated clean gas from the absorber is reheated with steam to 175°F prior to discharge to the atmosphere.

The scrubbing solution flows countercurrent to the flue gas at a rate of 10 to 16 gallons/1000 scf of gas depending on the vendor's design basis. The solution enters the tower SO_2 lean at a pH of 4.0 to 5.0 and leaves SO_2 rich at a pH of 3.5 to 4.5. The citrate/phosphate solution acts as a buffer maintaining this range of pH throughout the system. Citric acid and sodium carbonate, or phosphoric acid and sodium hydroxide are added to the absorber feed as necessary to maintain this pH range and a buffer concentration of .5 M citrate or 1.0 M phosphate, respectively.

Regeneration and Sulfur Separation

The SO_2-rich citrate/phosphate solution from the absorber is pumped directly to a series of regeneration reactors. An H_2S-rich gas stream is bubbled through these reactors countercurrent to the liquor. H_2S is admitted through an open pipe or sparger which produces large bubbles that are sheared into tiny bubbles by high speed agitators. The product gas has an H_2S to SO_2 mole ratio of 2.06 to 1 providing 3 percent H_2S above stoichiometric requirements. The excess H_2S-rich gas out of the last reactor is vented to the boiler or an incinerator.

The overall regeneration reaction is shown by Equation 6-6.

$$SO_{2\,(\ell)} + 2H_2S \rightarrow 3S + 2H_2O \qquad (6\text{-}3)$$

The chemistry of the regeneration reactions is much more complex than that indicated since chemical intermediates are involved in the rate-limiting step. Process vendors do not agree on the chemistry of the process. Available information has been based partly on a theoretical investigation of the reactions occurring in the process. The roles and reactions of intermediates such as polythionates do not appear to be completely understood. A thorough and exact understanding of the chemistry of the process remains to be demonstrated.

The regeneration reactors operate at a temperature of about 130°F in one design and at a temperature of 150-160°F in the others. The liquor from the absorber may be heated to the reaction temperature of 150-160°F by heat exchange with the hot regenerated solution out of the sulfur separation units (see the dotted line in Figure 6-1).

The sulfur slurry out of the last regneration reactor is pumped to a sulfur flotation unit where the sulfur is separated from the citrate liquor by kerosene or air flotation and from the phosphate liquor by a proprietary process. The buffered solution, essentially free of elemental sulfur, is recycled to the absorber feed, and a sulfur slurry of 50 percent solids (kerosene flotation) or 7-15 percent solids (air flotation) is continuously removed from the flotation cell. Slurry transporting equipment routes the sulfur slurry through a steam heated sulfur melter, operating at 280°F, to a decanter for final separation of molten sulfur from the regenerated citrate/phosphate liquor. Product molten sulfur for disposal or sale accounts for 1/3 of the sulfur produced while 2/3 of the molten sulfur is recycled for H_2S production.

Sulfate Purge

SO_2 oxidation results in a by-product of Na_2SO_4 that must be purged from the system. The sulfate purge system for the Citrate Process is based on an assumed oxidation of absorbed sulfur dioxide ranging from about one to four percent depending on the vendor design basis. Oxidation of roughly one percent is used as a basis in the Phosphate Process. Radian has chosen three percent oxidation for this evaluation since it is a conservative average of reported values. The purge systems could operate intermittently whenever analysis indicated high levels of sulfate in the solution or on a continuous basis as desired by the vendor. The reactions that result in the formation of sulfates are given below.

$$HSO_3^- + \tfrac{1}{2}O_2 \rightarrow HSO_4^- \qquad (6\text{-}4)$$

$$3S_2O_3^= + 2H^+ \rightarrow 2SO_4^= + H_2O + 4S \qquad (6\text{-}5)$$

The Na_2SO_4 is removed from the citrate/phosphate solution by crystallization. The solution is vacuum crystallized, centrifuged, melted to redissolve the hydrated sodium sulfate, recrystallized, and dried to anhydrous Na_2SO_4. The magnitude of the solid by-product for the Radian 500 Mw base case ranges from about 500 lb/hr anhydrous Na_2SO_4 to 2,000 lb/hr anhydrous Na_2SO_4 depending on the amount of oxidation occurring in the system.

H_2S Generation

One unique feature of the Citrate/Phosphate Process is the external generation of H_2S. Reducing gas or commercially pure hydrogen is reacted with 2/3 of the product sulfur to form H_2S for use in the regeneration step.

The H_2S gas leaves the H_2S generation unit at a temperature of about 400°F and is routed to the regneration reactor where the operating temperature is 130-160°F. Since unreacted sulfur vapors will condense upon cooling, care must be taken to prevent plugging of the gas lines by condensed sulfur. There are several proposed methods for reducing this problem. The H_2S gas could be cooled to near the liquor temperature by a water quench or heat exchanger to condense the sulfur vapors upstream of the regeneration reactors or it could be transported by heat traced pipe to the reactors with the sulfur vapors condensing in the reactors.

6.2 Environmental Considerations

The primary environmental consideration for any flue gas desulfurization process is the effectiveness of SO_2 removal. Other potential environmental effects associated with the process will also be considered and evaluated.

The Citrate/Phosphate Process can be designed to remove greater than 99 percent of the inlet SO_2. This would be accomplished by the addition of absorber trays or packing, depending on the absorber design. Both modifications would result in an increased pressure drop across the absorber.

The primary limitation in designing the packed tower for 99 percent removal is the number of transfer units and, therefore, the height of the tower. The liquor pumping rate would also increase about 10 percent for 99 percent removal.

One vendor has designed for 99 percent SO_2 removal using six impingement trays with an associated pressure drop of about 11 inches of water. To achieve a removal efficiency of 90 percent, the vendor reports the L/G would simply be reduced by about one-half with a similar reduction in the load on the rest of the system.

Temporary surges in SO_2 concentration may be controlled by increasing the L/G in the absorber. This would lead to a temporary overload on the regneration section and result in only partial regeneration of the citrate/phosphate liquor. One vendor has demonstrated in a pilot plant, however, that SO_2 absorption will occur while using a partially regenerated liquor. Since the effectiveness of the solution declines after each cycle, the duration and magnitude of the surge that the system can handle in this manner require examination.

Particulates remaining in the flue gas out of the electrostatic precipitator will be almost totally removed in the Citrate/Phosphate Process. Some will be removed in the quencher with the majority removed in the absorber. Vendors report that particulates such as fly ash are compatible with their systems. Pilot plants have been operated on coal-fired boilers and on oil-fired boilers with fly ash injected into the flue gas stream. Although the process has been demonstrated to operate in the presence of particulates (0.1-0.2 gr/scf), they are undesirable as they can contaminate the product sulfur. As a result, a regeneration reactor feed filter is included in some designs to remove acid insoluble species picked up in the absorber; acid soluble species dissolve in the liquor of the closed loop system.

The potential for removal of NO_x by the Citrate/Phosphate Process has not yet been examined. The effect of the process on NO_x emissions is, however, assumed to be negligible.

Chlorides are expected to be present in the flue gas. Some of the chlorides will be removed in the water quench, but the majority will be removed in the absorber and, therefore, will build up in the liquor of the closed loop process. Since chloride buildup might lead to corrosion in the system, some type of control may be necessary. Allowing the chloride concentration in the liquor to reach a steady state level of about 6,000 ppm and using appropriate materials of construction to prevent corrosion has also been proposed. This steady state level is maintained since some chlorides are present in the sulfate purge steam from the liquor loop. A venturi with an independent water loop might be used to remove chlorides prior to the absorber to reduce chloride concentrations in the system although no vendor has proposed this.

An environmental consideration unique to one developer of the Citrate Process is the potential hydrocarbon emission associated with the use of kerosene in the sulfur flotation unit. Vapor recovery techniques were not employed at the pilot plant, and high kerosene evaporation losses were observed. Although costly, the application of vapor recovery technology can probably be used to solve this emission problem.

The discharge of a phosphate solution would be environmentally unacceptable. Process developers feel, however, that the phosphate solution can be totally contained within the system. Nevertheless, some type of preventive design and operation will be necessary to guard against discharge of the phosphate solution. Although the citrate solution is biodegradable, discharge of this solution would not be desirable either. The chemical and biological oxygen demands as reported by Pfizer (KO-168) are .553 (COD) and .387 (BOD) pounds of oxygen per pound of anhydrous sodium citrate, respectively.

The use of externally generated H_2S gas as a reactant in the regeneration sections constitutes another potential environmental problem. Approximately 800 lb moles per hour of H_2S will be required for the Citrate/Phosphate Process for a 500 Mw installation.

Purge streams resulting from this process on a 500 Mw boiler include the sodium sulfate by-product, solids from a filter between the absorber and the regeneration reactors, and a stream from the quencher recycle loop. The by-product amounts to about 500 lb/hr of anhydrous Na_2SO_4 based on one percent oxidation and about 2,000 lb/hr based on four percent oxidation. The solids from the reactor feed filter are acid insoluble particulates picked up in the absorber. This stream will vary with coal composition but is expected to be very small. Vendors proposing a recycle loop on the quencher have an acid purge of about 210 gpm that will be neutralized by the client's water treatment facility.

If a water quench is used to cool the H_2S gas to the operating temperature of the regeneration reactors, a sour water purge stream would be produced and would have to be treated. The size and composition of this purge stream will depend on the amount and composition of gas to be cooled.

6.3 Material and Energy Balances

Vendor material and energy balance calculations were not prepared specifically for the 500 Mw Radian base case. The material and energy balances supplied by the vendors were based on the same 3.5 percent (wt.) sulfur content of the coal but differed in such areas as system size, SO_2 removal efficiency, coal heating value, and flue gas composition. Also, detailed stream compositions were not provided.

Results of Radian material and energy balance calculations were compared with those of the process vendors. In general, close agreement was found with the developers results although reconcilable differences were present due to variations in proposed designs and assumptions. For example, one vendor has proposed 90 percent removal of SO_2 as a design basis while some others use 98 to 99 percent. The reported oxidation of absorbed SO_2 to sulfate varies from 1.3 percent to 4 percent depending on the design basis. Energy and material balance calculations were performed on the basis of 90 percent removal of SO_2 and 3 percent oxidation of absorbed SO_2 to sulfate.

Due to secrecy agreement limitations detailed stream analyses for the process will not be reported. However, process raw material and energy requirements are summarized for each section of the process in Table 6-1.

6.4 Design Considerations

The key design features for each processing area will be discussed in this section. Possible alternative processing methods or sequences and the ability of the system to overcome potential problems will also be examined.

SO_2 Absorption

The flue gas is cooled with a water quench to its adiabatic saturation temperature. A gas pressure drop of about 2 inches of water occurs across the quencher and the demister. Quencher circuit materials of construction must be resistant to erosion and corrosion at a pH as low as 1. The quencher might also be designed for total evaporation of demineralized water with no acidic water loop resulting.

TABLE 6-1

ESTIMATED UTILITY AND RAW MATERIAL CONSUMPTION FOR CITRATE/PHOSPHATE PROCESS

Basis: 500 Mw: 3.5 Percent (wt.) S; 5,260 Hours
Per Year at Full Load

Process Section	Buffer (lb/hr)	Na_2CO_3 (lb/hr)	NaOH (lb/hr)	Steam (MM Btu/hr)	H_2O (M gal/hr)	Reducing Gas (MM Btu/hr)	Electric Power (Mw)
SO_2 Absorption	27^1 37^2	$1,750^1$	270^2	79	32	-	6.2
Regeneration and Sulfur Separation	-	-	-	25	-	-	.7
Sulfate Purge	-	-	-	14	-	-	.3
H_2S Generation	-	-	-	-	-	103	.8
TOTAL	27^1 37^1	$1,750^1$	270^2	118	32	103	8

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[1] Citrate Process

[2] Phosphate Process

An alternate processing method would be to use a venturi that would perform the duties of the quencher, plus remove HCℓ and some SO_3 from the flue gas. The venturi would also aid slightly in particulate removal. The advantages of the venturi must be weighed against its greater operating cost. No vendor proposes a venturi for the Citrate/Phosphate Process.

The absorption tower uses trays or packing, depending upon the design specified by the vendor, to provide a gas-liquid contacting area for SO_2 absorption. A packed tower using an open packing proposed by one developer will result in a pressure drop across the absorber of about three inches of water while an impingement tray tower will result in about eleven inches of water pressure drop. However, if 99 percent removal is required, a packing with more surface area will be used in the packed tower with an increase in pressure drop to about eight inches of water. The increase in the pressure drop across the tray tower associated with 99 percent removal efficiency should be very small.

The absorber liquor for the Citrate Process is a 0.5 molar sodium citrate solution while the Phosphate Process uses a 1.0 molar solution of sodium phosphate. Liquor pH values vary from about 4.5 to 5.0 at the scrubber inlet, absorber temperatures vary from about 125 to 130°F, and absorber liquid to gas ratios (L/G) vary from about 10 to 16 gallons per 1,000 scf of flue gas. Although optimum operating conditions have not yet been determined, each process has successfully demonstrated SO_2 removal ability at its design conditions.

The liquor loading ranges from 3 to 10 gm SO_2/liter of solution at the absorber outlet. The liquor loading is determined by such factors as temperature, liquor concentrations, and pH which vary with the process depending upon the developer.

The adiabatic saturation temperature of the flue gas entering the absorber is an important parameter in design of the absorption process area. The sulfur dioxide loading (gm of absorbed SO_2 per liter of solution) is a strong inverse function of the liquor temperature. For a gas stream containing 2,000 ppm SO_2 and a liquor composed of 0.5M citrate, 0.5M sodium hydroxide, and 0.25M sodium thiosulfate, the equilibrium loading is about 9 gm SO_2 per liter of solution at a temperature of 112°F and about 6 gm SO_2 per liter of solution at a temperature of 130°F.

Vendors have completed psuedo economic-technical optimizations of the liquor concentrations in the Citrate/ Phosphate Process. For the Citrate Process, the region of reasonable operation is 0.4 to 0.6 molar citrate. For the Phosphate Process, this region is 0.8 to 1.2 molar phosphate. Since the approach to equilibrium absorption varies with process vendor, the liquor loading for a given liquor concentration also varies. In general, a higher liquor concentration results in higher liquor loadings. However, the increase in liquor loading proceeds at a slower rate than the increase in concentration.

Korosy, Gewanter, Chalmers, and Vasan (KO-150) have presented the calculated solubility of SO_2 in water solutions at various pH values. They indicate that at a pH of 4 the solubility of SO_2 in water solutions is about 3 grams/liter, while at a pH of 5 the solubility is about 30 grams/liter. These calculated values indicate the sensitivity of the solubility of SO_2 in water solutions to pH.

Liquor loading is also a primary factor in sizing the regeneration section. A high liquor loading produces less solution for regneration and, therefore, a smaller regeneration unit. The low liquor loading in the Citrate/Phosphate Process relative to other wet regenerable processes, however, results in high capital and operating costs for the regeneration equipment.

Regeneration and Sulfur Separation

Regeneration reactor design is based on both reaction rate and mass transfer considerations. One developer reports that reaction kinetics are limiting; the mass transfer to H_2S into the solution occurs more rapidly than reactions involving intermediates formed in the system. Another vendor reports that the regeneration reaction is mass-transfer limited in the first reactor where the ratio of H_2S concentration to aqueous SO_2 concentration is lowest and kinetics limited in the other two reactors where the ratio of H_2S concentration to aqueous SO_2 concentration is greater. A model has been developed from pilot plant data which uses the above principles in designing the regeneration reactor system.

As previously indicated developers do not agree on the chemistry of the process. As a result, different rate controlling reactions are reported for the regeneration step. The intermediate reactions reported by some vendors are presented below. Reaction 6-9 is felt to be the slowest, and therefore, the rate-controlling step.

$$4HSO_3^- + 2H_2S \longrightarrow 3S_2O_3^= + 2H^+ + 3H_2O \qquad (6\text{-}6)$$

$$3HSO_3^- + H_2S + H^+ \longrightarrow S_4O_6^= + 3H_2O \qquad (6\text{-}7)$$

$$S_4O_6^= + H_2S \longrightarrow 2S_2O_3^= + 2H^+ + S \qquad (6\text{-}8)$$

$$S_2O_3^= + 2H_2S + 2H^+ \longrightarrow 3H_2O + 4S \qquad (6\text{-}9)$$

Another developer reports that thiosulfate ($S_2O_3^=$) reduction is too slow to be the principle reaction for the production of elemental sulfur. The following two reactions are suggested and evidence to support this mechanism is reported. Reaction 6-10 was determined to be the rate controlling step.

$$SO_2 + H_2S \rightarrow H_2S_2O_2 \qquad (6\text{-}10)$$

$$H_2S_2O_2 + H_2S \rightarrow 3S + 2H_2O \qquad (6\text{-}11)$$

The concentration of hydrogen sulfide in the gas fed to the regeneration reactors is another design consideration since it directly affects reactor size. Vendor specifications vary from a 39 percent to a 96 percent nominal H_2S gas stream.

Small bubbles of H_2S are desirable in the regeneration reactors to provide more liquid-gas interface. Pilot plants have used an open pipe or sparger generating large bubbles with a high tip-speed agitator shearing the large bubbles into tiny bubbles. The regeneration section will precipitate sulfur and, therefore, must be designed to minimize plugging problems.

An H_2S stream produced on site from reducing gas or hydrogen and sulfur will contain some elemental sulfur vapors. Potential condensation and solidification of these vapors upon contact with the liquor in the regeneration reactors must be considered in determining the method of introducing H_2S gas to the reactors.

Kerosene and air flotation units have been examined for use in separating the precipitated sulfur from the liquor out of the regeneration reactors. The flotation unit should produce an essentially sulfur-free citrate/phosphate solution for recycle, and a sulfur stream containing as little liquor as practicable. Kerosene flotation yields a powdery damp sulfur of about 50 percent solids, while air flotation yields a pumpable slurry of about 7-15 percent solids. The sulfur slurry produced with air flotation contains more liquor than that produced by kerosene flotation. As a result, systems using air flotation will have more solution exposed to the sulfur melting and decanting steps. A potential for buffer and thiosulfate degradation exists at the operating temperature of about 280°F in the melting and decanting steps. Kerosene flotation may affect product sulfur quality and may result in significant kerosene losses. An open vessel was used at the pilot plant with kerosene losses of about 90 lb/net ton of sulfur produced. A vapor recovery system on an enclosed vessel might reduce these losses to an acceptable level.

The sulfur melter is simply a steam heat exchanger that raises the temperature of the sulfur slurry out of the flotation cell to about 280°F. The equipment transporting the sulfur/liquor mixture to the melter and the melter itself must be designed for the appropriate slurry service and to minimize any potential for plugging. The decanter is a pressurized gravity flow separation unit. Molten sulfur is continuously or intermittently taken off the bottom while clear liquor is recycled to the absorber. All of the sulfur transfer lines must, of course, be heat traced to prevent solidification.

Citrate is subject to thermal decomposition during the sulfur melting step while phosphate is not. Some reported laboratory data indicates about one pound of citrate decomposition per ton of sulfur melted after 100 hours in an autoclave at 300°F (equivalent to about 300 melting cycles). However, the citrate solution showed no reduction in capacity to absorb SO_2

after 100 hours at 300°F. At a pH of 4.5, 260°F, with .5 molar citrate, the citrate decomposition was reported to be 0.11 percent per hour based on other laboratory data.

Thiosulfate ($S_2O_3^=$) decomposition was also examined in a continuous sulfur melting system at 275°F. For each ton of sulfur melted, about 3 pounds of sulfate was formed. For the Radian 500 Mw base case, thiosulfate decomposition would account for about 4 percent of the sulfate purge stream (assuming 3 percent oxidation in the system).

Sulfate Purge

The sulfate purge section should present no unique design problems. A crystallizer, refrigeration unit, and Glauber's Salt ($Na_2SO_4 \cdot 10\ H_2O$) separator are used to remove the sulfates from the citrate/phosphate solution. The by-product is then dried to produce anhydrous Na_2SO_4. The unit will be operated intermittently to control the sulfate concentration in the liquor. It should be noted that commercial sulfate removal units have not been operated at any of the pilot plants using the Citrate/Phosphate Process.

One design is based on producing hydrated sodium sulfate ($Na_2SO_4 \cdot 10\ H_2O$). However, for this evaluation it was assumed that the hydrated Na_2SO_4 is dried to give the anhydrous Na_2SO_4 as proposed by another vendor. The anhydrous form of the by-product was chosen since it is easier to handle, store, and transport than hydrated Na_2SO_4.

The relatively low oxidation in the Citrate/Phosphate Process has been largely attributed to the presence of thiosulfate ions. Laboratory data establishes a steady state concentration of about 0.25 moles/liter of thiosulfate in the circulating liquor. The effect of thiosulfates on oxidation in a citrate/phosphate solution based on laboratory data is presented in Table 6-2.

TABLE 6-2

EFFECT OF THIOSULFATE ON OXIDATION IN THE CITRATE/ PHOSPHATE PROCESS

Buffer	pH	Additive	Percent Oxidation
.5 M Citrate	5.0	.3 M Thiosulfate	0.15
.5 M Phosphate	5.0	.3 M Thiosulfate	0.20
.5 M Citrate	5.0	--	0.8-1.0

H_2S Generation

Three main points will be discussed relating to design considerations for the H_2S generation unit. These points are the concentration of H_2S gas produced, plugging, and turndown.

Hydrogen sulfide (H_2S) generation design considerations in the Citrate/Phosphate Process are different from most FGD processes that require H_2S because H_2S is produced externally by reacting elemental sulfur with hydrogen or reducing gas (H_2/CO). A gas stream with a high H_2S concentration is desirable for use in the regneration section. A higher H_2S partial pressure and mass transfer rate results in reduced reactor size. The H_2S concentration will, however, be determined mainly by the composition of the reducing gas or hydrogen fed to the H_2S generation unit rather than the process selected for H_2S generation.

Plugging of the system by condensed sulfur is one of the major operational problems with the H_2S generation facility. This unit must be designed so that condensation of sulfur vapors occurs only in knockout vessels included in the design.

Potential plugging at the entrance to the regeneration reactors could be reduced by several methods. Two parallel heat exchangers operated in a cyclic mode could be used. One would cool the H_2S gas and condense the sulfur vapors while steam was injected in the other to vaporize condensed sulfur. Alternately, a water quench could remove the sulfur and saturate the H_2S gas streams producing a sour water containing hydrogen sulfide as previously discussed under environmental considerations.

The ability to turn down the unit or store H_2S is important for a workable process design. The H_2S generation unit must be able to follow the load swings of the boiler since hydrogen sulfide requirements are directly proportional to the quantity of SO_2 absorbed. Turn down capability has not been fully developed or demonstrated at any of the pilot plants. The small amount of H_2S out of the regeneration reactors will be collected and combusted in the boiler or an incinerator.

6.5 Status of Development

Three pilot plants have been operated recently using the Citrate/Phosphate Process: (1) a .5 Mw installation by the Bureau of Mines; (2) a 1 Mw installation by Pfizer Inc., Arthur G. McKee and Company, and Peabody Engineering; and (3) a 100 scfm installation by Stauffer/CHEMICO. A summary of the experience at at these units is presented in Table 6-3. The Bureau of Mines and Pfizer-McKee-Peabody Processes employ citric acid as a buffer while the Stauffer/CHEMICO Process uses phosphoric acid.

Bureau of Mines Pilot Plant

The Bureau of Mines pilot plant has operated since February, 1974, at the Bunker Hill Lead Smelter in Kellogg, Idaho. The Bureau of Mines work initially emphasized control of SO_2 emissions from smelter operations rather than utility boilers.

During Phase I tests, the source of SO_2 laden gas was the flue gas from a coal-fired Lurgi up-draft lead sintering furnace. The flue gas passes through a baghouse, a packed wet scrubber, and an electrostatic mist precipitator in preparation for feed to the smelter's acid plant. A 100 scfm bleed stream of the acid plant feed gas (4.5 percent SO_2) was diluted 10 to 1 with air and fed to the pilot unit. The absorber, regeneration, and sulfur separation process areas were operated in Phase I. Commercially pure H_2S from a tank truck was supplied to the regeneration reactors, and no sulfate purge system was included.

During Phase II operations, an H_2S generation unit reacting methane with sulfur and steam was added. Operating time during Phase II was very short since the coil in the sulfur vaporizer burned out.

During Phase III tests the source of SO_2 laden gas for the pilot plant was changed from the acid plant feed gas to the lead sintering furnace tail gas. The tail gas (1000 scfm with .3 to 1 percent SO_2) was previously exhausted to the atmosphere.

TABLE 6-3

CITRATE/PHOSPHATE PILOT PLANTS

	Feed Gas		
Vendor or Developer	Source	Flow (scfm)	SO_2 (ppm)
Bureau of Mines (Citrate)	Lead sintering furnace tail gas	1,000	5,000
Pfizer, Peabody, McKee (Citrate)	Coal-fired industrial boiler	2,000	2,000
Stauffer/Chemico (Phosphate)	Low sulfur oil-fired utility boiler	100	700-2,800*

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[*] SO_2 content of flue gas was about 300 ppm. Additional SO_2 was introduced to the gas fed to the pilot plant.

A gas cooling and preparation train consisting of a baghouse, a packed wet scrubber, and a wet electrostatic precipitator was added on the tail gas stream prior to the SO_2 absorber.

The gas cooling and preparation unit, absorber, regeneration reactors, kerosene flotation cell, and sulfur melting and decanting unit have operated satisfactorily in Phase III of the Bureau of Mines program. Consistent SO_2 removal efficiencies of 96 to 99 percent were attained. The longest continuous run during this phase was 30 days. Operating problems have generally been associated with plugging due to precipitated or condensed sulfur in various parts of the system, particularly condensation of sulfur vapors in the H_2S generating unit. These problems have been reduced by employing heat tracing and knockout pots on the H_2S gas lines. However, a solution to the plugging problem has not yet been found.

The H_2S generation section of the Bureau of Mines Bunker Hill citrate pilot plant having a designed output of 1.25 tons H_2S per day was started up in September 1974. The sulfur-methane-steam reaction was carried out in two stages. In the first stage H_2S was produced as follows:

$$CH_4 + 4S \rightarrow CS_2 + 2H_2S \qquad (6\text{-}12)$$

This reaction takes place at over 1200°F with the gas subsequently cooled to about 300°F. In the second stage CS_2 was hydrolyzed to H_2S and CO_2 by the following reaction:

$$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S \qquad (6\text{-}13)$$

This second stage reaction occurs at about 700°F in a catalyst bed with the product gas again cooled to about 300°F. Initially difficulty was encountered in maintaining temperatures high enough for the reaction of sulfur-methane-steam. Modifications were made to overcome this problem, the plant was restarted, and successful turndown to about 0.6 tons H_2S per day (about 50 percent of design) was achieved. The final product gas composition, in percent, was 78.3 H_2S, 19.5 CO_2, 0.8 CS_2, 0.6 COS, with no detectable CH_4. Although the H_2S generator operated satisfactorily at this production rate, further turndown is necessary to accommodate reduced regeneration requirements. When continued turndown of H_2S production to 0.4 tons per day was attempted, the sulfur vaporizer coil plugged resulting in shutdown in November 1974. Sampling of the plug indicated a corrosion product of metal sulfides that was believed to be caused by excessively high temperatures in the sulfur vaporizer during initial startup and not as a result of the reduced H_2S production rate.

After mechanical reaming of the sulfur vaporizer coil, the unit was again started. Hot spots developed at points weakened by mechanical reaming and the coil burned out.

A new sulfur vaporizer coil was installed and the system modified to produce H_2S in one stage rather than two in July 1975. The unit normally operated to produce .6 ton/day H_2S (about 50 percent of design capacity) as this was sufficient to regenerate the citrate liquor out of the absorber. The turndown capability of the H_2S generation unit was not examined further. In September 1975 the second sulfur vaporizer coil burned out as a result of heating too rapidly during start-up. A third coil was installed and the unit began operation in October 1975.

Turndown of this unit at the Bureau of Mines pilot plant was accomplished by regulating the methane feed. The sulfur throughput remained constant so that the heat content of the excess gas would offset heat losses in the system.

Pfizer-Peabody-McKee Pilot Plant

The Pfizer-Peabody-McKee pilot plant treated 2,000 scfm of flue gas containing 1,000-2,000 ppm SO_2 from a coal-fired industrial boiler. The flue gas was adiabatically cooled with a venturi-type scrubber to both quench the gas and remove fly ash. No further preparation of the flue gas fed to the absorber was included. A mist eliminator between the venturi and the absorber was employed. An impingement tray absorber and and air flotation sulfur separation unit were used at the Pfizer-Peabody-McKee pilot plant. Commercial grade liquefied H_2S gas from a tank truck was mixed with CO from cylinders and the regeneration reactors.

Under the final equipment configuration, the pilot plant operated from March to September 1974, with a total of 2,300 operating hours logged. The longest sustained run was 180 hours. Consistent SO_2 removal efficiencies of 95 to 97 percent were attained with satisfactory operation of the gas cooling and preparation section, absorber, regeneration reactors, air flotation cell, and sulfur melting and decanting section. Commercial grade elemental sulfur was produced at the pilot plant.

Operating problems at the pilot plant were primarily associated with plugging due to sulfur deposition at the bottom outlet from regeneration reactors and plugging of pumps and level control valves in the regeneration unit. A change to a system of cascaded vessels with side outlets is proposed to overcome these problems. An H_2S generation unit was not included at the pilot plant. As a result, problems of producing H_2S from sulfur and hydrogen or reducing gas were not evaluated.

There was no evidence of degradation of the sulfur or citrate solution containing equipment or piping at the pilot plant. Stainless steel 316L and FRP were used to construct the facility. The materials proposed for a commercial installation are the same as those demonstrated at the pilot facility.

Stauffer-CHEMICO Pilot Plant

Stauffer/CHEMICO operated a skid-mounted pilot plant from January - June, 1974 on a low-sulfur oil-fired utility boiler. A 100 scfm flue gas stream containing about 300 ppm SO_2 was spiked with bottled SO_2 to vary the SO_2 content. The flue gas fed to the pilot unit varied from 700 to 2,800 ppm. This facility logged about 1,800 hours of operating time with an on-stream factor greater than 99 percent. The SO_2 removal efficiency was consistently maintained at 98 to 99 percent.

A coal burning operation was simulated by adding fly ash directly to the flue gas. The pilot plant was operated over 500 hours in this mode with no detrimental effects on the chemistry of the process noted. In addition, a commercial grade sulfur was produced in the pilot runs even with fly ash in the system.

No significant operating problems were reported for the Stauffer/CHEMICO pilot plant. Plugging did not occur in the packed tower absorber. The gas preparation section, absorber, regeneration reactor, air flotation unit, and sulfur melting and decanting equipment operated satisfactorily. Since commercial H_2S gas was supplied by a tank truck, problems associated with H_2S production from sulfur and reducing gas were not evaluated.

Evidence of corrosion was not found at the installation. Stainless steel was the material of construction at the pilot facility, but rubber or FRP lining is proposed for a commercial installation. These materials were not examined at the pilot plant.

6.6 Scale-Up Considerations

Potential scale-up problems are primarily concerned with the H_2S generator and and regeneration reactors. Other process areas have been demonstrated in other applications.

In the SO_2 absorption process area, the gas quencher is a commercial equipment item. Both tray and packed absorbers of the type proposed by vendors have also been commercially operated. Mass transfer correlations of absorbing SO_2 with the buffered liquor have been identified by system developers. A need to optimize the operating pH of the system exists since a higher pH favors the absorption step while a lower pH favors the regeneration step. The scale-up factor for a 125 Mw absorber would be about 125:1.

The unknown aspects of the process chemistry are a potential limitation to scale-up of the regeneration reactors. The high tip speed required for the reactor agitators might result in mechanical limitations on scale-up. Air flotation units to separate aqueous mixtures are commercially available up to 5,000 gpm capacity. However, air oxidation and evaporative cooling effects should be considered in the design and application of air flotation units to the citrate/phosphate process. Sulfur melting and decanting are relatively simple unit operations and, as with air flotation, sulfur separation should present no process limitations. Scale-up has not been demonstrated for the kerosene addition separation system.

Commercial sulfate purge units were not operated at any of the pilot plants. However, commercial equipment to crystallize and recovery hydrated sodium sulfate does exist. Therefore, no scale-up problems with the sulfate purge are anticipated.

An H_2S generator has been employed only at the Bureau of Mines pilot plant. The problems associated with this process have been discussed previously. However, hydrogen sulfide is a by-product of the commercial production of carbon disulfide from methane and sulfur. Also, production of H_2S from hydrogen gas and molten sulfur has been demonstrated commercially at a rate exceeding 10 tons per day. Uncertainties lie primarily in the use of reducing gas from coal to generate H_2S.

One vendor proposes steam-naphtha reforming, which is commercially available, as the method of producing reducing gas for H_2S generation. The use of steam-naphtha reforming would significantly lessen the uncertainties of scale-up of H_2S generation. The costs of the reducing gas are comparable to those for an air-blown gasifier, but the availabilty of naphtha may be a problem. Production of reducing gas is discussed in Section 13.

Neither a sulfate purge unit nor an H_2S generator using reducing gas produced from coal were operated at any of the pilot plants. Nevertheless, integration of the sulfate purge system should not be difficult. The ability to integrate reducing gas production from coal and H_2S generation with the process must be proven in future pilot demonstration facilities.

6.7 Utility Applicability

There should be few restrictions on the application of the Citrate/Phosphate Process to a new facility. The requirement of about 32,000 square feet for the absorption section of a 500 Mw installation could, however, limit the application of the process to an existing facility. Four absorbers would be used for 500 Mw of capacity. Each ranging from 25 feet by 25 feet rectangular by 20 feet high to about 25 feet in diameter by about 60 feet tall. The 45,000 square feet necessary for the remainder of the system could be located anywhere on the plot and, as a result, should not be a significant process limitation.

Pfizer, Inc. and Miles Laboratories, Inc. are the only commercial producers of citric acid in the United States. By 1977, their combined production capacity is projected to be 330 million pounds per year. If demand experiences an average annual growth rate of 6-7 percent as expected, the domestic demand for citric acid, excluding any FGD requirements, will be approximately 245 million pounds in 1978. The current price of citric acid is about $900/ton which includes a price increase of about 45 percent in 1974 due to increased costs of raw materials, energy, and transportation. Phosphoric acid is in ample supply with the current price about \$300/ton. Availability of citric and phosphoric acid should not be a problem, but the future cost of citric acid could be a handicap to the Citrate Process (BR-256).

Reducing gas production requirements for a 500 Mw facility are expected to be about 103 MM Btu/hr. This reducing gas is consumed in the H_2S generation section.

Using four absorber trains per 500 Mw capacity, the turndown capability of the absorption section is to about 15 percent of full load. This turndown results from operating only one of the absorber trains at about half of capacity. The turndown capability of the H_2S generator and reducing gas production unit has not been domonstrated at any of the pilot plants. Turndown capacity is important in the Citrate/Phosphate Process since the load on the entire process is determined by the load swings of the boiler. In the event of limited turndown, the excess reducing gas and H_2S would have to be stored or sent to boiler for combustion. Turndown is preferable to either of these alternatives.

An option not proposed by vendors is to include interstage tankage as surge vessels between the absorption section and the rest of the system. This tankage would act as a buffer and allow more gradual adjustments in the operation of the regeneration and H_2S generation units. The absorption section could return to design capacity with no time lag due to availability of stored regenerated liquor.

6.8 Economic Assessment

A detailed economic evaluation of the Citrate/Phosphate Process will not be attempted in this report. Raw material and utility costs based on energy and material balance calculations will be presented. Also, the relative contribution of each section of the process to these costs will be identified.

Raw material and utility costs were based on the energy, fuel, water, and raw material consumption for each process area based on energy and material balance calculations which produced the results shown in Table 6-4. Relative raw material and utility costs of each processing area are as follows:

Processing Area	Percent
SO_2 absorption	36
Regeneration and sulfur separation	4
Sulfate purge	3
H_2S generation	57

6.9 Process Summary

Radian's evaluation has identified some of the relative advantages and disadvantages of using a citrate versus a phosphate buffered solution. In laboratory experiments citrate buffer has been found to decompose at a rate of about 0.11 percent per hours. No degradation of the phosphate solution is anticipated. Pfizer Chemical (KO-168) has reported that in the pH range of 4.5 to 5.0 the citrate solution is a superior buffer based on laboratory data. A 2.4 molar phosphate solution has

TABLE 6-4

RAW MATERIAL AND UTILITY COSTS FOR CITRATE/PHOSPHATE FLUE GAS DESULFURIZATION PROCESS

Basis: 500 Mw; 3.5% Sulfur (Wt.) Coal; 5,260 hours per
year at full load

Process Area	Chemical and Energy Consumption	Annual Cost (10^3 S)
SO_2 Absorption	Power: 6,200 kw	652
	Steam for Reheat: 77 MM Btu/hr	416
	Process Water: 30 Mgal/hr	12
	Raw Materials:	
	27 lb/hr Citric Acid	57[1]
	1750 lb/hr Na_2CO_3	239[1]
	37 lb/hr Phosphoric Acid	29[2]
	270 lb/hr NaOH	121[2]
	Subtotal (Citrate Process)	1,376
	Subtotal (Phosphate Process)	1,230
Regeneration and Sulfur Separation	Power: 720 kw	76
	Steam: 25 MM Btu/hr	65
	Subtotal	141
Sulfate Purge	Power: 240 kw	25
	Steam: 14 MM Btu/hr	75
	Subtotal	100
H_2S Generation	Power: 800 kw	42
	Reducing Gas: 103 MM Btu/hr	2,167
	Subtotal	2,209
	TOTAL ANNUAL RAW MATERIAL AND UTILITY COSTS	
	CITRATE PROCESS	3,826
	PHOSPHATE PROCESS	3,680
	UNIT RAW MATERIAL AND UTILITY COST	1.4 mills/kwhr

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[1] Citrate Process

[2] Phosphate Process

the same buffering capacity as a .5 molar citrate solution at a pH of 4.5. A 1.7 molar phosphate solution is equivalent to a .5 molar citrate solution at a pH of 5.0. Availability of raw materials is not expected to be a factor in the choice of citrate or phosphate for the process. The costs of citric and phosphoric acid are about $900 and $300 per ton, respectively. However, this differential will probably not be a significant factor in the overall operating costs of the systems since material balance calculations indicate make-up requirements will be small. Leaks and process upsets resulting in solution discharge would be less acceptable with the Phosphate Process than with the Citrate Process.

The Citrate/Phosphate Process is a buffered aqueous absorption process which uses either a sodium citrate or sodium phosphate solution to absorb SO_2 from flue gas. The unique features of the process are the reaction of H_2S gas with absorbed SO_2 in the regeneration step, the separation of precipitated sulfur by flotation, and the external generation of H_2S from elemental sulfur and reducing gas. The major problems are the integration of H_2S generation with the process, the use of reducing gas from coal to generate H_2S, and the relatively low liquor loading. The process has been demonstrated at three pilot plants with the largest being 1 Mw. The raw material and utility costs of the process are competitive. A 10 to 25 Mw demonstration facility would seem to be the next logical step in process development as adequate design and scale-up information for a commercial unit is not available.

7.0 AMMONIA-AMMONIUM BISULFATE (ABS) PROCESS

The Ammonia-Ammonium Bisulfate (ABS) Process is a regenerable FGD process which removes SO_2 from flue gas by absorption in an aqueous ammonium sulfite and bisulfite solution. The solution is regenerated by acidulation to release the SO_2 which is subsequently converted to sulfuric acid or elemental sulfur. Crystalline ammonium sulfate is recovered from the liquor and thermally decomposed to ammonia and ammonium bisulfate (ABS).

7.1 Process Description

As shown in Figure 7-1 the ABS Process can be divided into the following processing steps:

1) SO_2 Absorption,

2) Regeneration, and

3) SO_2 Conversion.

Each processing area will be described in this section.

SO_2 Absorption

The flue gas flows through a prewash section containing a venturi-type element upstream of the absorber. The prewash section prepares the hot flue gas for treatment in the absorber. The gas is cooled with water to its adiabatic saturation temperature of about 125°F, and chlorides, SO_3, and fly ash are removed. The prewash section operates with an independent water loop. An acidic purge stream of chlorides and fly ash is

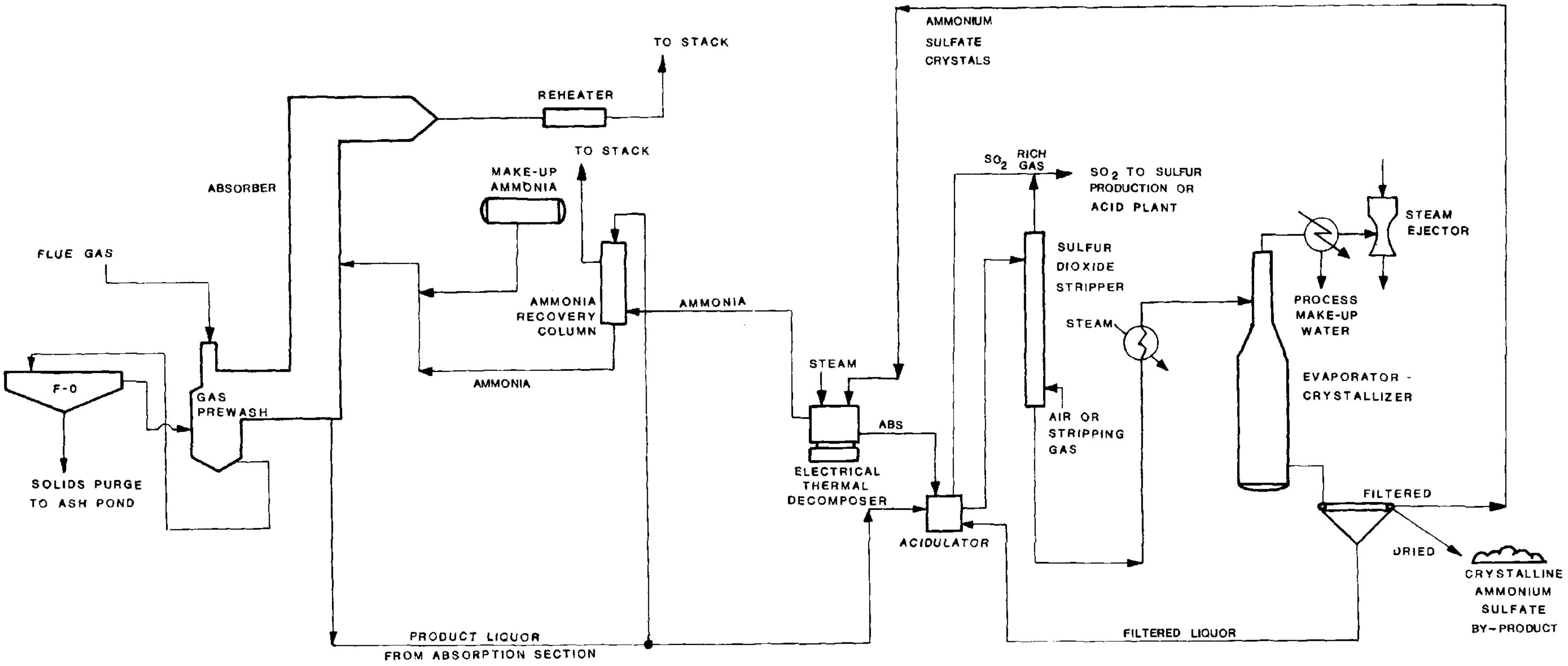

FIGURE 7-1

TVA AMMONIA ABSORPTION - AMMONIUM BISULFATE REGENERATION PROCESS continuously removed, neutralized if required, and sent to the ash pond.

A staged absorber (Figure 7-2), with a mist eliminator at the absorber outlet, is specified. A mist eliminator at the absorber entrance may also be required depending on liquid carry-over from the prewash section. The staged operation results in an outlet liquor with the high ammonium salt concentration necessary for regeneration. Also, low salt concentrations can be maintained on the final stage to reduce ammonia losses and the potential for fuming.

The chemistry of absorption is characterized by the primary reactions which are shown below:

$$SO_2 + (NH_4)_2SO_3 + H_2O \rightarrow 2NH_4HSO_3 \qquad (7\text{-}1)$$

$$NH_4HSO_3 + NH_3 \rightarrow (NH_4)_2SO_3 \qquad (7\text{-}2)$$

$$SO_3 + (NH_4)_2SO_3 \rightarrow (NH_4)_2SO_4 + SO_2 \qquad (7\text{-}3)$$

$$O_2 + 2(NH_4)_2SO_3 \rightarrow 2(NH_4)_2SO_4 \qquad (7\text{-}4)$$

The flue gas out of the prewash unit passes through a mist eliminator and enters one of the four 125 Mw absorber modules. Approximately 250,000 scfm of gas at about 125°F is treated by each absorber module. Liquor and gas contacting occurs on four semi-independent stages with the ammonia salt solution flowing countercurrently to the gas at a rate of 10 gallons/1,000 scf of flue gas for each stage of the absorber. The scrubbed gas is reheated to about 175°F with steam prior to release to the atmosphere.

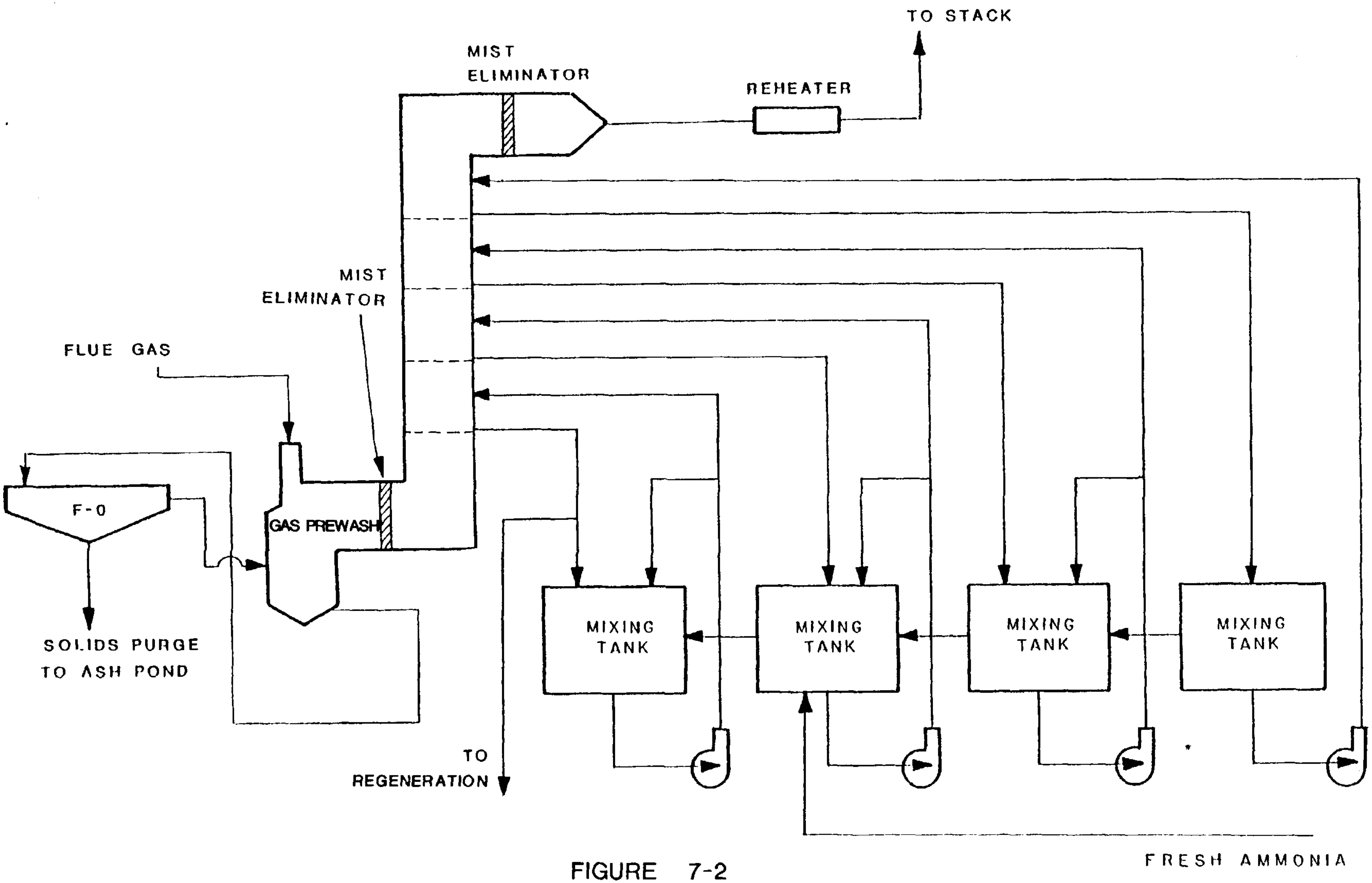

FIGURE 7-2
PROCESS FLOW DIAGRAM
ABSORPTION SECTION
TVA AMMONIA - AMMONIUM BISULFATE PROCESS

Each absorber stage has a separate, semi-independent recirculation loop as shown in Figure 7-2. A portion of the liquor outlet from each stage is fed to the next lower stage through a series of mixing tanks. Concentrated product liquor is withdrawn from the first stage and fed to the regeneration section through a surge tank.

Ammonia recovered in the regeneration section is recycled to the second-stage mixing tank. Fresh make-up ammonia is also fed to the second-stage mixing tank. Most of the SO_2 is removed in the first stage of the absorber but the other stages provide additional SO_2 removal capability.

Process make-up water is introduced through the fourth-stage mixing tank to reduce the concentration of dissolved ammonia and ammonium salts on the fourth stage, thereby minimizing ammonia losses and the potential for fuming.

Regeneration

The regeneration section of the Ammonia-ABS Process includes the following major processing steps:

1) acidulation and stripping,

2) crystallization and separation, and

3) thermal decomposition.

Each of these steps will be discussed below.

Acidulation and Stripping. The loaded liquor out of the absorber is fed to an acidulator where the liquor is mixed with an acid ion supplied by the ammonium bisulfate to chemically release SO_2 by the following reactions:

$$NH_4HSO_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4 + H_2O + SO_2\uparrow \qquad (7\text{-}5)$$

$$(NH_4)_2SO_3 + 2NH_4HSO_4 \rightarrow 2(NH_4)_2SO_4 + H_2O + SO_2\uparrow \qquad (7\text{-}6)$$

The ammonium bisulfate and absorber liquor are added concurrently to a mixing pot to obtain uniform acidulation of the liquor while also maintaining control of this exothermic reaction. The acidulator operates at a temperature of 140-150°F. A portion of the released SO_2 evolves as a gas in the acidulator.

The liquor from the acidulator overflows into a stripper where the remaining SO_2 is stripped from the liquor with a countercurrent flow of air. The packed column operates at about 100°F. The quantity of the free SO_2 in the liquor out of the stripper is approximately 0.4 grams per liter of liquor (400 ppm). Over 95 percent of the SO_2 in the ammonium sulfite-bisulfite liquor to the acidulator is removed during acidulation and stripping. The SO_2 gas streams from the acidulator and stripper are combined and sent to a sulfur production unit or an acid plant. This combined stream is about 65 percent SO_2. The liquor out of the stripper is sent to the evaporator/crystallizer. Steam could also be used to strip the SO_2 from the liquor and should result in a more concentrated SO_2 stream.

Crystallization and Separation. The stripped liquor (ammonium sulfate solution) is metered into the evaporator/crystallizer where water is evaporated to produce a slurry of ammonium sulfate crystals. The feed to this unit is heated to about 170°F in a steam heat exchanger. A vacuum of 20 inches of mercury is maintained in the evaporator-crystallizer.

The sulfate crystals in the slurry bottoms are separated from the mother liquor in a centrifuge and sent to the thermal decomposer. The mother liquor is recycled to the evaporator/crystallizer. The quantity of sulfate crystals produced is in excess of that required as feed to the electrical thermal decomposer so that a net by-product of ammonium sulfate results. The excess ammonium sulfate is dried with hot air from a steam/air heater and sent to disposal. The off-gas from the evaporator/crystallizer is sent through a water-cooled condenser to remove sulfur compounds with a vacuum pump used to maintain the vacuum. The aqueous stream out of the condenser and the off-gas from the vacuum pump are recycled to the absorber.

Thermal Decomposition

In the thermal decomposer, the ammonium sulfate crystals are decomposed at 700°F by the following reaction:

$$(NH_4)_2SO_4 \xrightarrow{700°F} NH_3 \uparrow + NH_4HSO_4 \qquad (7\text{-}7)$$

Approximately 85 percent decomposition of ammonium sulfate to ammonium bisulfate is accomplished. An electrically heated decomposer is presently specified in the ABS flow sheet. The ammonium bisulfate is fed to the acidulator. The off-gas is condensed with the ammonia subsequently stripped out with air and absorbed in a stream of absorber liquor for recycle to the absorption section.

SO_2 Conversion

Given the concentrated SO_2 stream produced by the acidulation and stripping operations, it is possible to use several processes to convert the sulfur values to a more desirable form. The process presently suggested is a contact sulfuric acid plant. Some recent studies indicate that a market may exist for sulfuric acid in many areas of the country. The acid product is less energy intensive than sulfur, although it is more difficult to store and transport.

For this evaluation, the process specified for production of elemental sulfur is the Allied Chemical catalytic reduction using reducing gas produced by coal gasification. In this process, a heated SO_2 stream is combined with a measured quantity of reducing gas. The resultant gas stream is passed over a catalyst to reduce part of the SO_2 to sulfur and H_2S. A condenser removes the sulfur from the gas stream with the H_2S-SO_2 mixture fed to a modified Claus Plant. Other processes under development which convert SO_2 to sulfur, such as RESOX and BAMAG, would also be applicable. A more detailed discussion of SO_2 conversion appears in Section 14 of this report.

7.2 Environmental Considerations

The first concern for a flue gas desulfurization process is the SO_2 removal efficiency, but consideration must also be given to other environmental factors. The most important problem facing the Ammonia-ABS Process is plume formation.

The Ammonia-ABS Process can be designed with an SO_2 removal efficiency up to 99 percent. However, this would require more absorber stages with associated liquor loops than needed for the base case design for 90 percent removal, as shown in Figure 7-2. Approximately 10 percent more ammonia would flow through the absorber and an increase of roughly 8 to 10 percent in raw material and utility costs would result.

The effect of temporary surges in flue gas SO_2 concentrations above design specifications has not been tested. However, the ammonia concentration in the absorber liquor can be increased to offset the increase in SO_2 concentration. This would lead to a temporary overload on the regeneration section. Excess ammonium sulfate is available for use in regeneration, but the ability of the equipment to process the increased throughput is unknown. A longer term alternative might be to install tankage and process the excess liquor in the regeneration section as operating conditions permitted.

Most of the particulates in the flue gas from the electrostatic precipitator should be removed in the prewash section of the absorber. Particulates picked up in the absorber will probably leave the system with the by-product ammonium sulfate or the purge from the liquor out of the evaporator/crystallizer. These contaminants would be recycled to the regeneration section with the ammonium sulfate fed to the decomposer. Purges from the regeneration liquor loop must be sufficient to prevent a buildup of contaminants.

The effect of the Ammonia-ABS Process on NO_x emissions has not yet been examined. For the purposes of this study, NO_x removal capability is assumed to be negligible.

Chlorides from the coal are expected to be present in the flue gas, however, essentially all of the chlorides are removed from the flue gas in the prewash operation. Chloride removal is required primarily due to fuming considerations but also due to the potential for corrosion with chloride buildup. The fate of chlorides not removed in the prewash section has not been determined as yet. The chlorides might exit the system with the purge on the evaporator/crystallizer bottoms or with the ammonium sulfate by-product. Chlorides might also be recycled with the ammonium sulfate feed to the decomposer and the overhead from the evaporator/crystallizer.

The formation of an ammonium salt plume is an environmental consideration unique to ammonia processes. The discharge of a plume, particularly one that eventually oxidizes to very fine (0.2 micron) ammonium sulfate particles, would be a serious process liability.

Various methods of controlling the plume have been tested at TVA's Colbert Station 1.2 Mw pilot plant. The severity of the plume is judged by the opacity of the clean flue gas. The plume has been controlled to five percent opacity or less with the following operating conditions:

- Liquor temperature of about 120°F,
- Use of a prewash to remove particulates, SO_3, and chlorides,
- Maintaining a low salt concentration on the top stage, and
- Reheat of the clean gas 10 to 20°F above the temperature necessary to dissipate the steam plume.

However, even with these restrictions, the plume often reformed outside the stack on cold humid days.

In general, control of the plume has not been satisfactory with any technique used. The use of fine particulate control technology to solve the fuming problem is presently under consideration. Fuming will be discussed further in Sections 7.4 and 7.5 dealing with Design Considerations and Status of Development.

The primary waste or by-product streams from the Ammonia-ABS Process include ammonium sulfate crystals and a particulate slurry. Approximately 6,300 lb/hr of by-product ammonium sulfate is produced. This by-product should be relatively pure compared to sulfate by-products from other wet FGD systems. Also, a market for the ammonium sulfate may exist in the fertilizer industry. A particulate slurry of roughly 100 gpm (56,000 lb/hr) from the surge tank in the prewash water loop is sent to neutralization and/or the ash pond as required. A purge on the mother liquor stream out of the ammonium sulfate separation equipment may also be necessary. The process has not been adequately tested at the TVA pilot plant to determine if such a purge will be necessary.

7.3 Material and Energy Balances

The material and energy balances prepared by Radian for the 500 Mw base case play a key role in this evaluation. These calculations allow a more independent view of the process by serving as the basis for raw material and energy requirements. The magnitude and nature of waste streams, the approximate sizes of equipment for a commercial system, and the degree of difficulty of scale-up of operating units can also be estimated.

TVA made available to Radian a preliminary flow diagram and material and energy balance. Although the material and energy balance was not prepared for this evaluation, the calculations have a basis almost identical to the 500 Mw Radian base case. No stream compositions were included.

Results of Radian calculations were in reasonable agreement with those of TVA. Process raw material and utility requirements are summarized for each section of the process in Table 7-1.

7.4 Design Considerations

Principal factors that should be considered in the design of each processing area will be discussed in this section. Potential problems associated with the process and the ability of the system to overcome them will also be examined.

SO_2 Absorption

A basic design criterion for an ammonia FGD process is elimination of the plume. To control fuming, chlorides, particulates, and SO_3 should be removed from the flue gas before it contacts the ammonia solution. Also, the partial pressures of NH_3, SO_2, and H_2O must be kept at such levels that a gas phase reaction to form ammonium salts does not occur.

A low pressure drop, prewash venturi is used to humidify and cool the gas and remove particulates, chlorides, and SO_3. This prewash venturi has a gas-side pressure drop of 5 to 6 inches of water and operates at an L/G of about 9 gallons per 1000 scfm. The materials of construction must withstand erosion and corrosion at a pH as low as one.

Some of the more important design considerations for the absorber are related to the vapor-liquid equilibria of the system and the approach to equilibrium chosen. Equilibrium absorption of SO_2 is enhanced by the following:

1) decreasing the solution temperature,

TABLE 7-1

RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE AMMONIA-ABS PROCESS

Basis: 500 Mw; 3.5 wt. % S coal; 5,260 hours per year at full load

Process Section	Ammonia (lb/hr)	Steam (MM Btu/hr)	Reducing Gas (MM Btu/hr)	Electric Power (Mw)
Absorption	1800	79	-	8.9
Regeneration	-	60	-	18.0
SO_2 Conversion	-	-	-	.3
TOTAL	1800	139	-	27.2

2) minimizing liquor loading (pounds SO_2 per pound of solution),

3) minimizing the S/C_A ratio (the ratio of the moles of SO_2 in solution as sulfite and bisulfite to the moles of ammonia in solution as sulfite and bisulfite), and

4) increasing the total NH_3 concentration in solution.

Minimizing ammonia concentrations in the gas leaving the absorber is equally important. Ammonia losses are reduced by:

1) decreasing the solution temperature,

2) decreasing the total NH_3 concentration in solution, and

3) maximizing the S/C_A.

Obviously, the conditions under which SO_2 removal is maximized and NH_3 losses are minimized are not all compatible. These considerations in combination with other system parameters must be optimized for a given application.

Removal of SO_2 from flue gases occurs primarily on the first stage of the absorber with ammonia, other volatiles, and lesser amounts of SO_2 removed on the remaining three stages. Weepage and entrainment from one absorber stage to the next are undesirable due to fuming considerations.

The pH and the liquor temperature on each stage have a significant impact on SO_2 pickup, ammonia losses, and the potential for fuming. Absorption of SO_2 drops off markedly with a liquor pH below 5.6, while NH_3 losses are very high with a pH above 6.8. TVA found that the liquor pH on the top tray must be less than 6.1 to control NH_3 emissions to 50 ppm or less. The pH is also important due to its effect on the vapor pressure of NH_3 and SO_2. As previously indicated, lower liquor temperatures increase SO_2 removal and reduce ammonia losses. However, the liquor temperature cannot be reduced below the adiabatic saturation temperature of the flue gas without cooling the liquor. As a result, the temperature can only be controlled within rather narrow bounds.

A liquor with a high concentration of ammonium salts is desirable as a feed to the regeneration section. However, increasing the salt concentration in the absorber bottoms increases liquor concentration throughout the column, and thus, increases NH_3 and SO_2 vapor pressures above every stage. The result is greater ammonia losses and a higher potential for fuming. A water wash after the top stage can be used to reduce ammonia losses.

Regeneration

The processing steps included in regeneration are acidulation and stripping, crystallization and separation, and thermal decomposition. The design considerations for each of these operations will be discussed below.

Acidulation and Stripping. The acid ion is metered to the acidulator to give a molar ratio of acid ion to ammonium ion (as sulfite and bisulfite) of 1.05. A slight excess of acid ion is specified to insure complete acidulation of the liquor. The acidulation step must result in a uniform and complete reaction of the acid and ammonium salts. For maximum release of SO_2, and reasonable process control of an exothermic reaction involving acid species.

The method of contacting the acid and the liquor is important. Uniform acidulation of the liquor is difficult to accomplish if the acid is added slowly to a large quantity of absorber liquor. If the liquor and acid are added concurrently at the top of the stripper, a violent reaction takes place with excessive heat generation. Also, the materials for the acidulator must be chosen carefully due to the corrosive atmosphere.

Reactions (7-5) and (7-6) indicate that a high bisulfite to sulfite ratio (high S/C_A) in the absorber product liquor reduces the amount of acid ions required for acidulation and, therefore, the equipment size for the regeneration cycle. This potential advantage must be weighed against restrictions on the S/C_A in the absorber.

Data for the design of the acidulator has been based on the use of sulfuric acid as the source of acid ions. A commercial unit would use ammonium bisulfate as the source of acid ions. Laboratory work indicates that ammonium bisulfate acts very similarly to sulfuric acid in the acidulator. Nevertheless, since the use of ammonium bisulfate is an integral part of the process and since additional considerations in the design of the acidulator might be identified after testing with ammonium bisulfate, data for pilot plant operation with ammonium bisulfate is very important.

The stripper must have the capability to remove virtually all the free SO_2 in the liquor overflow from the acidulator.

Air, which has been used successfully at the TVA pilot plant, has been specified as the stripping gas. The specified gas flow is 10 cubic feet per gallon of acidulated liquor throughout. A packed column is used to provide the necessary gas-liquid contacting. As with the acidulator, the materials must withstand the corrosive liquor. Steam would also be used to strip the SO_2 from the liquor. The liquor is heated with steam prior to being fed to the evaporator/crystallizer and a more concentrated SO_2 stream would be produced. The load on the evaporator/crystallizer would be increased due to condensation of steam in the stripper, however.

Crystallization and Separation. Water is evaporated and ammonium sulfate crystals are formed in the evaporator/crystallizer. The acidulated and stripped liquor is heated with steam to about 170°F prior to being fed to the evaporator/crystallizer. This unit, as found in the pilot plant, is operated under a vacuum of 20 inches of mercury to enhance the removal of water and reduce steam requirements. The possibility exists of using an atmospheric evaporator system which should result in reduced equipment costs and require steam of only slightly higher pressure.

Provision must be made to handle condensables and noncondensables that come overhead from the evaporator/crystallizer. Residual SO_2 is released with steam which is subsequently condensed with part of the SO_2 dissolved in the water. This liquid stream is recycled to the absorber due to the SO_2 content. The gas out of the condenser containing the remaining SO_2 and the noncondensables is fed to a steam ejector. Equipment designed for slurry service will be required to handle and transport the bottoms from the evaporator/crystallizer.

The separation step includes dewatering and drying the ammonium sulfate crystals. Some of the variables that will affect the load on the separation equipment are the salt concentration of the absorber bottoms, the amount of oxidation in the absorber, and the water concentration in the slurry from the evaporation/crystallizer. An aqueous purge may be necessary to prevent buildup of contaminants in the regeneration loop.

A yellow solid that is sometimes present in the slurry fed to the separation equipment has made separation more difficult at the TVA pilot plant. This yellow solid has been tentatively identified as an homogeneous iron-ammonia-sulfur compound. The fly ash absorbed in the liquor is assumed to be the source of iron. Attempts to remove this solid by filtration have not been successful because the precipitated solids and fly ash form a gelatinous, thixotropic material that blinds the filter media. More must be learned about this yellow solid so that it can either be eliminated or accommodated in the design of the separation equipment.

As the salt concentration in the liquor leaving the absorber decreases, the total water that must be removed from the crystals increases. The moles of active ammonia (as bisulfite and sulfite) per 100 moles of total water are defined as the C_A of the solution. A product liquor with a C_A=12 which represents reasonable absorber operation would result in a total evaporation-dewatering-drying load of about 2.9 pounds of water per pound of SO_2 product from the regeneration section.

Thermal Decomposition. Thermal decomposition of ammonium sulfate can be accomplished in an electrical or a direct-fired fossil-fuel decomposer. An electrical decomposer is currently used in the process design.

The decomposer must be designed to thermally disassociate the ammonium sulfate to ammonium bisulfate and NH_3 without further decomposing the NH_3. A reducing atmosphere or, as a minimum, no excess oxygen is required for proper operation of the decomposer. Temperature control and residence time for the 700°F melt are very important due to the sensitivity of the decomposition reaction to these parameters. Also, a very corrosive atmosphere in the decomposer requires the use of appropriate materials for the unit.

SO_2 Reduction

The choice of sulfuric acid or elemental sulfur as a product will have to be made with each application of the process. For production of sulfur to be a viable alternative, a process able to use a reductant other than methane might be necessary. In some isolated cases, availability of methane may not be a problem, but generally, the most reliable sources of reducing agent will be coal or coke. Coal might be used in solid form as in Foster Wheeler's RESOX process or as a source of H_2/CO producer gas. Unfortunately, production of elemental sulfur from SO_2 is still developing technology with only the Allied Chemical process using methane demonstrated on a large scale. The impact of using H_2/CO reducing gas on the Allied Process remains to be demonstrated. Potential problems such as the effectiveness of their catalyst with the H_2/CO reductant are numerous.

7.5 Status of Development

The Ammonia-ABS Process which is currently under development by TVA and EPA was initially patented in 1946 by Hixson and Miller. The technical feasibility of the individual unit operations has been demonstrated in industrial applications. However, integration of the process on a significant scale has not been accomplished.

The use of ammoniacal solutions to remove SO_2 from gas streams is considered proven technology. Acidulation of the absorber liquor to release SO_2 and form ammonium sulfate has been practiced commercially by Cominco using sulfuric acid since the 1930's. Also, acidulation with phosphoric and nitric acid to produce SO_2 and fertilizer has been reported in Czechoslavakia and Romania. Thermal decomposition of ammonium sulfate to yield NH_3 and ammonium bisulfate was accomplished in a program sponsored by the U.S. government during WW II. An electric furnace processed about 550 tons per day of $(NH_4)_2SO_4$ to produce ammonium bisulfate for mineral extraction. A direct-fired fossil-fuel decomposer has been reportedly tested more recently in France, but the status of this unit is not known.

The Tennessee Valley Authority began studies on ammonia scrubbing at TVA's Colbert Steam Plant in 1968. A 1.2 Mw pilot plant treats a 3000 cfm slipstream from a coal-fired boiler. All the processing steps with the exception of the decomposer are included at the pilot facility. Extensive tests have been run to establish important operating parameters and develop solutions to problems encountered.

Plume formation is the primary area of concern in the adsorption section. This fuming problem parallels that of the Catalytic/IFP Process discussed in Section 5 of Volume II. TVA is examining the impact of more efficient removal of chlorides in the prewash unit on fuming. TVA is also considering the use of fine particulate control technology to solve this problem. Since adjustments in operation of the absorber have not satisfactorily prevented fuming, control equipment downstream of the absorber might be necessary.

The acidulation and stripping and crystallization and separation units at the pilot plant have operated successfully. Problems with the uniform and controlled acidulation of the absorber product liquor have been overcome. The formation of a yellow solid that blinds the filter in the separation step has not been adequately explained. However, a centrifuge which is specified in the TVA conceptual design of the process should be less susceptible to this problem. Testing of a centrifuge at the pilot plant is planned in the near future. The contaminants in the ammonium sulfate produced at Colbert have not been determined. This analysis may provide some insight as to the fate of contaminants that enter the system and the suitability of this by-product for marketing to the fertilizer industry.

Sulfuric acid has been used exclusively to acidulate the liquor. The production of NH_4HSO_4 and NH_3 from $(NH_4)_2SO_4$ and the use of NH_4HSO_4 in the acidulator have not been tested at the pilot unit. However, laboratory work indicates that NH_4HSO_4 should act very similarly to H_2SO_4 in the acidulation step. Also, bench scale units have successfully produced NH_3 and NH_4HSO_4 crystals from ammonium sulfate with no appreciable degradation of NH_3 observed. Total integration of the Ammonia-ABS Process, solution of the fuming problem, and design and operating data for the thermal decomposer are necessary before a demonstration size unit is feasible.

Construction materials have also been evaluated at the pilot unit. The original prewash section of 316L stainless was severely corroded due to the low pH in the water loop. New design will use FRP with a neoprene lining for the venturi throat. Type 316L stainless was found to be suitable for the absorber but marginal in the demister areas. Mild steel with a corrosion resistant lining is specified for the acidulator and stripper.

The crystallization and separation equipment should not present any material problems due to the commercial nature of these operations. Materials for the decomposer are yet to be evaluated.

7.6 Scale-Up Considerations

Most of the considerations that affect scale-up have already been presented under Design Considerations or Status of Development. Uncertainties of scale-up exist in the absorption and regeneration process steps. These areas that are currently under development will be emphasized with scale-up factors for a 500 Mw facility presented where appropriate.

Absorption

TVA has constructed and operated a 1.2 Mw Ammonia-ABS FGD Process. They are proposing 125 Mw absorber modules which would require tower diameters to be on the order of 25 feet. On a Mw basis the scale-up would be about 100:1 for 500 Mw capacity.

Even though the scale-up factor is large, scale-up of the absorber from the standpoint of SO_2 removal should not present a serious process limitation as commercial units are in existence. However, scale-up of operating technology that would solve the fuming problem remains to be demonstrated as all ammonia scrubbing processes suffer from plume formation.

Regeneration

The stripping, crystallization, and separation operations should not present any unsolvable problems on scale-up. Equipment of this type is applied commercially in numerous industries. The acidulator and thermal decomposer will present a more difficult scale-up problem. Uniform and controlled acidulation of the absorber liquor will be become harder with greater throughputs and larger equipment. Examination of the thermal decomposition of ammonium sulfate by TVA has been limited to bench scale and, then, to only a batch operation.

The TVA pilot plant at the Colbert Station is partially integrated. A thermal decomposer is not included and sulfuric acid is used in the acidulator rather than ammonium bisulfate. With the addition of a decomposer, the ammonium bisulfate should also be available for testing. Integration of the process is very important to its continued development.

7.7 Utility Applicability

Application of the Ammonia-ABS Process to a new facility should not present serious limitations. The space requirements for a 500 Mw installation have not been estimated by TVA. However, the space requirements which should be comparable to other wet systems could limit the retrofitability of the process. Only the absorption section needs to be located close to the stack and boiler.

TVA has been involved with ammonia production and availability as a result of their involvement with the fertilizer industry. TVA reports that the availability and price of ammonia should not be a limitation to the application of this process.

The use of an H_2/CO reducing gas produced from coal in the Allied Chemical Process has not been demonstrated. Numerous potential problems have not been adequately examined. Earlier reports by Allied on various reducing agents indicate that an H_2/CO mix is a technically feasible reductant. The current status of this development is unknown. It should be noted that TVA recommends conversion of the SO_2 to sulfuric acid rather than sulfur (TE-233).

Turndown of the absorption section to about 15 percent of full load should be readily attainable by operating one 125 Mw absorber train at about 50 percent of design. The ability of the regeneration section to turndown is not known. However, the thermal decomposer might result in significant limitations on the overall turndown of the system.

7.8 Economic Assessment

Raw material and utility costs based on energy and material balance calculations will be presented. A detailed economic analysis of the Ammonia-ABS Process will not be attempted in this evaluation.

The raw material and utility requirements and costs are shown in Table 7-2. The energy and material balance calculations performed by Radian are the basis for these results. The annual raw material and utility costs are $6,704,000 or 2.5 mills per kwhr. The relative contribution of each process section is as follows:

	Percent
Absorption	39
Regeneration	31
SO_2 Conversion	30

The cost of the reducing gas consumed in the SO_2 reducer accounts for about 29 percent of the annual cost while the electric power consumed in the thermal decomposer accounts for about 28 percent. The other primary considerations in the cost analysis are ammonia

TABLE 7-2

RAW MATERIAL AND UTILITY COSTS FOR THE AMMONIA-ABS PROCESS

Basis: 500 Mw; 3.5 wt. % S coal, 5,260 hours per year at full load

	Annual Cost (10^3 dollars)
Absorption	
Electric Power: 8,900 kw	936
High Pressure Steam: 79 MM Btu/hr	416
Ammonia: 1,800 lb/hr	1,280
Subtotal	2,632
Regeneration	
Electric Power: 18,000 kw	1,894
High Pressure Steam: 22 MM Btu/hr	116
Low Pressure Steam: 38 MM Btu/hr	100
Subtotal	2,110
SO_2 Conversion	
Electric Power: 300 kw	32
Reducing Gas: 92 MM Btu/hr	1,930
Subtotal	1,962
Total Annual Raw Material and Utility Costs	$6,704

Unit Raw Material and Utility Cost 2.5 mills/kwhr make-up (19 percent), power consumption for the rest of the process (14 percent), and steam (3 percent).

7.9 Process Summary

The Ammonia-ABS Process absorbs SO_2 from flue gas streams with an aqueous ammonium sulfite liquor. The unique features of the process are the staged absorber, the acidulation of the ammonium sulfite-bisulfite liquor with ammonium bisulfate (ABS) to release SO_2, and the thermal decomposition of ammonium sulfate to ammonia and ammonium bisulfate. The process produces a concentrated stream of SO_2 that can be converted to either sulfur or sulfuric acid.* The major by-product or waste stream is excess ammonium sulfate that results from oxidation in the absorber. The primary technical problems are formation of a plume in the absorber and the availability of design and operating data for the thermal decomposer. The use of H_2/CO reducing gas as a reductant in the Allied Chemical Process also remains to be examined.

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* TVA proposes that the SO_2 be converted to sulfuric acid (TE-233).

8.0 IONICS ELECTROLYTIC REGENERATION PROCESS

The Stone & Webster/Ionics process was a complete SO_2 recovery and concentration process developed jointly by the two companies and demonstrated in a pilot facility at Wisconsin Electric Power Company under EPA auspices. Stone and Webster provided the scrubbing, acidulating and stripping equipment and know-how while Ionics provided the heart of the system, the chemical reaction sequence and their proprietary electrolytic cell technology for regeneration. However, Ionics is no longer associated with Stone & Webster and thus Radian's approach had to be modified to take into account the fact that Ionics does not market a full system. Ionics feels that the other parts of the process are fairly simple or well known operations, and should be considered as being available without further development.

The technology that Ionics has developed consists of a workable electrolytic cell, the SULFOMAT cell, which electrolyzes moderately concentrated sodium sulfate solutions to sulfuric acid and caustic, both of which also contain some sodium sulfate. Sodium sulfate in the acid solution will be present as $NaHSO_4$. With the addition of another membrane, the basic cell can be modified to produce a pure dilute sulfuric acid solution in order to eliminate sulfate formed by oxidation without purging the sodium ions. This electrolytic cell know-how can be used either as the regeneration system for an alkaline scrubbing system or as a means of putting the sodium sulfate purge from other processes back into a usable form. Ionics, however, does not have the capability to design or build the main scrubbing, acidulating, stripping or SO_2 processing equipment which is also part of a complete SO_2 recovery process. As a result, the complete system which Radian wished to evaluate does not exist and it was necessary to make a number of assumptions to provide a basis for process evaluation. Information from similar types of sodium scrubbing schemes was used to develop a reasonable set of processing assumptions.

Therefore, it should be kept in mind that the discussion of the Ionics Process is based only on a very rudimentary conceptual design and is much less accurate than the other process evaluations, except in regard to the electrolytic cells. The system could be designed to use different types of absorbers, strippers, or SO_2 conversion steps. The Ionics cells were evaluated for both applications - a total process using caustic scrubbing and as a purge treatment in combination with other sodium scrubbing processes.

8.1 Process Description

The Ionics process as evaluated by Radian consists of four steps:

1) Absorption,

2) Acidulation and stripping,

3) Regeneration, and

4) SO_2 conversion.

Except for regeneration and SO_2 conversion, the sections are very simple and not technologically new. The process flow sheet appears in Figure 8-1.

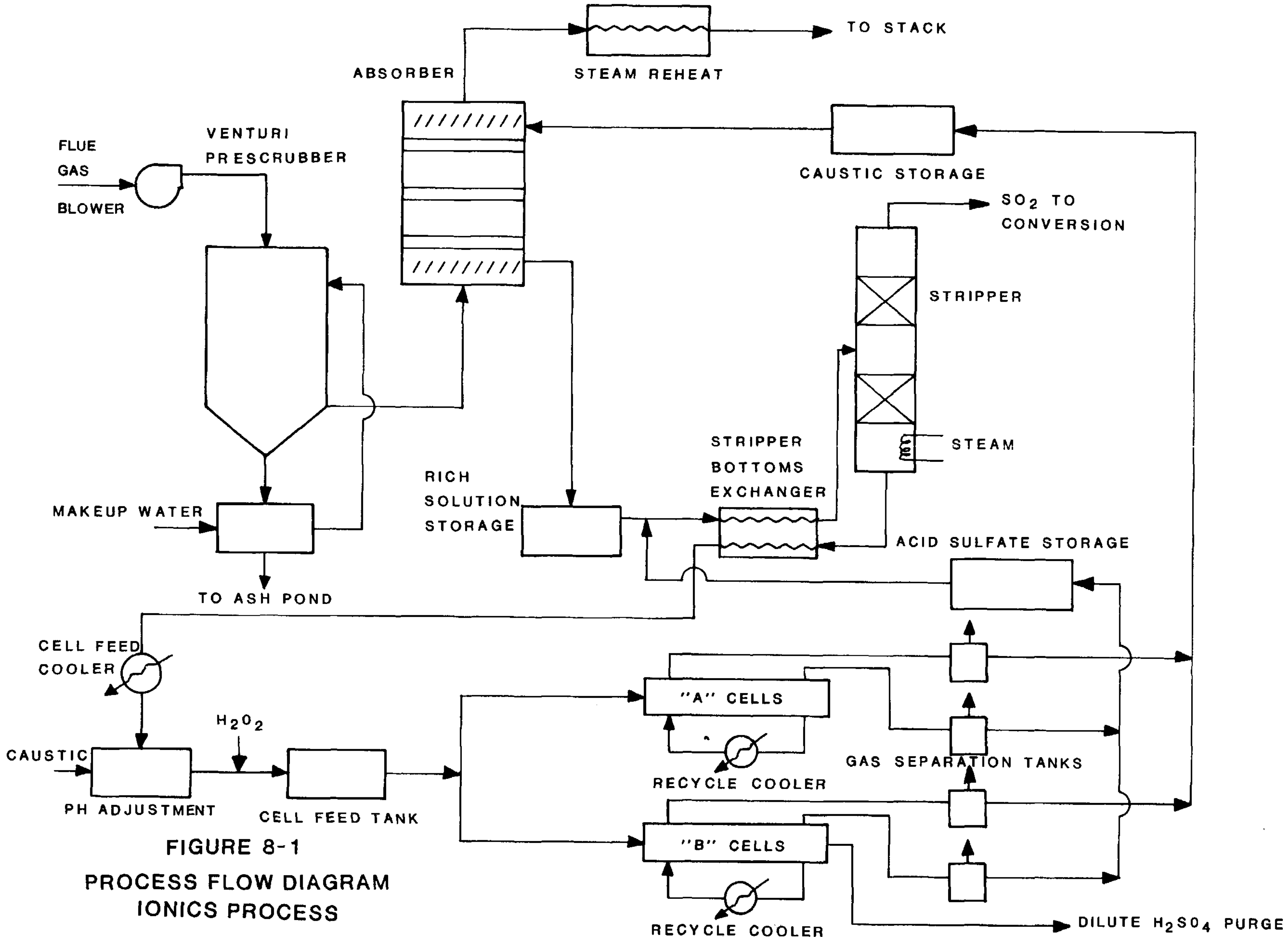


FIGURE 8-1
PROCESS FLOW DIAGRAM
IONICS PROCESS

Absorption

The absorption section employs a venturi type prescrubber to humidify and cool the inlet flue gas from the electrostatic precipitator (ESP). The humidification is necessary to control evaporation of water from the scrubbing solution. The prescrubber also collects about 80 percent of the particulates escaping the ESP, disposing of them as a 5 percent solids slurry to the ash pond, and about 90 to 95 percent of the chlorides in the flue gas. The scrubber itself operates at about 130°F and in this case uses valve trays with recirculation on each stage although a packed tower or even a spray scrubber could be used. The L/G ratio assumed was about 3 gal/mscf per tray with a gas velocity of around 10 feet per second. The total flue gas pressure drop across the venturi and absorber was assumed to be 25 inches of water. The scrubbing solution is a moderately concentrated mixture of sodium sulfate and 2 normal caustic. The caustic absorbs SO_2 according to Reactions 8-1 and 8-2.

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \tag{8-1}$$

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \tag{8-2}$$

The second reaction is the one occurring in the Wellman-Lord process. The most efficient use of caustic and most economical operation occurs when bisulfite concentrations in the exit solution are kept high. Data collected by Ionics indicates that high bisulfite concentrations also deter oxidation and they theorize that sodium sulfite is the oxidized species as in Equation 8-3.

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \tag{8-3}$$

The efficiency of caustic utilization is often represented in terms of the s/c ratio which is defined as the total concentration of sulfite and bisulfite divided by the concentration of the associated sodium ions. A 100 percent bisulfite solution has an s/c ratio of 1 and 100 percent sulfite has an s/c ratio of 0.5. The best s/c ratio which can generally be obtained is about 0.925. Oxidation was taken to be equivalent to 5 percent of the total amount of SO_2 removed for purposes of this study. Ionics researchers feel that the main parameters affecting oxidation are oxygen content of the flue gas, sulfite content of the solution, and gas-liquid contact area in the scrubber.

Acidulation and Stripping

The product scrubbing liquor from the absorber, containing sodium sulfite, sulfate and bisulfite is acidulated with a solution of one normal sulfuric acid and sodium bisulfate. This causes Reactions 8-4 and 8-5 to take place, releasing SO_2 from the solution.

$$NaHSO_3 + NaHSO_4 \rightarrow Na_2SO_4 + H_2O + SO_2 \qquad (8\text{-}4)$$

$$Na_2SO_3 + 2NaHSO_4 \rightarrow 2Na_2SO_4 + H_2O + SO_2 \qquad (8\text{-}5)$$

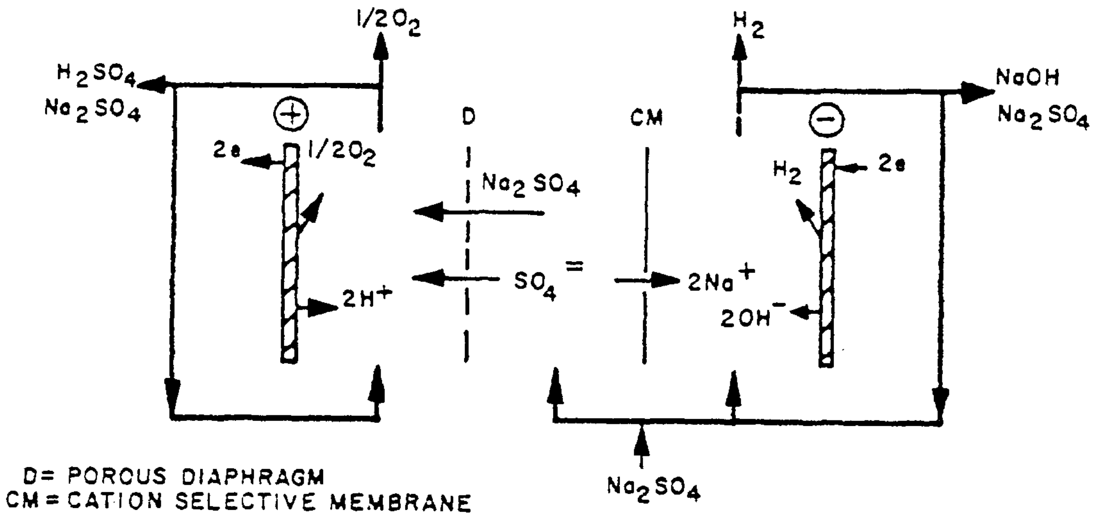
The temperature of the acidulated solution is raised to 200°F by heat exchange and then this solution is fed to the stripper. The steam stripper drives the SO_2 out of the liquor along with large quantities of water vapor. The stripper overhead is partially condensed to reduce the water vapor content to 10 or 15 percent by volume and the condensed water is returned as reflux. The stripper bottoms are cooled by exchange with the feed stream in the stripper bottoms exchanger. Despite the stripping operation, the acidulated solution still contains about 100 ppm residual SO_2.

Cell Feed Treatment

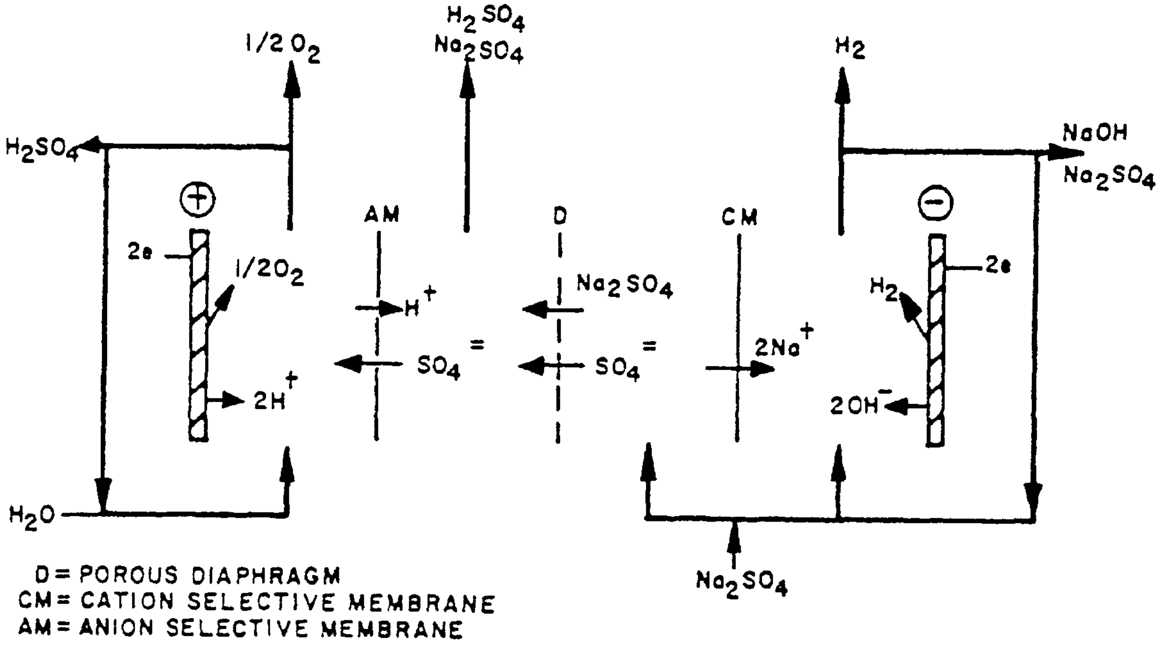
The acidulated and stripped solution of sodium sulfate must be cleaned before being fed to the cells in order to protect the membranes and electrodes from fouling which increases the cell voltage and thus the power consumption. The main contaminants are metal salts, particularly, iron, aluminum, magnesium, and calcium which can be picked up either from equipment corrosion or dissolution of fly ash which gets carried into the system. Removing these contaminants to very low levels is accomplished by adjusting the solution pH to about 8 and adding hydrogen peroxide to oxidize some ions, particularly ferrous iron, and precipitate most metal ions as their hydroxides so they can be filtered out. However, the residual SO_2 also consumes peroxide. The final step in cell feed treatment after filtration is cooling to guarantee a cell feed at about 100°F.

Regeneration System

The regeneration system consists of the electrolytic cells and their auxiliary units: 1) the electrical switch gear for rectification and power control and 2) pumps, piping and exchangers to recirculate and cool the electrolyte solution. This is the equipment which Ionics has developed and is prepared to market. The electrolytic cells are the heart of the process and therefore they will be described in considerable detail. Figure 8-2 illustrates the basic configuration of the two types of electrolytic cells used by Ionics. The "A" cell consists of two electrodes, a nickel-plated carbon steel cathode and a noble metal coated titanium anode, a microporous diaphragm, and a cation selective membrane. The "B" cell contains an additional anion selective membrane. Both types of cell produce solutions of sodium hydroxide and sulfuric acid, each of which also includes



A. SCHEMATIC DIAGRAM OF "A" ELECTROLYTIC CELL



B. SCHEMATIC DIAGRAM OF "B" ELECTROLYTIC CELL

FIGURE 8-2
DIAGRAM OF ELECTROLYTIC CELLS

SOURCE: IO-017

sodium sulfate but the "B" cell in addition produces a dilute solution of pure H_2SO_4 to purge nonregenerable sulfate ions formed due to oxidation. Also, some gaseous hydrogen and oxygen are produced at the electrodes. The hydrogen ions formed at the anode of the "A" cell are prevented from migrating into the catholyte compartment by maintaining sufficient flow of solution from the catholyte side, through the diaphragm to sweep the hydrogen ions back. For this reason the acid solution is diluted with sodium sulfate solution. In the "B" cell the anion selective membrane is successful at preventing sodium from entering the anode compartment but some hydrogen ions escape into the mid-anolyte compartment. The weak, mixed acid thus formed is added to the mixed acid from the "A" cell. Due to the additional resistance caused by the anion selective membrane, the "B" cells require slightly higher voltage. The power consumed by the cells is converted to heat which must be removed. A large amount of electrolytic solution is recirculated and cooled externally to maintain temperature control in the cells. The mixed caustic and sulfate solution is sent to a storage tank from which the scrubbing solution fed to the absorber is drawn. The mixed acid and sulfate is used to acidulate the rich absorber product solution. Dilute acid from the "B" cells is disposed of in order to purge sulfate ions from the system.

SO_2 Conversion

The concentrated SO_2 stream off the stripper can be handled in several ways. The two most likely alternatives are to convert it to either sulfur or sulfuric acid but liquid SO_2 could also be produced. The production of sulfuric acid is easily accomplished but its desirability will depend on the power plant location and the acid market. Production of sulfur is not as easy or as economical due to the use of fuel and reducing agents. The only commercially proven process for reducing

SO_2 to sulfur in environmental applications is the Allied Chemical Process using methane as the reductant. Other processes such as BAMAG or RESOX could be used if demonstrated but the primary consideration will be what type of reducing media is required. For the purposes of this evaluation, the use of the Allied Chemical Process using H_2/CO produced from coal gasification as a reductant was assumed. A further look at the question of SO_2 conversion is to be found in Section 14 where the various schemes are examined in more detail and their usefulness is evaluated.

8.2 Environmental Considerations

Sodium hydroxide solution is a highly effective SO_2 absorbing media and holds a large amount of SO_2 per volume. Therefore, it will not be difficult to achieve greater than 90 percent removal of SO_2 from flue gas. However, slightly higher oxidation may result as SO_2 removal is increased. Alkaline solutions have also been reported to remove about 20 percent of flue gas NO_x due to co-absorption of NO and NO_2 (BA-003). Limited data from the Wisconsin Electric Power Company pilot plant run by Stone & Webster and Ionics indicated NO_x removal approaching 40 percent, but instruments used there showed poor reliability.

The system produces two product streams which present possible environmental hazards. The dilute (10 percent) sulfuric acid purge stream of about 30 gpm must be disposed of. If the process is applied in a situation where production of sulfuric acid is acceptable, the weak acid could be used in the acid plant. In other cases, Ionics has proposed storing the acid for short periods then using it to regenerate the ion exchange resins used by the power plant to treat feed water. Whether this latter method would be accepted by a utility is unknown. The most likely route would be reaction with lime to produce gypsum for disposal.

A second source of potential trouble is the chlorides in the flue gas. A venturi prescrubber should remove 90 to 95 percent of the chlorides but if a simple water quench is used instead of the venturi most of the chlorides would enter the absorber solution. In the electrolytic cells, these chlorides can cause two problems. The chlorides can foul the electrodes and membranes by precipitating with dissolved metal ions and if they remain in solution they will be preferentially reduced instead of oxygen at the anodes, resulting in chlorine gas being given off at the anodes. Since the quantity of oxygen gas produced is rather small it will be vented to the atmosphere and if chlorides do get into the cell feed, the chlorine produced will also be vented. Fortunately, the chlorine should be in small enough quantities to make it little more than a potential nuisance.

8.3 Material and Energy Balances

As mentioned in the introduction, the information which Radian received from Ionics was rather limited and applied mainly to the cell system. In order to have a complete process to evaluate, it was necessary to make several basic assumptions about logical processing steps and about the chemical behavior they would exhibit. Because of the similarity between the Wellman-Lord process and the basic chemistry involved in Ionics' conceptual scheme, most of the assumptions were based on more substantiated information from Davy-Powergas. From these assumptions about the absorber, acidulation, and stripping units and the information about the electrolytic equipment provided by Ionics, it was possible to develop material and energy balances for a full-scale process and for a purge treatment system to be used in conjunction with other sodium-based scrubbing processes. From these balances, estimates could be made of the raw material and utility requirements of each case. These are presented in

Table 8-1. However, because so many unconfirmed assumptions had to be made, the reliability of these estimates will be less than those for other processes.

8.4 Design Considerations

The primary design considerations center around the electrolytic cell regeneration scheme since it is the only new technology in the system. Each cell electrode contains about five square feet of electrode area but a complete assembled cell including membranes is only one to two inches thick. The inter-electrode spacing is kept as small as is feasible in order to have a low cell voltage. Increasing the electrode spacing increases the current path length and thus the electrical resistance of the cell. The cell components are still under-going development but Ionics has already shown that noble metal coated titanium anodes, although more expensive than the lead alloy anodes originally used, are more cost effective because they reduce cell voltage and thus reduce power consumption. Assuming the low current density of 80 amps per square foot Radian's base case requires about 1800 "B" cells and 10,000 "A" cells, each with about 5 square feet of area. The cells would have a current efficiency of 90 to 95 percent based on hydroxide ion production and further improvements will be small. Ionics has had long experience in designing and building electrolytic and electrodialysis cells similar to the SULFOMAT cell under evaluation.

Cell Voltage

The main cost item for the Ionics system will be the electric power to run the SULFOMAT cells. Power usage hinges on the cell voltage which must be applied since the amperage is fixed by the amount of caustic needed for scrubbing and Faraday's

TABLE 8-1

RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE IONICS PROCESS

Basis: 500 Mw, 3.5% Sulfur Coal

Processing Area	Electric Power (Mw)	Steam-H.P. (MM Btu/hr)	Steam-L.P. (MM Btu/hr)	Sodium Carbonate (lb/hr)	Hydrogen Peroxide (23.5%, lb/hr)	Reducing Gas (MM Btu/hr)	Process Water (M gph)	Cooling Water
Pretreatment and SO_2 Absorption	9.3	77	-	300	-	-	42	-
Acidulation and Stripping	-	-	46	-	-	-	-	-
Electrolytic Regeneration	24.5	-	-	-	125	-	-	480
SO_2 Conversion	0.3	-	-(12)	-	-	92	-	-
TOTAL	34.1	77	34	300	125	92	42	480

constant. The cell voltage is a function of four items: the theoretical electrode potential difference, the activation overvoltage due to the slowness of the electrode reactions, the concentration overvoltage which is a result of formation of ion concentration gradients by diffusion limitations, and ohmic losses due to the electrical resistivity across the electrode gap. The theoretical cell potential is beyond control. The activation overvoltage depends on the choice of electrode materials and Ionics has probably finalized its efforts in this area. The concentration overvoltage is controlled by proper design of fluid inlet and outlet ports to keep the electrolyte agitated and by increasing the operating temperature.

Several factors influence ohmic losses. Gas bubbles formed in the interelectrode gap increase electrical resistance; however, fluid agitation and fluid recirculation aid in minimizing this problem. The electrical conductivity of the solution is increased by operating at higher temperatures. The electrical conductivity of the diaphragm is important too but it is mainly a function of construction material. Ionics researchers are still developing the equipment components and feel that the cell voltage can be reduced up to another volt from its present 4.5 volts (80 amps per square foot) by a combination of these methods including higher temperatures, smaller interelectrode gap, and thinner membranes. The membranes now used have a fluorocarbon fabric backing and a lifetime in normal use of several years.

Oxidation

Use of antioxidants to reduce the amount of sulfate formed was considered as it was for Wellman-Lord but was abandoned because all the compounds tested wound up in the electrolytic cells as sludge which hampered cell operation. Antioxidants were tried because "B" cells, which purge the sulfate formed as dilute sulfuric acid, are more energy demanding. The additional anion selective membrane causes them to have a higher cell voltage than "A" cells. In addition to having technical drawbacks due to fouling of the cells, antioxidants were also found to be cost ineffective as they were by Davy-Powergas. Ionics found that a much more effective way of controlling oxidation and at the same time maintaining efficient caustic utilization is by designing and operating the absorber to maximize the concentration of bisulfite ion in the solution and to minimize the amount of time and area where solution containing mostly sulfite ion is contacted by the oxygen bearing flue gas.

The actual amount of oxidation which will take place is not really certain. Davy-Powergas has fairly consistent and complete data for oxidation in their absorber operated with oil-fired flue gas which was used to estimate the oxidation for Radian's version of the Ionics Process. Ionics and Stone & Webster experienced somewhat higher oxidation in their WEPCO pilot plant. The limited amount of data that was collected on oxidation was interpreted by Ionics and Stone & Webster in different fashions. Measured data fell in the range of 7 to 25 percent but Ionics questioned the accuracy of the measurement techniques while Stone & Webster felt the higher measurements should be accepted to be conservative (ME-086). Ionics feels oxidation should be controllable in the range of 5 to 10 percent while Stone & Webster would have said 10 to 15 percent.

One problem in comparing the Ionics and Wellman-Lord absorbers is that while Wellman-Lord's solution starts off as sulfite and any SO_2 pickup reduces its concentration in solution, the Ionics' absorber starts off with caustic and as the solution passes through the absorber progressive SO_2 absorption creates first sulfite and then bisulfite. Thus the profiles down the absorber of solution sulfite and bisulfite composition will be very different for the two processes and the validity of comparing the net result in terms of oxidation may be doubtful. Ionics feels that sulfite is the species being oxidized but Davy-Powergas and others feel that bisulfite is the oxidized species.

Although the use of the "B" cells to purge sulfate ions as dilute sulfuric acid rather than sodium sulfate theoretcially eliminates a sodium ion makeup requirement, some sodium carbonate makeup is, however, required to replace sodium solution lost as entrained mist and mechanical losses from pumps, lines, and tanks. The appropriate quantity is uncertain but Radian has assumed a rate of loss equivalent to 0.5 percent of the circulation rate of caustic solution.

The same considerations about the L/G ratio of the absorber and the need for internal recirculation to maintain good hydraulic characteristics and solution mixing that apply to the Wellman-Lord process apply here as well. The small quantity of flow required to actually absorb the SO_2 is too small to maintain even liquid distribution and mixing across a tray in a tray absorber and is also too small to adequately wet packing in a packed tower so internal recirculation is practiced on each stage to achieve an L/G of about 3 gallons per 1000 standard cubic feet of flue gas passing up through the absorber.

Stripper pH Control

Another factor influencing the design which will affect the efficiency of caustic utilization is the control of pH in the stripper. If considerable excess acid is used to acidulate the absorber product, the equibrilium involving SO_2 in the liquid and sulfurous acid is shifted toward SO_2 which can be easily driven out of the solution by the heat of the stripper. This means a lower residual SO_2 value in the stripper bottoms, however, it also means more recycle caustic is needed to neutralize the excess acid prior to cell feed treatment which must take place in the range of pH 8 to 9. On the other hand, if less acid is used, the residual SO_2 will be higher and when this SO_2 is treated with hydrogen peroxide in the cell feed treatment area a greater amount of sulfate ion is formed. The result is increased usage of peroxide and increased dilute sulfuric acid purge (which requires more "B" cells). The optimum for this situation lies somewhere around a stripper bottoms pH of 3.

As with most wet processes, the Ionics process will require stack gas reheat. However, because the gas is being scrubbed with caustic it is highly unlikely that SO_3 or acid mist would escape to the atmosphere in significant quantities.

Fly ash carryover from the prescrubber can cause two problems. First, it can increase oxidation through a catalytic effect and it can contribute metal ions which could foul cells. To control the metal ions and protect the cells, the cell feed is treated with peroxide and filtered to collect certain metals as their insoluble hydroxides. Hydrogen peroxide addition is expensive, however, and work needs to be done on use of air or oxygen as an oxidizing agent in its place.

As with some other processes, Ionics can store both rich and lean scrubbing solutions to smooth out power plant operating peaks but it can also store solution so it can be regenerated during off-peak hours when excess generating capacity is available. An analysis of the use of off-peak power to cut costs will be made in Section 8.7 on Utility Applicability. SO_2 conversion has been discussed several times previously but it will be reiterated that choice of product and process depends on available markets, available reductants or fuels, and current development efforts by other researchers.

8.5 Status of Development

The Ionics Process, with the exception of the electrolytic equipment, is in a very rudimentary stage of development. Of course, the electrolytic section is the only new technology involved so no real handicap may exist.

WEPCO

The major pilot plant work using actual power plant flue gas was done in 1973 and 1974 at Wisconsin Electric Power Company's Valley Station in Milwaukee using flue gas from a coal-fired boiler. The pilot unit treated 2200 cfm (0.75 Mw) of flue gas containing 2000 ppm of SO_2. The original purpose of this unit was to demonstrate the technical feasibility of the conceptual process design and the operation of the electrolytic regeneration system on the actual product solution of a flue gas desulfurization system. Due to this limited goal, the parts of the system other than the cell area were not adequately instrumented to provide much significant data for absorber or stripper design. Mechanical reliability of the equipment outside the cell area was very poor, resulting in eleven days being the longest continuous period of operation in over one year of test operation. Integration of the process was demonstrated but only after many difficulties during the early operations.

Under the same EPA test program which partially funded the WEPCO pilot plant, Ionics built and satisfactorily tested in their labs a module of full scale cells. However, development work is still going on in the areas of cell feed treatment and cell materials for the purpose of reducing cell voltage and power usage. Plans to build a 75 Mw demonstration plant at WEPCO were dropped when the capital cost of the system was estimated. The cost would have been around $200/kw because of space and retrofit limitations. The small amount of space available was a particular problem and it would have required a very complex equipment arrangement.

Ionics recently announced the sale of a large scale electrolytic system using their SULFOMAT cells to a Japanese company for use in a stack gas scrubbing process. The overall process is basically a Double Alkali Process producing gypsum, but the sodium sulfate formed will be reconverted to caustic and sulfuric acid by the SULFOMAT cells.

Although it might be possible to construct and operate a complete full-scale Ionics system based on Ionics cell developments and a general knowledge of scrubbing and stripping, an integrated demonstration with the aim of gathering design data for the whole system would be desirable. Use of the Ionics electrolytic technology for regeneration of caustic from sodium sulfate solution is already a commercial reality.

8.6 Scale-Up Considerations

The major scale-up problems will be those associated with the electrolytic cell area, as the absorber and stripper are fairly common pieces of equipment and they should present no serious limitation. And, in fact, scale-up of the cell area is already accomplished because Ionics has tested a cell with electrodes with 5 square feet of area which they foresee as being the basic component size for a full-scale plant. The flow volumes required for a 500 Mw installation would call for thousands of cells. In other words, there would be no real scale-up, only a duplication of units.

8.7 Utility Applicability

The Ionics Process should not be limited for any reason in new plant applications. However, as with several of the other processes, the plot area required could limit some retrofit applications even though only the absorption towers need to be close to the boiler. Actual space requirements are still unknown but the absorption and stripping sections will be similar in size to those used by the Wellman-Lord and Citrate/Phosphate Processes (25,000 to 35,000 square feet). The large number of cells needed (approximately 12,000) for regeneration will also occupy a large area but possibly not as large as might be expected because of the way in which they are assembled. Cells are put together back to back in modules of eight and several of these modules can be mounted on one flow manifolding system. Each cell is less than 2 inches thick and thus 12,000 cells may take up much less room than all the electrical switchgear, piping, and auxiliary equipment they require. The large number of cell units employed in a large system gives the process a great deal of flexibility. The modules can be switched out of service easily for maintenance or to follow variations in sulfur content or power plant load. For long term shifts modules could be traded between all plants using the Ionics scheme. Thus, the capital costs of overdesign can be partially recouped by reselling excess electrolytic cell modules.

Raw Materials

The only raw materials required are make-up sodium carbonate and hydrogen peroxide for cell feeding treating. Sodium carbonate is only required in small quantities compared to most sodium processes and will not be a supply problem. A 500 Mw unit also consumes around 450,000 lb/yr of 35 percent hydrogen peroxide. This should not be a problem either since U.S. production is around 120 million lb/yr on a 100 percent peroxide basis. Thus, a 500 Mw Ionics unit boosts hydrogen peroxide use by about 0.1 percent.

Energy

Energy requirements fall into three areas: steam for stack gas reheat and stripping, H_2/CO reducing gas for SO_2 reduction, and electric power for the cells and various system auxiliaries. The steam requirements are relatively minor and problems with the use of a H_2/CO reducing gas in the Allied Chemical Process are discussed in Section 14. The major hindrance in use of the Ionics Process is the large amount of electrical energy which is needed. This energy serves two needs. First, is the power to drive the pumps and fans, the most important being the flue gas booster blowers which consume 7.8 Mw in overcoming the gas side pressure drop across the prescrubber and the absorber. Second, and of overwhelming importance is the energy consumed by the electrolytic cells - about 24.5 Mw for a 500 Mw plant. Together this means that an Ionics system where the cells were operated in synchrony with the power plant load would derate that plant by 6.8 percent.

However, this may not accurately represent the situation because the cells are readily interruptible and the regeneration system could be completely decoupled from the absorption system by provision of sufficient solution storage capacity. In this case, the big power consumer, the regeneration system, could be shut down when the plant was peaking while solution to be electrolyzed was stored. Then during off peak hours when extra capacity was available, regeneration could be run at full capacity using solution from storage.

Off-Peak Regeneration

Some studies were made by Stone & Webster and Ionics during their association on the economic consequences of using off-peak power for regeneration. Most plants must maintain a sizable fraction of their capacity as spinning reserve at all times to meet any sudden demand surges and to fulfill their commitments to the power grid. If this reserve could be put to useful work such as the Ionics regeneration while still being available almost instantly, the actual cost of the electricity could be reduced significantly. This, of course, would require a larger initial cost for a sufficient number of cells to regenerate all the solution necessary during off-peak hours. An additional consideration is that when regeneration is to be di continued for periods longer than a couple of hours the cells must be drained to prevent damage to the membranes from salt crystallization. A study to verify the feasibility of this idea and to compare the economic tradeoff of reduced electricity cost versus increased regeneration system capital cost in each specific case would be necessary to completely evaluate the system's economic applicability.

The use of large storage tanks to decouple the absorption, stripping, and regeneration steps increases the operability and flexibility of the process. Turndown will be about the same as that achievable on the Wellman-Lord process, reduction down to 35 percent of capacity for each absorber module, with 3 or 4 modules being used.

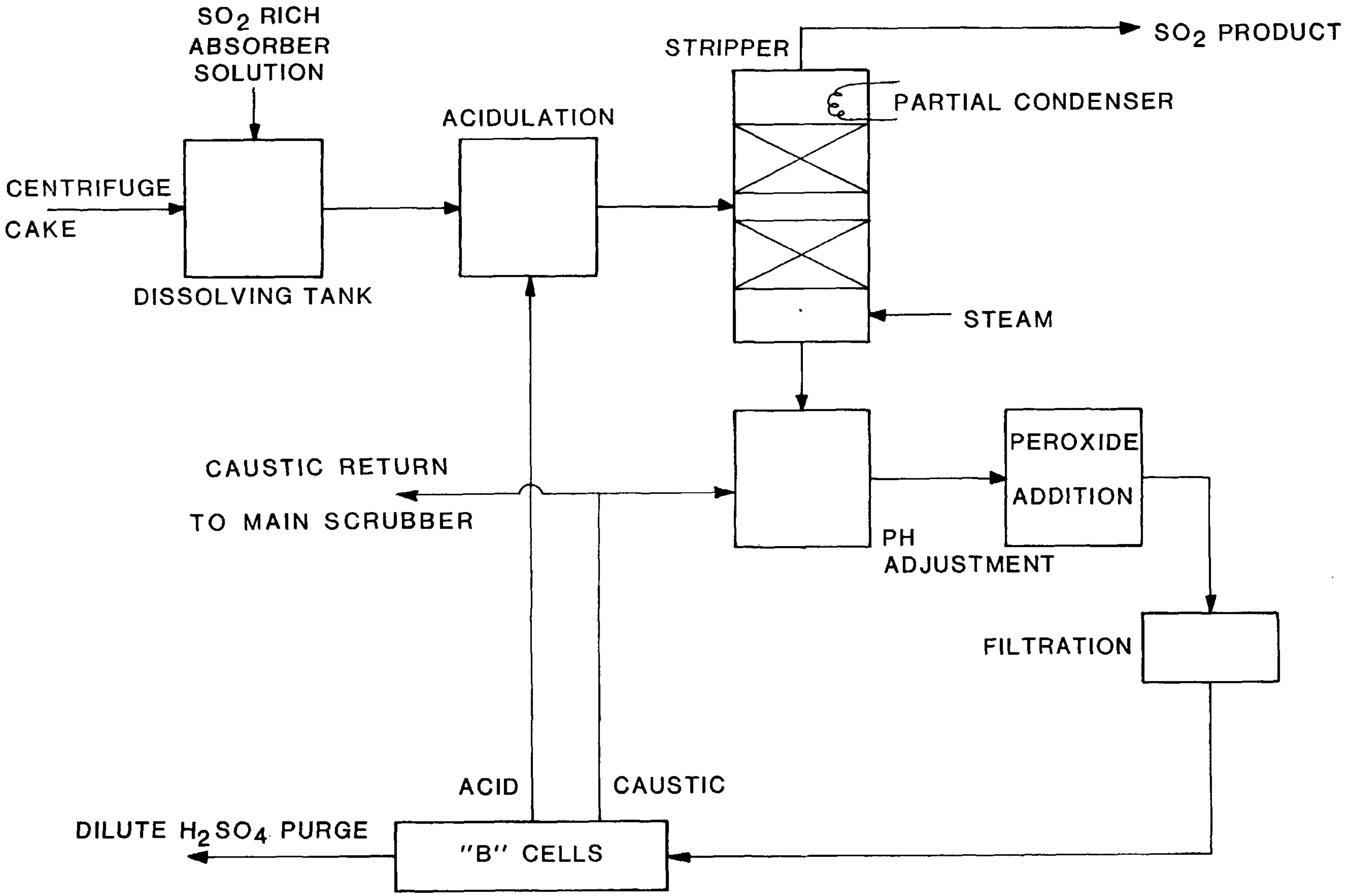


FIGURE 8-3 PROCESS FLOWSHEET FOR SODIUM SULFATE PURGE TREATMENT

Sulfate Purge Treatment

The Ionics' SULFOMAT cell is also applicable to treatment of sodium sulfate purge streams from other FGD processes, such as Wellman-Lord and Citrate/Phosphate. At the present time such streams are either discharged to a large receiving body or concentrated for storage or sale with the primary markets being the paper and pulp industry and glass making. The value of the sulfate is low and it would be beneficial to be able to return the sodium ions to the scrubbing system in an active form such as caustic soda. In this area the Ionics' SULFOMAT "B" cell has very positive technical contributions to make. To evaluate the feasibility of using Ionics technology to convert sodium sulfate to caustic and sulfuric acid, a conceptual flow scheme (Figure 8-3) was devised using the same "B" cell configuration and solution concentration as in the complete process to treat the mixed sodium sulfate and sulfite purge from the Wellman-Lord process (see Section 9).

First, sodium sulfate/sulfite centrifuge cake is dissolved and combined with a small side stream of SO_2 rich absorber liquor (about 3.5 percent of the total absorber output). This sulfate, sulfite, and bisulfite solution is acidulated with the mixed sulfuric acid and sodium bisulfate solution from the cells, then the solution is stripped of SO_2 in a reboiled column. The SO_2 product is combined with the main SO_2 product stream. The stripper bottom is neutralized with caustic and treated for metal removal before being fed to the electrolytic cells. About 1800 "B" cells produce approximately 30 gallons per minute of pure 10 percent sulfuric acid and 60 gallons per minute of caustic and 120 gallons per minute of acid mixed with sodium bisulfate. Most caustic produced is returned to the absorber with a small portion used for pH adjustment after stripping. The mixed acid solution is used in acidulation to release SO_2 in solution as sulfite and bisulfite. This system converts the sodium sulfate purge to a dilute sulfuric acid purge reducing the need for makeup sodium carbonate. If no use can be found for the dilute acid purge stream, it must be neutralized with lime or limestone before disposal.

Technically there is nothing to prevent such a system from being used successfully. The only question is whether or not the Ionics cells regenerate caustic from sodium sulfate at a cost lower than the purchase of sodium carbonate and sale of sodium sulfate.

8.8 Economic Assessment

Annualized raw material and utility requirements and costs for a complete Ionics Process are presented in Table 8-2. The results indicate that the approximate distribution of raw material and utility costs is: Absorption Section - 23 percent, Acidulation and Stripping Section - 2 percent, Regeneration Section - 44 percent, and SO_2 Conversion - 31 percent. The SO_2 conversion cost is based on the assumption that an Allied Chemical plant to reduce SO_2 to sulfur would be used. The total annual raw material and utility costs for the 500 Mw base case power plant is approximately $6.2 million or 2.4 mills/kwhr.

The Ionics Process is energy intensive only in the extent to which it uses electrical power. The steam requirements of 46 MM Btu/hr for stripping are relatively minor. Most other processes which use steam stripping consume 6 to 10 pounds of steam per pound of SO_2 but because Ionics strips SO_2 from very acid solution they need only about 2.5 pounds of steam - 1 pound for feed heating and 1.5 pounds for stripping and heat losses. The electrical energy goes to two major consumers: the flue gas booster blowers using about 7.8 Mw or 1.6 percent of the power

TABLE 8-2

UTILITY AND RAW MATERIAL COSTS IONICS PROCESS

Basis: 500 Mw; 3.5% Sulfur Coal; 5,260 Hours Per Year

Absorption System	Consumption	Unit Price	Annual Cost, $	
Electric Power	9.3 Mw	$0.02/kwhr	978,360	
Sodium Carbonate	800 tons/yr	$52/ton	41,600	
Steam (H.P.-Reheat)	77 MM Btu/hr	$1.00/MM Btu	405,020	
Process Water	700 gpm	$0.08/M gal	17,670	
			1,442,650	23%
Acidulation & Stripping				
Steam (L.P.)	46 MM Btu/hr	$0.50/MM Btu	120,980	
			120,980	2%
Electrolytic Regeneration				
Hydrogen Peroxide (23.5%)	126 lb/hr	$190/ton	60,070	
Electric Power	24.5 Mw	$0.02/kwhr	2,577,400	
Cooling Water	8000 gpm	$0.03/M gal	75,740	
			2,713,210	44%
SO_2 Conversion to Sulfur				
Natural Gas	92 MM Btu/hr	$4.00/MM Btu	1,935,680	
Electric Power	0.3 Mw	$0.02/kwhr	31,560	
Stream Credit	12 MM Btu/hr	$0.50/MM Btu	-(31,560)	
			1,935,680	31%
TOTAL RAW MATERIAL AND UTILITY COST			6,212,520	
			or 2.4 mills/kwhr	

plant capacity and 24.5 Mw or 5 percent of capacity used by the regeneration section. As discussed earlier the electrolytic cells may not actually require derating of the plant by the full 5 percent if the solution can be stored for regeneration during off-peak hours.

Another way of looking at the power usage is to calculate the fuel equivalent of the electrical energy. Assuming that it takes 10,000 Btu of fuel to produce each incremental kilowatt hour, the total energy usage of the regeneration section amounts to 245 MM Btu/hr and that of the flue gas blower amounts to 78 MM Btu/hr. The H_2/CO reducing gas used for SO_2 conversion is equivalent to 92 MM Btu/hr. Overall, electrical energy accounts for 58 percent of the total utility and raw material cost. The economic impact of using off-peak power at the cost of fuel, operating, and maintenance charges would be significant since this might reduce the cost of electric power for the Ionics Process from $0.02/kwhr to $0.01/kwhr or less.

Particularly for the Ionics Process, Radian was unable to determine capital charges. However, on the basis of very limited information (IO-017), it is estimated that the absorption and acidulation/stripping will represent about 30 percent of the capital cost, the regeneration section 60 percent, and the SO_2 conversion section 10 percent. Capital costs for the Ionics Process, however, should be high due to the power replacement costs.

A preliminary economic assessment was also made of the Ionics SULFOMAT cells use for sulfate purge regeneration. As noted above, the electrical energy for the regeneration system is the predominant cost of the Ionics Process. The electrical energy amounts to almost 90 percent of the costs in the acidulation/stripping and regeneration section. Therefore, the only cost which was actually calculated for an Ionics cell system for sodium sulfate purge conversion was the power cost. The power consumed to treat the purge stream from the Wellman-Lord Process for Radian's 500 Mw base case plant assuming 5 percent oxidation was 3.6 Mw. Thus, the power cost would be about $400,000/yr. For comparison, the difference between the carbonate make-up cost and the sodium market value without drying would be $270,000/yr. Thus, the power alone, charged at the prime rate of $.02/kwhr, would make the Ionics regeneration scheme uneconomic for purge treatment and inclusion of capital costs would make the situation even worse since the cells themselves are expensive. Again, if off-peak purge treatment were feasible at reduced power cost, it is possible that this application would become viable.

8.9 Process Summary

The Ionics Process consists of caustic scrubbing of SO_2 laden flue gas with release of SO_2 by acidulation and stripping and electrolytic regeneration of the caustic solution. Conversion of SO_2 to either sulfur or sulfuric acid is possible. This process is simple with regard to both chemistry and equipment but the electrolytic regeneration, although flexible, is expensive in terms of capital cost and electric power consumption. The only by-product is a small stream of dilute, pure sulfuric acid which might be used by the power plant to regenerate the boiler feed water demineralizers. The process's SO_2 removal properties are good. Areas of concern in design are the cells, the cell feed treatment system, oxidation, and integration of the scrubbing system with power plant operation and SO_2 conversion. The electrolytic cells have been developed to full scale and large applications will require only the replication of present equipment but some improvements are still being made.

As an integrated process, however, it is in an early stage of development, the only pilot plant run with flue gas being an 0.75 Mw unit at WEPCO.

The SULFOMAT cells are applicable both as the regeneration system for a complete caustic scrubbing design or as a sodium sulfate purge treatment system for other sodium based scrubbing processes. Economically, the utility and raw material cost of 2.4 mills/kwhr could be substantially reduced if regeneration during off-peak hours could be done at a lower electricity cost. It should be noted that Ionics, Inc., does not market a complete FGD process, only the electrolytic equipment. This evaluation and the costs presented are qualified by many assumptions.

9.0 WELLMAN-LORD SULFITE SCRUBBING PROCESS

The Wellman-Lord Sulfite Scrubbing Process marketed by Davy Powergas, is based on the ability of sodium sulfite solution to absorb SO_2 thus forming a solution of sodium bisulfite which can be thermally regenerated. It is a regenerable process and is presently being commercially employed on a large scale. A concentrated stream of SO_2 is produced which can be processed to elemental sulfur, sulfuric acid, or liquid SO_2. A by-product purge of sodium sulfate is produced as the result of sulfite oxidation.

9.1 Process Description

The Wellman-Lord Process consists of five basic processing steps:

1) Gas pretreatment,

2) Absorption,

3) Purge treatment,

4) Regeneration, and

5) SO_2 conversion.

No unusual or unique equipment is used in any of these areas with the possible exception of the SO_2 conversion step which is licensed technology. A simplified process flow sheet appears in Figure 9-1. The gas pretreatment and absorption sections are essentially the same as those found in most aqueous scrubbing systems.

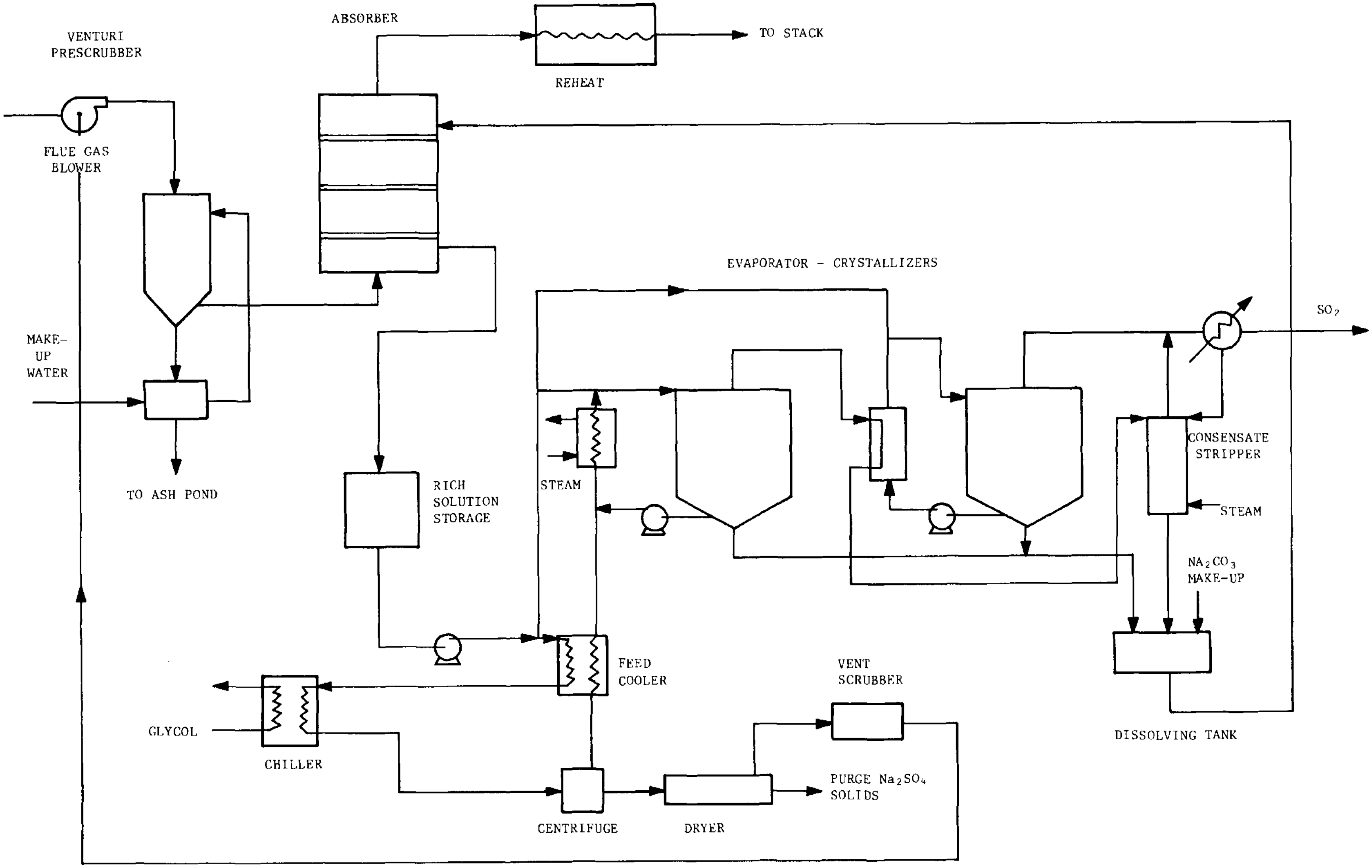


FIGURE 9-1. PROCESS FLOW DIAGRAM
WELLMAN-LORD SULFITE SCRUBBING PROCESS

Gas Pretreatment

The flue gas to be treated is taken after the electrostatic precipitator at a temperature of about 300°F and passed through a venturi or tray type prescrubber where the gas is cooled to around 130°F and humidified. The venturi is preferred because with it 70 to 80 percent of the remaining fly ash and 95 to 99 percent of the chlorides are removed. A tray-type prescrubber is satisfactory for cooling and humidifying the gas with low pressure drop but provides lower reductions in fly ash and chlorides. The humidification of the flue gas in the prescrubber prevents the evaporation of excessive amounts of water in the absorber. Scaling and plugging problems are virtually eliminated by use of the prescrubber and clear scrubber solutions, and due to the fact that the absorption product, sodium bisulfite, is more soluble than sodium sulfite. A well-designed prescrubber will remove up to 99 percent of all chlorides in the flue gas which should help maintain a low level of chloride in the scrubbing liquor, thus reducing the potential occurrence of stress corrosion. The fly ash and other solids collected by the prescrubber are pumped to the ash disposal pond as about 5 percent slurry, after neutralization with lime when necessary. The absorption of chlorides and some SO_2 and SO_3 can cause the water to become fairly acidic.

Absorption

Humidified gas from the prescrubber is passed up through the absorption tower where the SO_2 level is reduced by at least 90 percent. The cleaned gas is reheated to at least 175°F by heat exchange with high-pressure steam and exhausted to the atmosphere. There are various alternatives to this method of reheating the gas but use of steam allows coal to be used indirectly rather than premium fuels such as oil or natural gas. The total pressure drop across the FGD system which must be overcome by flue gas booster fans is about 25 inches of water.

The absorption of SO_2 proceeds according to Equation 9-1.

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \qquad (9\text{-}1)$$

Make-up sodium carbonate also reacts with SO_2 in the absorber to form sodium sulfite by Equation 9-2.

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \qquad (9\text{-}2)$$

A very important side reaction which will be discussed in detail later is the oxidation of sulfite to sulfate by oxygen in the flue gas as in Equation 9-3.

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \qquad (9\text{-}3)$$

Some sodium sulfate is also formed by absorption of SO_3 from the flue gas as in Equation 9-4.

$$2Na_2SO_3 + SO_3 + H_2O \rightarrow 2NaHSO_3 + Na_2SO_4 \qquad (9\text{-}4)$$

Davy Powergas offers two types of absorption units, a packed tower for small volume applications and a valve tray tower for large volume applications. The valve tray unit is generally built in a square configuration and includes three to five trays depending on the inlet SO_2 concentration and the degree of desulfurization required. For a 500 Mw installation, three or four absorbers would be used although a single unit in Japan is treating flue gas from a 220 Mw boiler. Because of the large capacity of concentrated sodium sulfite solution to absorb SO_2, the feed liquor flow is fairly small and recirculation is practiced on each stage to maintain good hydraulic characteristics over the trays. With the recirculation, the L/G ratio is kept at about 3 gal/mscf, per tray. Superficial gas velocity in the absorber is about 10 feet per second.

Purge Treatment

About 15 percent of the absorber product liquor is drawn off to the purge treatment area for separation of sodium sulfate. The feed liquid is cooled by heat exchange with treated liquid. In a chiller-crystallizer, the purge is further cooled to about 32°F and a mixture of sodium sulfate and sulfite is crystallized out. The slurry is put through a centrifuge to produce a 40 percent solids cake and the cake is dried by steam. A small liquid purge stream is also drawn off the evaporators and added to the cake to remove some of the thiosulfate formed in the system. The crystalline product is a mixture of anhydrous sodium sulfate (70 percent) and sodium sulfite (30 percent), plus small amounts of thiosulfates, pyrosulfites, and chlorides. The vent gases from the dryer are scrubbed to remove dust and recycled to the main flue gas stream. The centrate is heated by passing through the feed cooler and is returned to the product liquor stream entering the evaporator loop. Refrigeration for the chiller-cyrstallizer is provided by an ethylene glycol system.

Regeneration

The regeneration section consists of a set of double effect, forced circulation evaporators, condensers, a condensate stripper, and a dump dissolving tank. The regeneration of sodium sulfite is performed by simply reversing the absorption reaction through addition of heat.

$$2NaHSO_3 \rightarrow Na_2SO_3 + H_2O + SO_2 \qquad (9\text{-}5)$$

However, higher temperatures also increase the formation of thiosulfate by the disproportionation reactions 9-6 and 9-7.

$$6NaHSO_3 \rightarrow 2Na_2SO_4 + Na_2S_2O_3 + 2SO_2 + 3H_2O \qquad (9\text{-}6)$$

$$2NaHSO_3 + 2Na_2SO_3 \rightarrow 2Na_2SO_4 + Na_2S_2O_3 + H_2O \qquad (9\text{-}7)$$

The combined stream of absorber product liquor and purge centrate is split between the two evaporator effects, each of which operates under a vacuum, with 55 percent going to the first effect and 45 percent going to the second effect. The first effect operates at 200°F and is heated with low pressure steam by way of an external shell and tube exchanger. The SO_2 and water vapor driven off in the overhead from the first effect are used to heat the second effect which operates at about 170°F. In each effect the undissolved solids content of the recirculated liquor is about 45 percent, primarily sodium sulfite. Operating at such a high solids concentration eliminates the need to centrifuge the product stream going to the dissolving tank. The regeneration reaction is limited by the equilibrium concentration of sulfite ion in solution. Fortunately, since sodium sulfite is less soluble than sodium bisulfite, it is continuously removed from solution by crystallization, driving the reaction forward.

The SO_2 and water vapor from the evaporators is subjected to partial condensation to remove most of the water and thus concentrate the SO_2. The condensate contains several hundred ppm of dissolved SO_2 and is steam stripped to lower these values. The stripped condensate is returned to the dump dissolving tank along with a small amount of make-up water and sodium carbonate and agitated with the sodium sulfite slurry from the evaporators to provide absorber feed. The SO_2 stream exiting the condenser contains only 5 to 10 percent water. It is compressed and turned over to the SO_2 conversion section.

SO_2 Conversion

Given the concentrated SO_2 stream produced by the Wellman-Lord gathering system, it is possible to utilize several processes to put the sulfur content in a more useful or acceptable form. The process presently used by Davy Powergas when sulfur is the desired product is the Allied Chemical catalytic reduction using methane. For this evaluation, Radian will use H_2/CO produced by coal gasification as the reductant rather than methane. In this process, the SO_2 would be heated, mixed with the correct amount of H_2/CO and introduced over a catalyst to reduce part of the SO_2 to sulfur and part to H_2S. The sulfur is condensed out and the H_2S-SO_2 mixture is fed to a modified Claus unit. Other processes under development which convert SO_2 to sulfur such as the RESOX and BAMAG processes would be applicable, if successfully demonstrated.

Another alternative for SO_2 conversion would be to add a contact sulfuric acid plant to convert the SO_2 to sulfuric acid. Some studies have shown that a market may exist for sulfuric acid in many areas of the country. Acid production is less comsumptive of fuel and reducing media than sulfur production, although it is more difficult to store and ship. A more detailed discussion of these SO_2 conversion alternatives appears in Section 14 of this report.

9.2 Environmental Considerations

The Wellman-Lord Process is capable of achieving very high SO_2 removal levels by varying the number of trays used in the absorber, but each additional tray adds at least 3 inches of water to the pressure drop. However, 100 to 150 ppm SO_2 in the outlet gas is about the most economically obtainable value due to equilibria relationships. Increasing SO_2 removal also has another effect.

Oxidation of sulfite is largely a function of the oxygen content of the flue gas and the contacting system. Oxidation is controlled by the transfer of oxygen through the liquid film along the gas-liquid interface so any steps which increase the liquid contact may increase the oxidation rate.

Some alkaline scrubbing systems have reported about 20 percent removal of NO_x due to absorption of NO and NO_2, perhaps as in Equation 9-8 (BA-003).

$$Na_2SO_3 + NO + NO_2 \rightarrow 2NaNO_2 + SO_2 \tag{9-8}$$

The Wellman-Lord system has not been able to show appreciable reduction in the NO_x content of flue gas in actual practice. Moreover, the NO_2 is suspected of being a major contributor to oxidation.

Wellman-Lord yields two by-product streams besides the main SO_2 product. For a 500 Mw plant burning 3.5 percent sulfur coal, about 1350 lb/hr of neutralized fly ash solids as 5 percent slurry, including most of the chlorides, must be disposed of to the ash pond. The other by-product is 2725 lb/hr of mixed, anhydrous sodium sulfate and sulfite which is a result of the purge. This product has only limited economic value but there is currently a market for it in the paper industry although the size of the market is unknown. Davy Powergas reports that samples of sodium sulfate purge solids have been tested and found satisfactory for paper industry consumption.

Some possible environmental side effects could be caused by carry-over of entrained mist from the absorber and fugitive dust escaping from the sodium sulfate drying operations. In both cases, the primary offender would be sulfates, whose health effects are still under investigation. However, well designed mist elimination devices on the absorber and a well designed vent scrubber on the dryer should reduce these sources to insignificance.

9.3 Material and Energy Balances

As with the other processes, material and energy balances were performed for the Wellman-Lord Process as it might be applied to a 500 Mw boiler burning 3.5 percent sulfur coal. From these calculations, estimates of the raw material and utility requirements of the process could be made.

One very important assumption had to be made about the oxidation rate in order to carry out the study. Based on information provided by Davy Powergas, Radian has assumed that sulfite oxidation is controlled mainly by oxygen transfer into the liquid and that the rate of transfer and hence oxidation is dependent on the oxygen flow. Design correlations obtained from Davy Powergas enabled Radian to estimate the sulfate formation fairly accurately. The configuration assumed for the regeneration section was based on advice from Davy Powergas to use double-effect evaporator-crystallizers rather than single effect for the SO_2 loadings typical in flue gas applications. This results in a net savings of about 45 percent in steam consumption by the regeneration section, although at a higher capital cost.

In the past, Davy Powergas has usually proposed a natural gas-fired, stack gas reheat system when the Wellman-Lord

Process is used in conjunction with the Allied Chemical methane reduction system to produce sulfur. However, for the purposes of this study, a high pressure steam reheat will be employed and H_2/CO reducing gas will be used as the reductant. A summary of the utility and raw material requirements is presented in Table 9-1.

9.4 Design Considerations

The design area of major concern in the Wellman-Lord Process is sulfite oxidation. Other areas of concern are the evaporator-crystallizer, stack gas reheat, and the availability of reducing agents.

The oxidation rate of the sulfite scrubbing solution is a function of several factors, the first being most important: impurities in the solution, recirculation rate, temperature and oxygen content of the flue gas, contact efficiency, pH, and solution strength.

It is probable that certain components of fly ash such as iron and manganese catalyze the oxidation and thus increase the total sulfate formation. Despite the upstream electrostatic precipitator and venturi prescrubber some small amounts of fly ash will be picked up by the scrubbing liquor. The liquor is routinely filtered as it leaves the absorber to prevent build-up of these solids. Davy Powergas has noted about a 25 percent increase in oxidation for oil-fired boiler applications over acid plant tail-gas applications where fly ash is not present. This information was obtained from data on Wellman-Lord units now in commercial operation. Short term tests on coal-fired boiler flue gas, however, indicated that fly ash from coal does not increase the oxidation rate over that obtained in oil-fired boiler applications. Long term data on oxidation in applications with fly ash

TABLE 9-1

RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE WELLMAN-LORD PROCESS

Basis: 500 Mw, 3.5 % Sulfur Coal, 5,260 Hours Per Year
at Full Load

Processing Area	Electric Power (Mw)	Steam-H.P. (MM Btu/hr)	Steam-L.P. (MM Btu/hr)	Reducing Gas (MM Btu/hr)	Sodium Carbonate (lb/hr)	Process Water (mgph)	Cooling Water (mgph)
Pretreatment and SO_2 Absorption	9.3	77	-	-	2,120	-	-
Regeneration	1.6	-	160	-	-	25.5	430
Purge Treatment	1.0	-	20	-	-	-	-
SO_2 Conversion	0.3	-	-(12)	92	-	-	-
TOTAL	12.2	77	168	92	2,120	25.5	430

from coal-fired boilers will be obtained from the 115 Mw demonstration unit at Northern Indiana Public Service Company's Dean H. Mitchell Station, which will start up in 1976.

The liquor recirculation rate on each stage of the absorber is governed by the need to maintain adequate flow for good hydraulic characteristics. If liquid flow across the trays is too low, poor distribution of liquid occurs and stagnant areas will result. Any recirculation above that needed for this reason merely increases the oxidation rate without increasing SO_2 removal. The reason for this is that SO_2 transfer from gas to liquid is controlled by gas film resistance while oxygen transfer is controlled by liquid film resistance. Increasing liquid recirculation decreases liquid film resistance to oxygen transfer.

The absorption temperature is fixed at the adiabatic saturation temperature of the gas, about 125°F. Oxygen content of the flue gas is determined by the amount of excess air fired. Flue gas NO_2 may be a significant contributor to oxidation but the major cause is direct oxidation of sulfite to sulfate by oxygen from the gas.

Oxygen transfer is impeded by salts in solution so the fresh scrubbing liquor is originally saturated with sodium sulfite which also minimizes the amount of solution to be circulated. The pH range of 7 to 5.5 is controlled by the sulfite-bisulfite equilibrium. Contact efficiency is a function of tray design which is set by the level of SO_2 removal.

As a result of the oxidation problem several approaches have been tried to reduce the amount of purge and the amount of make-up sodium carbonate. The most successful method so far has been the development of a fractional crystallization technique to increase the concentration of sodium sulfate in the purged solids to about 70 percent. This step will be demonstrated in the U.S. for the first time at NIPSCO. It has been used three times previously in Japan. Further improvements in sulfate concentration are still possible.

For a while, Davy Powergas and their Japanese licensees investigated the use of an antioxidant material to decrease the rate of sulfate formation. This idea was shown to be feasible but was cost ineffective and, therefore, was abandoned in favor of simply controlling operating conditions to minimize oxidation as much as possible. An idea still under consideration involves development of a process to convert sodium sulfate to sodium carbonate or sodium hydroxide.

Because the Wellman-Lord is a wet process it will be necessary to reheat the treated flue gas to at least 175°F to get adequate dispersion of the plume and the remaining SO_2. Recent data on sulfuric acid dew points indicates that reheat to some temperature even higher than 175°F may be necessary to completely eliminate acid mist and corrosion problems. The reheat energy is a significant debit against the system.

Another point in the system where energy consumption is important is the evaporator section. Reversing the absorption reaction and driving off SO_2 from solution requires a substantial quantity of heat which is supplied by low pressure steam. By using double-effect rather than single-effect evaporators, the consumption of steam is reduced but the capital costs for the equipment are increased.

In sophisticated or complicated processes such as some of the second-generation regenerable processes, integration of various treatment steps is sometimes difficult, but in the Wellman-Lord system the unit operations are all fairly simple and are all continuous. The variation in flows to the absorption section from the boiler can be accommodated by insertion of surge storage between the absorption and regeneration areas.

The question of what to do with the SO_2 product stream will have to be answered separately for each individual site but for production of sulfur to a viable alternative in many cases a process able to use a reductant other than methane will be necessary. In some isolated cases, methane may be readily available but in general the most reliable sources of reducing agent will be coal or coke. Coal might be used in solid form as in Foster Wheeler's RESOX process or as H_2/CO producer gas. Unfortunately, this whole area is a source of uncertainty because to date, only the Allied Chemical Process using methane has been demonstrated on a large scale. The use of reducing gas from coal gasification in the Allied Process is still in the relatively early developmental stage. Consequently, the design considerations for SO_2 conversion have not been adequately identified.

9.5 Status of Development

The Wellman-Lord Process was first conceived in 1966 and a pilot plant using potassium sulfite rather than sodium sulfite was operated in 1967. The problems encountered with scaling and high steam consumption on this original pilot induced a switch to the sodium system. Potassium bisulfite is less soluble than potassium sulfite, while sodium bisulfite is more soluble than sodium sulfite. This means that in a sodium system the tendency in the absorber as SO_2 is picked up is toward the more soluble compound so that despite considerable evaporation of water, the saturation point of the solution will not be exceeded.

The first sodium sulfite system was installed for Olin Corporation in 1970 to treat a 45,000 scfm stream of acid plant tail gas. Despite some initial difficulties, the plant operated successfully. Subsequently, the process was applied to an oil-fired industrial boiler of the Japan Synthetic Rubber Company in 1971. Again, the plant was operated successfully after some initial difficulty. This unit has since been able to achieve better than 90 percent removal of SO_2 with an on-stream factor of better than 97 percent. Growing experience allowed a continued improvement in design and operating techniques.

The process has since been applied to other sources of sulfur dioxide. Altogether, 17 plants are on-stream, 12 in Japan and 5 in the U.S., and 15 more have been contracted for. Of these 32 installations, the two most significant for this study are the unit in operation since 1973 for Chubu Electric Power's Nagoya Station and the unit under construction at Northern Indiana Public Service Company's Dean H. Mitchell Station. The Chubu plant is significant because it is the largest Wellman-Lord system which has a fairly long operating history. The application is a 220 Mw, oil-fired peaking plant. The Wellman-Lord unit has been highly successful, achieving 90 percent removal of SO_2 consistently with a high on-stream factor. The nature of the source is such that the FGD system has had to follow rapid load swings from 35 to 105 percent of plant nameplate capacity, thus its flexibility and turndown capabilities are well proven. The flexibility is obtained mainly by the provision of large solution surge storage.

The NIPSCO plant is important because it will be the first large scale installation in the U.S. and the first full scale demonstration of the process on a power plant burning high sulfur coal. The Wellman-Lord unit is being installed on the Number 11 boiler at the Mitchell station. The nameplate rating of the boiler is 115 Mw and it is burning 3.5 percent sulfur coal.

Current areas of concern are improvement in evaporator and purge treatment design. The fractional crystallization method of purge concentration was developed by Davy Powergas's two Japanese licensees. Some effort has also been spent to devise an economical means of converting the sodium sulfate to a form such as sodium carbonate or caustic soda which could be returned to the system in order to reduce the sodium make-up requirements. So far this work has not been completed. Ionics' SULFOMAT electrolytic cell and various techniques from the paper industry have shown that sodium conversion or reduction is possible, but the economics are still uncertain and some technical problems remain. Also, some purge will still be necessary to eliminate chlorides, thiosulfates and other trace components from the recirculation loop.

The use of an antioxidant has been evaluated by the process developer in order to reduce the quantity of sodium sulfate formed. However, the chemical compounds which were able to substantially decrease the oxidation rate turned out to be so expensive that the cost of using the antioxidants was greater than the cost of simply replacing the sodium sulfite which was converted to sodium sulfate. Therefore, use of antioxidants has been dropped in favor of various operational techniques to minimize oxidation by reducing oxygen transfer.

Obviously, with 17 commercial plants in operation, the Wellman-Lord Process has been largely demonstrated. The NIPSCO unit will, however, answer a few remaining questions about integrating the basic absorption and regeneration technology with the Allied Chemical Process to reduce SO_2 to sulfur.

Data for selection of the materials of construction is plentiful due to the large amount of previous experience. The materials which will be employed are generally fiberglass reinforced polyester-lined carbon steel, 304, 316 and 316L stainless steel, all of which are fairly common. The only area where material problems are still encountered is the prescrubber. There the chlorides and ash may make the use of Hastelloy G necessary.

9.6 Scale-Up Considerations

Scale-up is not a problem in application of the Wellman-Lord system because like lime/limestone scrubbing, large scale units are already in operation or under construction. This aspect was discussed earlier under status of development. The Wellman-Lord system has undergone only minor modifications in the last few years. These were the shift to double-effect evaporators and more recently the inclusion of the fractional crystallization method of purge treatment. Double-effect evaporators are well understood and have been used on some Wellman-Lord units presently in operation.

The first large scale use of the fractional crystallization technique will be the NIPSCO unit. Scale-up of this type of process should be very straight forward since the equipment used is very well known and the scale-up factors from units already in use are fairly low.

In general, the Wellman-Lord process is very simple and consists only of unit operations which are well understood. It does not have components like the multistage fluid beds in Westvaco or the uniquely designed fixed beds in the Shell Flue Gas Desulfurization Process which make those processes unusual and new, thus making their scale-up uncertain.

9.7 Utility Applicability

The simple nature of the Wellman-Lord Sulfite Scrubbing Process puts it in a very favorable position with regard to utility applications, where operational personnel will have to be retrained to run the unit. Process simplicity also reduces maintenance problems and increases operational reliability. Space requirements for the system are about the same as those for the other FGD systems, but only the absorbers need be close to the boilers in order to keep expensive flue gas ducting to a minimum. The other processing steps, *i.e.*, regeneration, purge treatment, storage tankage, and SO_2 conversion, can easily be located some distance away.

Turndown on the Wellman-Lord process has already been amply demonstrated by the Chubu Electric Company plant. The unit is a 220 Mw peaking plant and the FGD system has shown the capability for turndown to 35 percent of design load in less than 30 minutes. The limiting factor in turndown is the gas rate through the absorber necessary to maintain normal behavior. The reason Davy Powergas prefers valve tray towers for large units is that they give better turndown than sieve trays and are structurally and economically more sound than packing in large cross section vessels. A 500 Mw unit would consist of 3 or 4 absorbers and two parallel regeneration trains so even greater turndown is achievable by taking one or more absorbers out of service.

Operating flexibility and reliability is maintained by inclusion of large solution tanks for both absorber feed and product solution. In this way changes in load can be accommodated by using the tanks as surge capacity to smooth out the variations. Also, the absorber system can be kept running while the regeneration system is shutdown for maintenance or repair. Davy Powergas recommends at least 16 hours of storage capacity be provided for both absorber feed and product which amounts to two 600,000 gallon tanks. Each tank would be about 30 feet high and have a 60 foot diameter.

The system has one disposal problem and one raw material supply problem. About 2700 lbs per hour of purge solids are produced at full boiler load and presently this must be disposed of outside the Wellman-Lord complex. Perhaps, it will be possible at some later time to convert the sodium values in the sulfate to a form which could be reused. Currently, the most promising avenue of disposal is sale of the sodium sulfate solids to the paper industry. The Allied Chemical reactor might be adaptable to use of an H_2/CO mixture which could be supplied by coal gasification. Earlier reports by Allied on various reducing agents indicate that an H_2/CO mix is a technically feasible agent. Whether further development by Allied has taken place in this area is unknown. Other reduction systems using reductants in more assured supply are also under development.

A favorable point for the Wellman-Lord Process is that it has been operated successfully several times on different SO_2 sources and although modifications are still being made, the process is well defined. Commercial scale units are already running so no unanticipated problems should arise in any new unit being built. Proven commercial scale operability and reliability are a considerable advantage for the Wellman-Lord Process.

9.8 Economic Assessment

From the material and energy balances which were performed it is possible to estimate the raw material and utility requirements of the Wellman-Lord Process. These are summarized in Table 9-2. The absorption section contributes 38 percent of the raw material and utility cost, the regeneration section 15 percent, the purge treatment 4 percent, and the sulfur production section 43 percent. The overall scheme includes sulfur production rather than acid production but either alternative is feasible. The annual raw material and utility cost is about $4,428,000 per year or about 1.7 mills/kwhr. These costs are higher than those developed by TVA (MC-136) due to the conversion of SO_2 to sulfur using H_2/CO reducing gas at $4.00/MM Btu.

Table 9-2 also provides a breakdown of the process's energy consumption by both type of fuel and point of use. The total power requirement of approximately 12 Mw for the 500 Mw base case plant is equivalent to 2.4 percent of the power plant rating and is the amount by which the boiler must be derated. In instances where the venturi prescrubber has been designed so that it can cope with the entire particulate loading during precipitator outages the total power consumption could be considerably higher due to higher gas pressure drop across the venturi.

Major cost items are reducing gas, electric power, and steam for reheat and the evaporators. Sodium carbonate makeup is the only other major cost. The steam costs are based on use of double-effect evaporators which reduce the steam used in regeneration by about 45 percent.

The necessity of further improvement in purge reduction may be open to economic argument because even in the present process configuration, the sodium carbonate makeup is only the fourth most important utility and raw material cost item, at about 0.11 mill/kwhr. In addition, the main reason why processes to convert sodium sulfate to sodium carbonate or sodium hydroxide are lagging is their inherently high cost due to high energy consumption.

TABLE 9-2

ANNUAL UTILITY AND RAW MATERIAL COSTS FOR THE WELLMAN-LORD PROCESS

Basis: 5,260 Hours/Year at Full Load, 500 Mw,
3.5% Sulfur Coal

Absorption System	Consumption	Unit Price	Annual Cost, $	
Electric Power	9.3 Mw	\$.02/kwhr	978,360	
Steam (H.P.) (Reheat)	77 MM Btu/hr	\$1.00/MM Btu	405,020	
Sodium Carbonate	2,120 lb/hr	\$52/ton	289,930	
			1,673,310	38%
Regeneration System				
Electric Power	1.6 Mw	\$.02/kwhr	168,320	
Steam (L.P.) (Evaporators)	160 MM Btu/hr	\$.50/MM Btu	420,800	
Cooling Water	7,170 gpm	\$.03/M gal	67,890	
Process Water	425 gpm	\$.08/M gal	10,720	
			667,730	15%
Purge Treatment System				
Electric Power	1.0 Mw	\$.02/kwhr	105,200	
Steam (L.P.) (Dryer)	20 MM Btu/hr	\$.50/MM Btu	52,600	
			157,800	4%
SO_2 Conversion System				
Electric Power	0.3 Mw	\$.02/kwhr	31,560	
Reducing Gas	92 MM Btu/hr	\$4.00/MM Btu	1,929,920	
Steam Credit (L.P.)	12 MM Btu/hr	\$.50/MM Btu	-(31,560)	
			1,929,920	43%
		UTILITY AND RAW MATERIAL COST	1.7 mills/kwhr	100%

9.9 Summary

The Wellman-Lord system is a first-generation regenerable FGD process which is based on the aqueous absorption of SO_2 by sodium sulfite to form sodium bisulfite and subsequent regeneration of the sulfite with release of SO_2 upon heating. It produces a stream of concentrated SO_2 which can be converted to either sulfur or sulfuric acid. As an SO_2 removal system, it is highly efficient but it has negligible effect on flue gas NO_x and yields by-product sodium sulfate due to oxidation in the absorber.

Oxidation is the primary technical problem facing the system. The sulfate formation necessitates a significant makeup of sodium carbonate and the inclusion of a purge treatment system to remove the sulfate in as concentrated a form as possible. A second consideration is the use of multiple effect evaporators to reduce the amount of energy used in regeneration. The use of H_2/CO reducing gas in the Allied Chemical Process would also be a major concern for this process.

Scale-up of the system will not be a problem since large scale units are already in operation worldwide. As of December, 1975, 17 plants were operating and 15 more were contracted for. Economically, prospects for the Wellman-Lord Process look very good relative to most other regenerable FGD systems, with raw material and utility costs around 1.7 mills/kwhr.

10.0 CATALYTIC OXIDATION PROCESSES

The Cat-Ox Processes for flue gas desulfurization (FGD) were developed by Enviro-Chem Systems, Inc. The Cat-Ox Processes are divided into an Integrated and a Reheat Process. The Integrated Process was designed to be installed on new power units while the Reheat Process was designed to be installed on existing power units. Both of the Cat-Ox Processes utilize a vanadium pentoxide catalyst to oxidize the sulfur dioxide to sulfur trioxide. The sulfur trioxide then combines with water in the acid absorber to form a 78 percent H_2SO_4 product acid.

10.1 Process Description

The Integrated and the Rehat Cat-Ox Processes can be divided into four and five processing areas, respectively. The processing areas for the Integrated Process are:

- particulate removal,
- catalytic oxidation,
- acid absorption, and
- heat recovery.

The processing areas for the Reheat Process are:

- particulate removal,
- flue gas heat exchange,
- flue gas reheat,
- catalytic oxidation, and
- acid absorption.

These sections of the Cat-Ox Processes are illustrated in Figures 10-1 and 10-2.

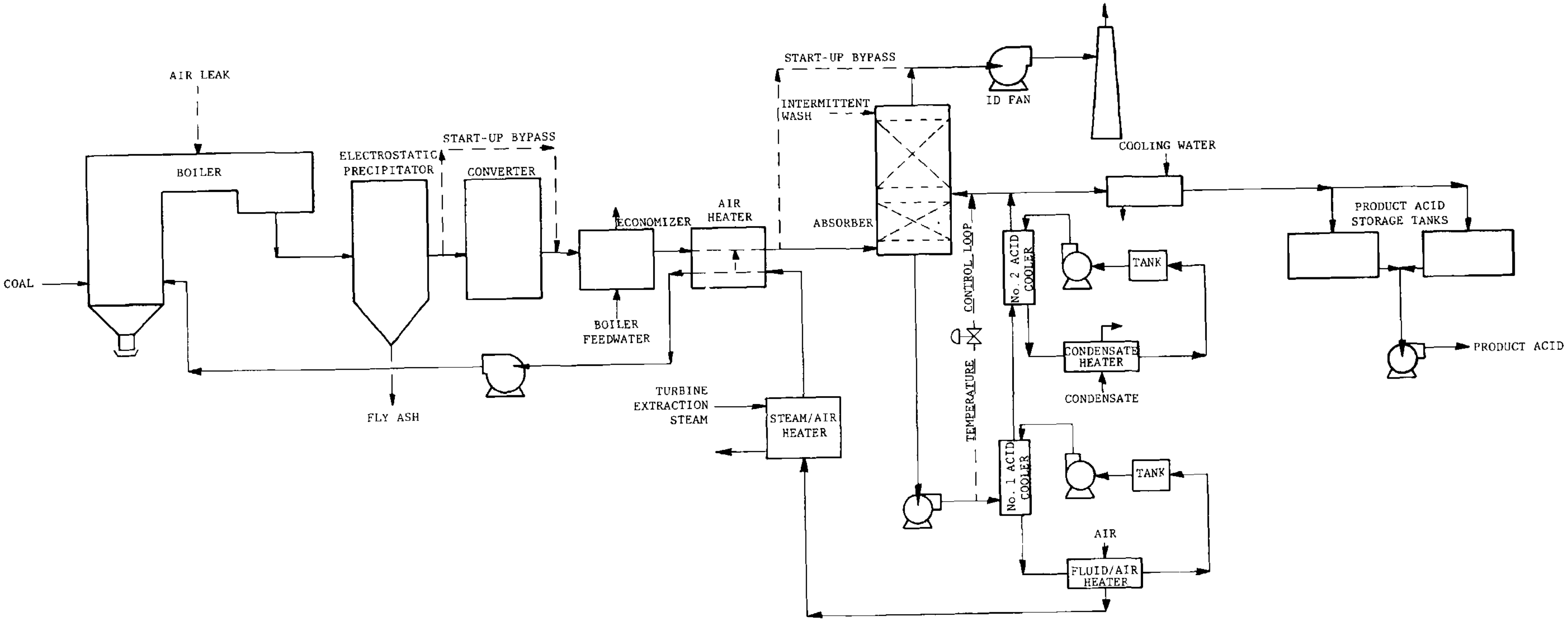


FIGURE 10-1

PROCESS FLOW DIAGRAM
FOR THE INTEGRATED CAT-OX FGD PROCESS

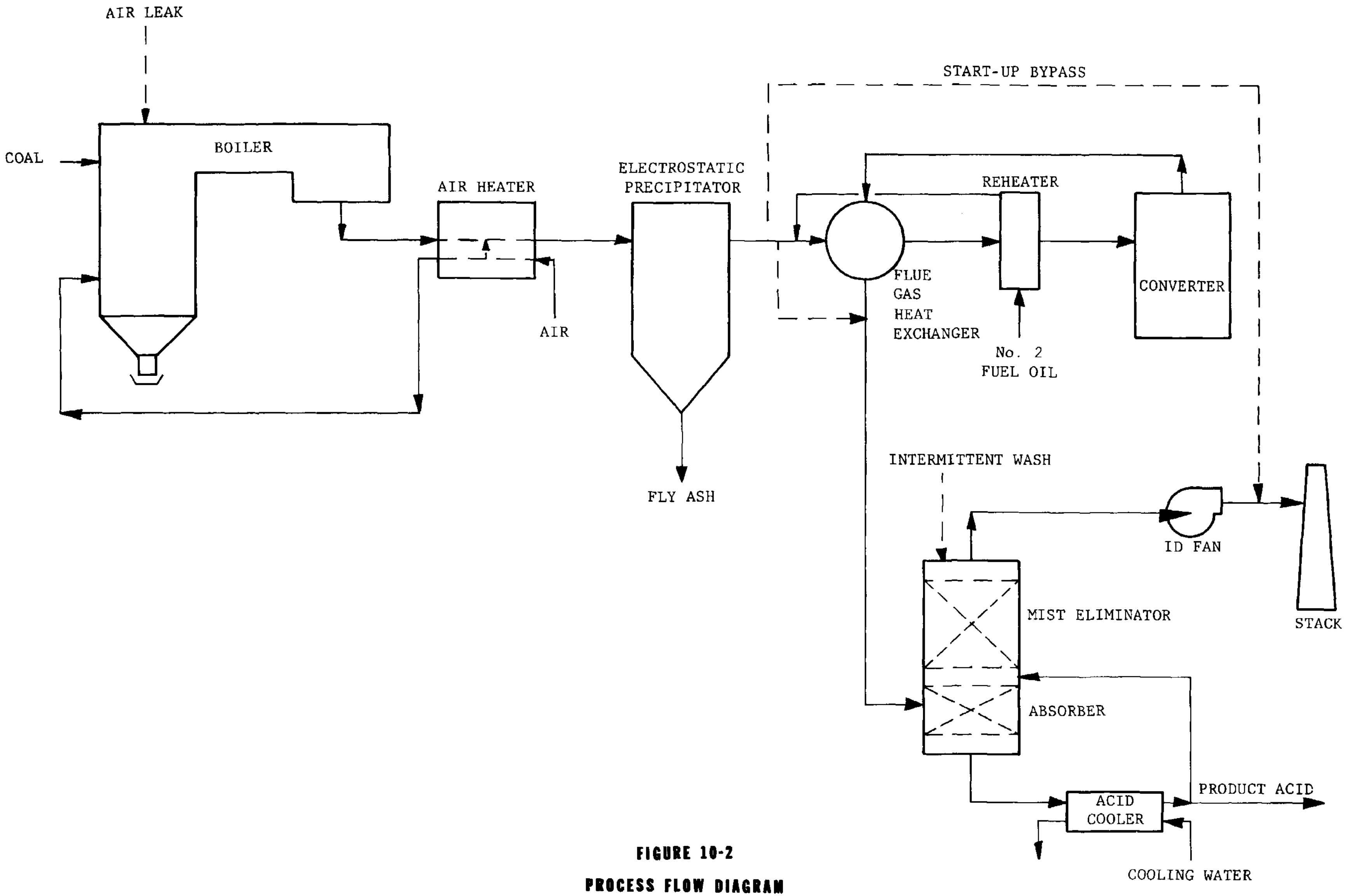


FIGURE 10-2

PROCESS FLOW DIAGRAM
FOR THE REHEAT CAT-OX FGD PROCESS

Both of the Cat-Ox Processes require high efficiency electrostatic precipitators (ESP's) to reduce the flue gas particulate loading to 0.005 grains per standard cubic foot or less to minimize catalyst fouling. The reheat Cat-Ox ESP operates at conditions similar to precipitators on existing power units. However, the Integrated Cat-Ox ESP would operate at temperatures 400 to 500°F above normal ESP operating temperatures.

The catalytic oxidation of SO_2 to SO_3 requires a temperature of approximately 850 to 900°F. For the Integrated Process, the catalytic converter is installed upstream of the economizer and air preheaters to eliminate the need for additional heat transfer equipment. However, for the Reheat Cat-Ox FGD Process, direct oil-fired heaters with external combustion air are required to reheat the flue gas to the specified reaction temperature. The catalyst also requires periodic cleaning due to a continuous build-up of particulate matter in the catalyst bed. For the specified flue gas grain loading entering the converter, the catalyst must be cleaned four times per year. The amount of catalyst lost during cleaning is approximately 2.5 percent.

Sulfur trioxide and a portion of the flue gas water vapor are absorbed by a circulating stream of sulfuric acid in the absorption towers. An acid concentration of 78 percent is maintained in the absorber by controlling the recirculating acid temperature. Entrained sulfuric acid and acid mist in the flue gas are collected by high efficiency Brink demisters.

For energy conservation, about half of the heat from the Integrated Cat-Ox Process is transferred to the power plant boiler combustion air by means of a heat transfer loop as illustrated in Figure 10-1. Additional heat is transferred to the boiler feed water by another heat transfer loop. For the Reheat Process, cooling water is used to remove this heat; however, heat transfer loops to recover this heat could be installed. The product acid for both processes is further cooled using cooling water.

To prevent contaminating the catalyst bed and product acid during start-up, the Integrated Cat-Ox Process is equipped with bypass ducts. These ducts route the flue gas around the catalytic converter and absorber during start-up. The Reheat Process uses a damper at the tie-in point to the power unit ducts to provide a start-up bypass which routes the flue gas directly to the stack.

10.2 Environmental Considerations

The Cat-Ox Processes were developed primarily to remove SO_2 from flue gas; however, the Processes remove 99.9+ percent of the particulates, SO_3, and halogens in the flue gas. The waste streams from the Cat-Ox Processes include fly ash and vanadium pentoxide catalyst solids, sulfuric acid liquid, and SO_2, H_2SO_4, and NO_x vapor. The solid emissions, fly ash and catalyst, from the Cat-Ox Processes arise from the electrostatic precipitator and from catalyst cleaning, respectively. The sulfuric acid liquid stream is from leakages in pump seals. The acid mist emission is emitted from the acid absorber demister pads. The vapor emissions, sulfuric acid and SO_2, are due to (a) vapor-liquid equilibria for aqueous sulfuric solutions at the absorber gas exit temperature (117°C), (b) the amount of SO_2 not oxidized to SO_3 in the catalytic converter, and (c) the gas leakage in the flue gas heat exchanger used in the Reheat Process. The Cat-Ox Process does not affect the nitrogen oxides in the flue gas.

Sulfur Dioxide Emissions

The amount of sulfur dioxide removed by the Cat-Ox FGD Processes is governed by: (a) the fraction of SO_2 oxidized to SO_3 in the catalytic converter, (b) the flue gas heat exchanger leakage, (c) the fuel sulfur content, (d) the type of fuel, and (e) the acid collection efficiency of the acid absorber. For example, if 90 percent of the SO_2 is oxidized to SO_3, 5 percent of the flue gas leaks across the gas heat exchanger seals, and 98 percent of the sulfuric acid is collected in the absorber, the total SO_2 removal efficiency would be 83 percent.

The effects of the fuel type (coal or No. 6 fuel oil) and fuel sulfur content on the SO_2 emissions from the Cat-Ox Processes are illustrated in Figure 10-3. This figure is based on a 90 percent sulfur dioxide conversion fraction and a 500 Mw power unit with a 9200 Btu/kwh heat rate. From Figure 10-3, the SO_2 emissions increase with respect to increasing fuel sulfur content, and the SO_2 emissions are greater for a power unit burning coal rather than fuel oil. This figure also indicates that the SO_2 emissions from the Reheat Process are greater than for the Integrated Process. This is due to the 5 percent leakage in the gas heat exchanger.

The effects of coal sulfur content and gas heat exchanger leakage on SO_2 emissions from a Reheat Cat-Ox Process are illustrated in Figure 10-4. These SO_2 emissions are also compared to EPA emission standards (1.2 lb SO_2/MM Btu, or 11.7 g-mole SO_2/sec). This figure indicates that the SO_2 emissions increase with increasing leakage in the gas heat exchanger, and the maximum leakage and fuel sulfur content which could be tolerated in order for the Reheat Cat-Ox Process to meet EPA SO_2

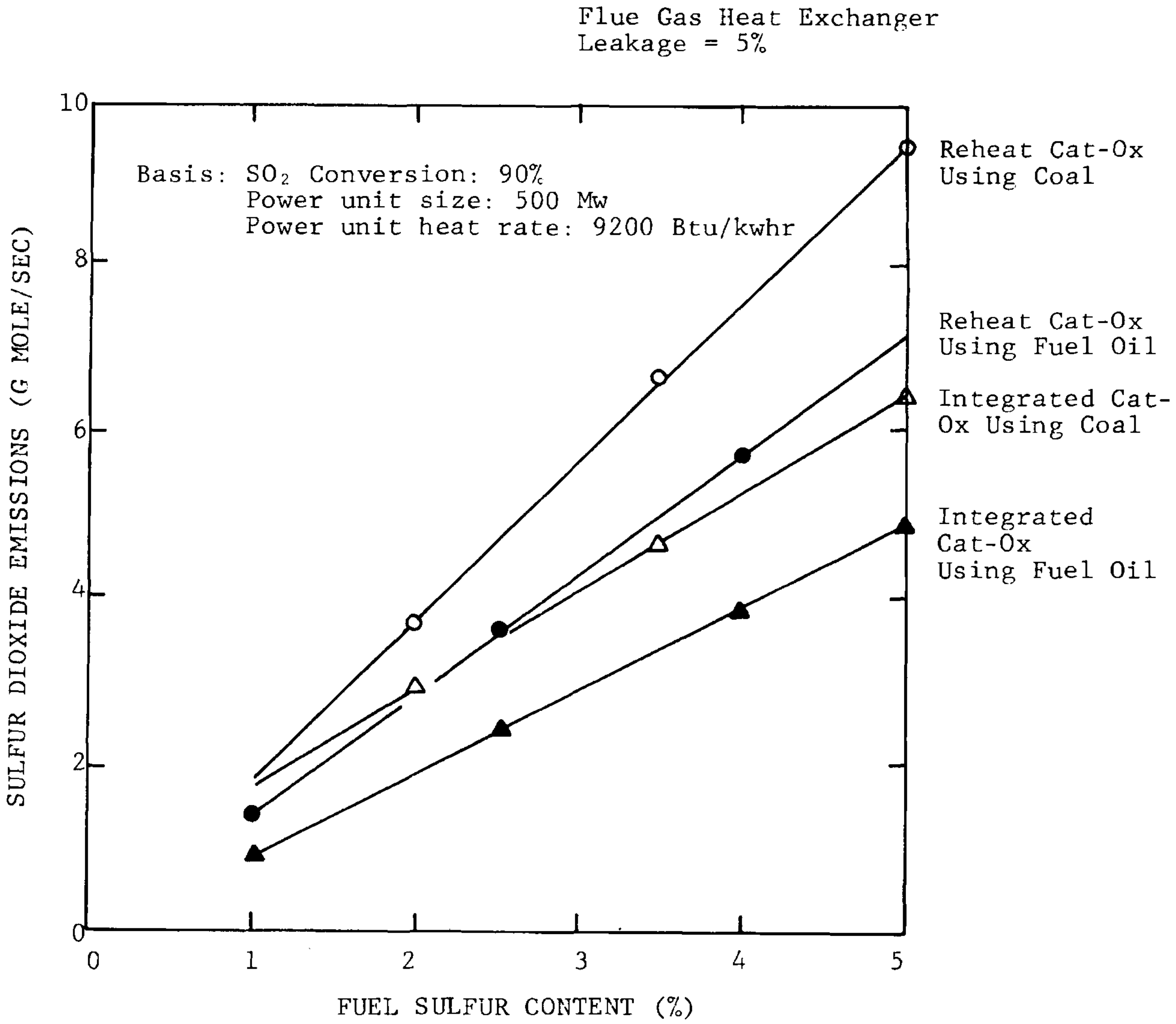


FIGURE 10-3. SULFUR DIOXIDE EMISSIONS FOR THE REHEAT AND INTEGRATED CAT-OX PROCESSES USING VARIOUS FUEL OIL OR COAL SULFUR CONCENTRATIONS

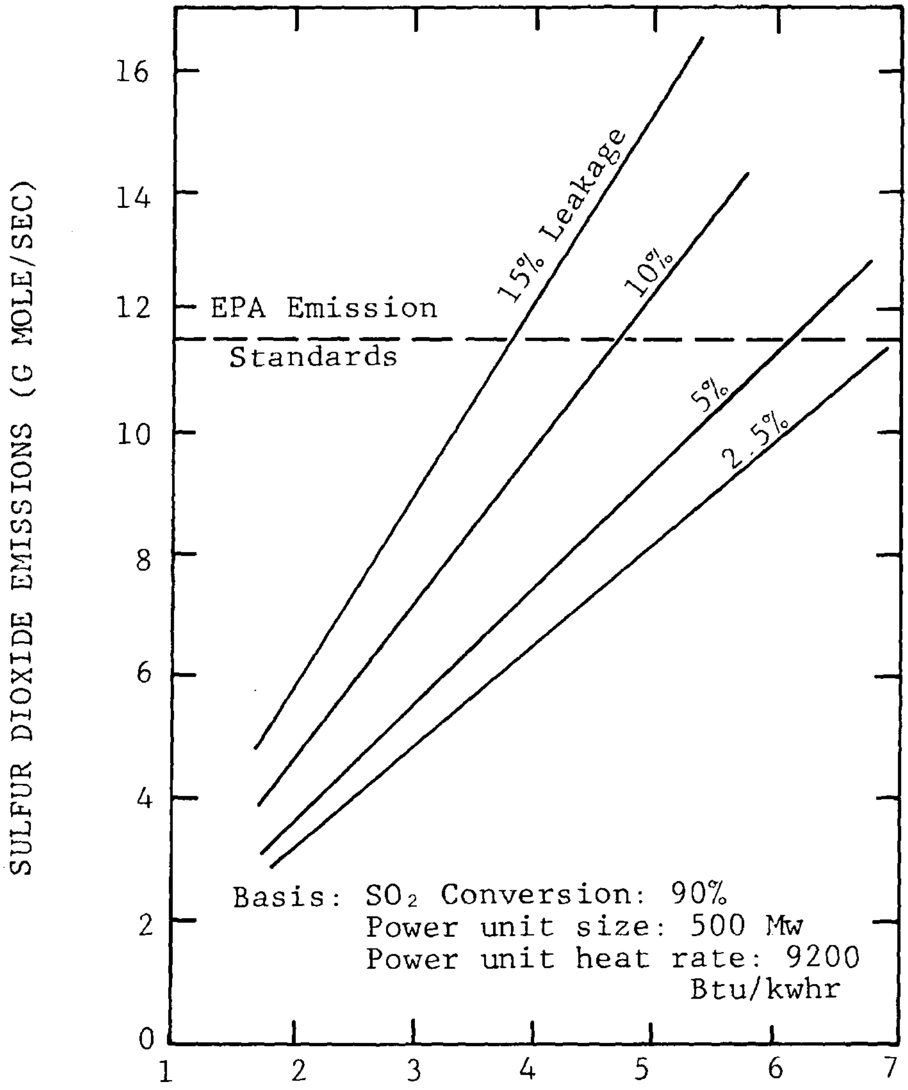


FIGURE 10-4. SULFUR DIOXIDE EMISSIONS AS A FUNCTION OF FLUE GAS HEAT EXCHANGER LEAKAGE AND COAL SULFUR CONTENT

emission requirements. For example, for a 10 percent gas leakage in the heat exchanger, the maximum fuel sulfur content would be 4.7 percent; and for a 15 percent leakage, the maximum fuel sulfur content would be 3.8 percent.

The SO_2 emissions from the Cat-Ox Processes are also affected by the fraction of SO_2 oxidized to SO_3 in the catalytic converter. This catalytic oxidation is controlled by temperature, gas flow rate, and catalyst volume. The effect these parameters have on SO_2 oxidation is shown by Equation 10-1.

$$\frac{p^{\frac{1}{2}}\left[k_f\, y_{O_2} + k_r (y_{O_2})^{\frac{1}{2}}\right] w}{F_g (y^{o}_{SO_2})^{\frac{1}{2}}} = \left\{ 2\left[1-(1-x)^{\frac{1}{2}}\right] + Q \ln\left|\frac{Q+(1-x)^{\frac{1}{2}}}{Q-(1-x)^{\frac{1}{2}}}\right| - Q \ln\left|\frac{Q+1}{Q-1}\right| \right\} \qquad (10\text{-}1)$$

where $Q = (1-x_{eq})^{\frac{1}{2}}$

$\log_{10} k_f = -\dfrac{6774}{T} + 5.242$

$\log_{10} k_r = -\dfrac{11,730}{T} + 9.92$

k_f = forward rate constant

k_r = reverse rate constant

y_{O_2} = flue gas oxygen concentration

$y^{O}_{SO_2}$ = initial flue gas sulfur dioxide concentration

w = catalyst weight (grams)
F = flue gas flow rate (g moles/sec)

x = SO_2 conversion fraction

x_{eq} = equilibrium SO_2 conversion fraction

T = temperature (°K)

p = pressure (atm)

Equation 10-1 was developed from kinetic data obtained from Calderbank, et al. (CA-268) and by assuming a constant temperature and oxygen concentration in the converter. Based upon this equation, equilibrium conversion data (PH-029), and the amount of catalyst specified by Enviro-Chem Systems, Inc. (MO-179), 94.9 percent of the SO_2 in the flue gas would be converted to SO_3 at 477°C (890°F) and 97.0 percent of the SO_2 would be converted to SO_3 at 443°C (830°F). These conversions would indicate that the Integrated Cat-Ox Process could remove 93 to 95 percent of the flue gas SO_2 and the Reheat Process could remove 88 to 90 percent of the SO_2. These SO_2 removal efficiencies were calculated using a 5 percent gas leakage in the Reheat Process' heat exchanger and a 98 percent acid removal efficiency in the absorber.

Two modifications could be made to increase the SO_2 removal efficiencies of the Cat-Ox FGD Processes. First, the Ljungstrom gas heat exchanger used in the Reheat Process could be replaced by a shell and tube heat exchanger. This would eliminate the gas leakage problem associated with the Reheat Process. Second, a two-stage acid absorber shown in Figure 10-5 could be designed to increase the acid absorption efficiency from 98 to 99 percent. This two-stage absorber could produce a more concentrated product acid (up to 86 percent H_2SO_4, and would reduce acid emissions. If these modifications were incorporated in the Cat-Ox Processes, the SO_2 removal efficiencies could be increased to 94 to 96 percent.

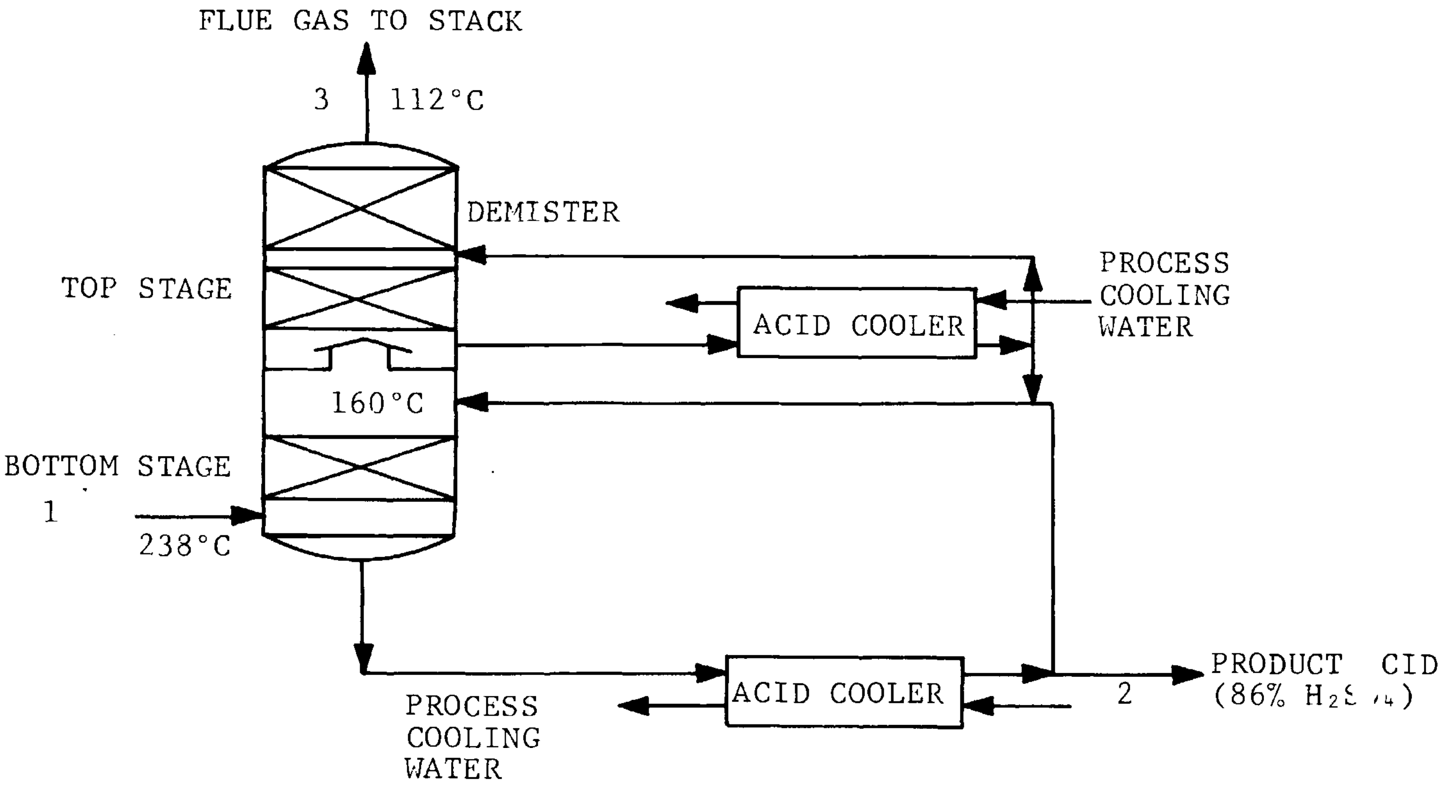


FIGURE 10-5. TWO-STAGE ACID ABSORBER

Sulfuric Acid Emissions

Sulfuric acid emissions as both vapor and mist are potential environmental problems that are associated with the Cat-Ox Processes. The potential problem is illustrated using the sulfuric acid emissions regulations for the State of Texas (TE-219). For the base-case, 500 Mw plant, Texas regulations would allow 2.2 g-mole/sec of sulfuric acid. This acid emission rate is greater than the 0.8 g-mole/sec acid emitted from the Cat-Ox Processes. However, the acid emission rate from the Cat-Ox Processes exceeds this standard when the absorber acid concentration rises above 80 percent H_2SO_4. The acid emission problem could be significantly reduced if a two stage acid absorber was incorporated in the Cat-Ox Processes. As stated previously, the acid mist exiting the absorber is governed by the collection efficiency of the absorber demister.

10.3 Material and Energy Balances

The material and energy balance calculations for the Cat-Ox Processes were based on the operating parameters for the base-case, 500 Mw power unit and the Cat-Ox Process Design Manual (MO-179) for the Wood River Steam Station. Five additional assumptions were also used in these calculations. These included: (1) the particulate loading of the gas exiting the electrostatic precipitator is 0.005 gr/scf, (2) the atmospheric pressure is 750 mm Hg, (3) the gas exiting the acid absorber contains 1.0 mg $H_2SO_{4(\ell)}$/acf, (4) the gas heat exchanger leakage is 5 percent, and (5) 90 percent of the sulfur dioxide is converted to sulfur trioxide in the catalytic converter. A detailed material balance will not be presented, however, the flow rates, temperatures, and compositions of major streams will be discussed for each major section of the Integrated and Reheat Cat-Ox Processes.

Integrated Cat-Ox Process Sections

There are four major process sections in the Integrated Cat-Ox Process. These sections include (1) particulate removal, (2) catalytic oxidation, (3) acid absorption, and (4) heat recovery.

In the particulate collection section, 2495 lb mole/hr of gas enters the electrostatic precipitator at 450°C (850°F). The particulate and sulfur dioxide flow rates in this gas stream are 562 lb/hr and 6.1 lb mole/hr, respectively. In order to achieve the specified outlet particulate loading, 0.005 gr/scf, the precipitator must remove 99.88 percent of the incoming fly ash or 561.3 lb/hr of particulates.

The gas exiting the electrostatic precipitator then passes to the catalytic converter where 90 percent of the sulfur dioxide is oxidized to sulfur trioxide. The gas exiting the converter consists of 5.5 lb mole/hr of SO_3 and 0.6 lb mole/hr SO_2. The catalyst bed in the converter also collects approximately 50 percent of the incoming particulate matter or 0.35 lb/hr.

After passing through an economizer and a gas/air heat exchanger, the gas flows to the acid absorber. In the absorber, the sulfur trioxide combines with water to form sulfuric acid. Water vapor in the gas is also absorbed by the circulating acid. The temperature and flow rate of the gas exiting the absorber are 117°C (242°F) and 2713 lb moles/hr, respectively. The amounts of sulfur dioxide and sulfuric acid leaving with this gas are 0.6 lb mole/hr and 0.1 lb mole/hr, respectively. The circulating acid leaves the absorber at 146°C (294°F) and is cooled to 83°C (180°F) in the heat transfer loops. The product acid is generated at the rate of 13.6 lb mole/hr of 77.7 percent H_2SO_4.

The heat recovery section includes the economizer, air heater, fluid/air heater, and condensate heater. The total amount of heat recovered in this section is 1.4×10^8 Btu/hr.

Reheat Cat-Ox Process Sections

The Reheat Cat-Ox Process is divided into five sections. These sections include (1) particulate removal, (2) gas heat exchange, (3) flue gas reheat, (4) catalytic oxidation, and (5) sulfuric acid absorption.

In the particulate collection section, the temperature and flow rate of the gas entering the electrostatic precipitator are 155°C (310°F) and 2729 lb mole/hr, respectively. As in the Integrated Process, the outlet particulate loading from the precipitator is 0.005 gr/scf. This gives a particulate flow of 0.7 lb/hr in the gas exiting the precipitator.

Flue gas then passes to a gas heat exchanger. Exit gas from the heat exchanger has a temperature of 414°C (776°F) and a flow of 2593 lb moles/hr. The 5 percent leakage across the heat exchanger seals reduces the gas flow by 136 lb mole/hr. It should be emphasized that 0.3 lb mole/hr of SO_2 is also lost due to this leakage.

After the gas heat exchanger, the gas is heated to 450°C (850°F) by the flue gas reheater. The total gas flow exiting the reheater is 2687 lb mole/hr which includes the combustion products and excess air from the combustion of No. 2 fuel oil used in the reheater. The sulfur dioxide flow from the reheater is 5.8 lb mole/hr.

In the catalytic converter, 90 percent of the incoming SO_2 is converted to SO_3 and 50 percent of the particulate matter is deposited on the catalyst bed. 2684 lb mole/hr of gas exits the converter carrying 5.2 lb mole/hr of SO_3, and 0.6 lb mole/hr of SO_2.

After the converter, the sulfur trioxide combines with water to form sulfuric acid in the acid absorber. Water vapor in the flue gas is also absorbed y the circulating acid in the absorber. The gas and component flows exiting the absorber are 2803 lb mole/hr, 0.9 lb mole/hr of SO_2, and 0.1 lb mole/hr H_2SO_4. The temperature of this gas is 117°C (242°F). Sulfuric acid is produced at the rate of 13.6 lb mole/hr of 77.7 percent H_2SO_4.

Raw Material and Utility Requirements

The raw material and utility requirements for the sections of the Integrated and the Reheat Cat-Ox Processes are tabulated in Table 10-1 and Table 10-2, respectively. These requirements were calculated using the operating parameters for the base case 500 Mw power unit. Checks on these requirements have been made to insure their validity.

10.4 Design Considerations

The major design areas of concern associated with the Integrated and the Reheat Cat-Ox Processes include the following:

- flue gas heat exchanger design,
- acid absorber design,
- electrostatic precipitator design,
- catalytic converter design, and
- reheater design.

TABLE 10-1

RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE INTEGRATED CAT-OX PROCESS

Basis: 500 Mw, 3.5 percent sulfur, 5260 hr/hr

Processing Area	Steam (MM Btu/hr)	Process Water (GPM)	Electric Power (kw)	Catalyst (ℓ/hr)
Particulate Removal	-	-	3917	-
Catalytic Oxidation	-	-	39	15
Heat Recovery Loop(a)	30(b)	-	495	-
Fans	-	-	7548	-
Acid Absorption	-	743(c)	821	-
TOTAL	30	743	12,820	15

(a) 1.4 x 10^8 Btu/hr are recovered in this loop

(b) Steam used for heating boiler combustion air

(c) Water used for cooling product acid only

TABLE 10-2

RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE REHEAT CAT-OX PROCESS

Processing Area	Fuel Oil (MM Btu/hr)	Process Water (GPM)	Electric Power (kw)	Catalyst (ℓ/hr)
Particulate Removal	-	-	500	-
Catalytic Oxidation	-	-	39	15
Flue Gas Reheat	210	-	20	-
Fans	-	-	9,543	-
Acid Absorption	-	19,000	454	-
TOTAL	210	19,000(a)	10,556	15

(a) Water used for cooling total amount of recirculated acid

The major design consideration for the flue gas heat exchanger is the amount of leakage across the seals as this effects the sulfur dioxide removal efficiency of the Reheat Process. The design considerations for the acid absorber consist of dilute acid production during start up, and demister collection efficiency. Design considerations for the gas heat exchanger and the absorber's exit gas temperature and mist collection have been previously discussed in the Environmental Considerations.

The electrostatic precipitator design considerations are centered upon the ability of "hot-side" and "cold-side" precipitators to achieve a reliable outlet particulate loading of 0.005 gr/scf. The catalytic converter considerations consist of the effects that temperature, composition, and flow rate variations of the flue gas have on sulfur dioxide oxidation, catalyst poisoning by the flue gas constituents, and the dynamic temperature response of the catalyst bed. The flue gas reheater design considerations include the effect that reheater fuels, particulate emissions, and types of reheaters have on reheater performance.

Acid Absorber Design

According to MITRE (BE-326), dilute acid would be formed in the acid absorber during start-up of the Cat-Ox FGD Processes. This has caused major concern about the applicability of the construction materials specified for the Cat-Ox FGD Processes (MO-179). Various solutions to the problem of producing hot, dilute acid have been proposed. These solutions include: (a) using construction materials that could adequately handle the hot, dilute acid, (b) modifying the recirculating acid coolers so that the coolers could be used to heat the recirculating acid prior to start-up, and (c) using 98 percent sulfuric acid as the initial acid charge.

In order to minimize the corrosion problems associated with producing a hot, weak acid during start-up, the acid lines should be constructed of Teflon-lined piping. The construction materials of the flue gas ducts leaving the demister should be corrosion-resistant.

The major reason weak acid is produced during start-up is that it takes time for the absorber to reach design temperatures. In order to solve this problem, MITRE (BE-326) indicated that the recirculating acid coolers should be modified so that steam could also be introduced. This modification would give the Cat-Ox Processes the capacity to preheat the recirculated acid prior to start-up. This preheat capability could also be used to add heat to the system to maintain the design temperature in the absorber, if the power unit is operated at very low load levels.

Another solution to the potential problem of producing dilute acid during start-up would be the use of 98 percent acid as the initial acid charge instead of 78 percent acid. Using MITRE's basis for calculating the amount of water absorbed by the acid during start-up (BE-326), the effects of absorber temperature on acid concentration for initial acid charges of 98 and 78 percent acid are illustrated in Figure 10-6. This figure indicates that acid concentrations of 57 percent could be produced in the absorber for an initial charge of 78 percent H_2SO_4. However, if 98 percent acid were used for the initial charge, the lowest acid concentration that would be produced would be approximately 71 percent. These calculations indicate the corrosion problems from producing hot, dilute acid during start-up could be significantly reduced by using a 98 percent acid for the initial acid charge.

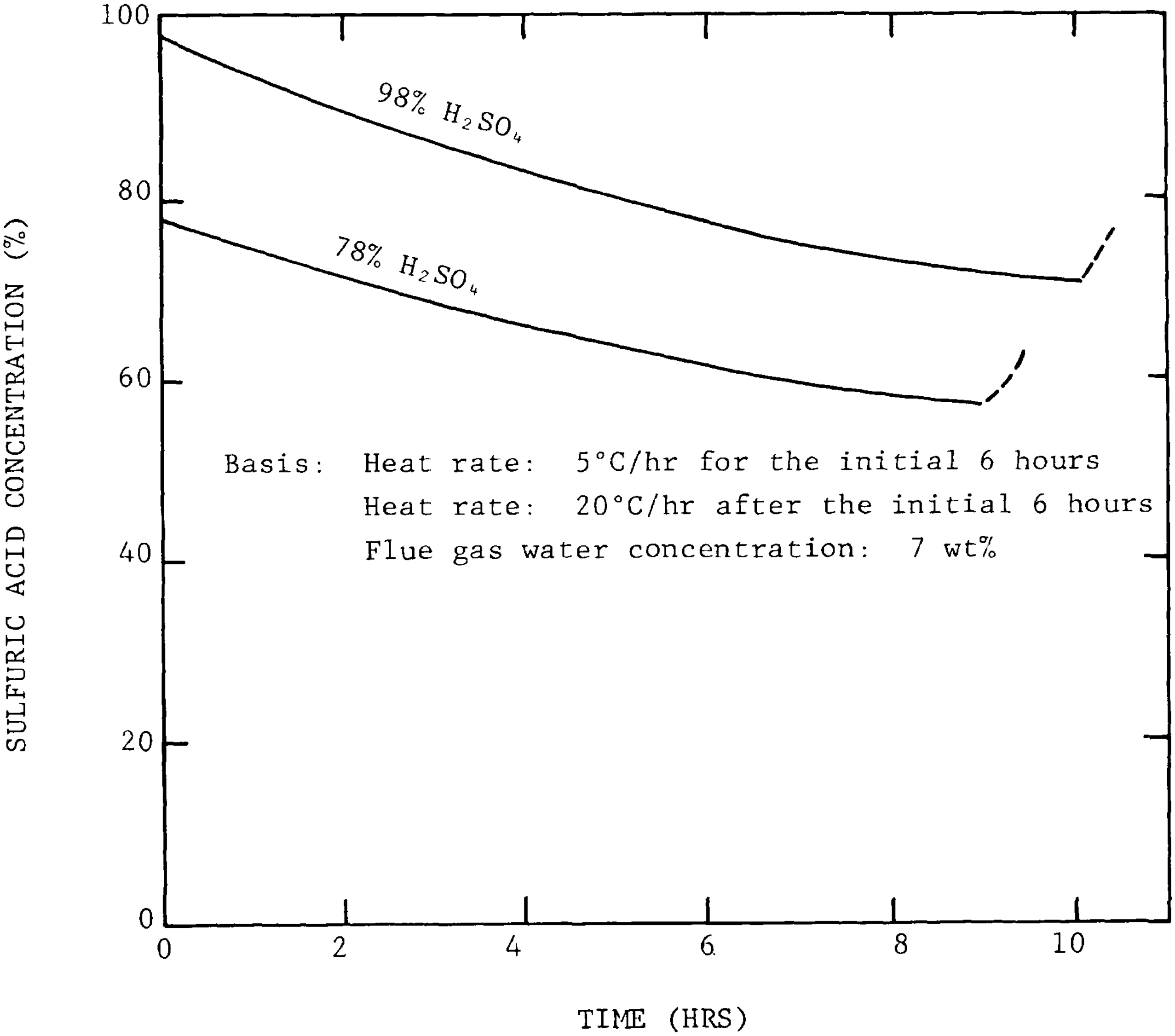


FIGURE 10-6. ACID CONCENTRATIONS IN THE ABSORBER DURING START-UP FOR VARIOUS INITIAL ACID CHARGE CONCENTRATIONS

These solutions for the problem of producing hot, dilute acid during start-up are all technically feasible and should be considered in constructing new Cat-Ox Processes. These process and material modifications should also be considered in refurbishment of the Cat-Ox Process at Wood River.

Electrostatic Precipitator Design

This section discusses the technical aspects of "hot-side" and "cold-side" electrostatic precipitator (ESP) performance during power unit operation. The ESP performance criteria are based on the ability of the equipment to maintain a reliable outlet particulate loading of 0.005 gr/scf.

One of the main concerns of the feasibility of the Integrated Cat-Ox Process is the ability of an ESP to operate at temperatures around 482°C (900°F). To date, there has been a significant amount of operating experience with these "hot-side" ESP's. Their generally successful operation indicates that current design practices are adequate for designing "hot-side" ESP's for application to the Integraded Cat-Ox Process. Figure 10-7 illustrates actual performance data for "hot-side" ESP's as reported by Walker, et al. (WA-215).

On the design of "hot-side" ESP's, ash resistivity is rarely a design issue. This is mainly due to the effect of temperature on ash resistivity. For example, at 900°F, ash resistivities vary from 10^8 to 10^{11} ohm-cm compared to 10^7 to 10^{13} ohm-cm at 300°F (WA-215). According to Oglesby, et al. (SO-005), the design parameters that have to be considered in determining "hot-side" ESP size are: (1) gas leakage between sections, (2) gas velocity distribution in the sections, and (3) the total gas flow rate and composition which includes SO_3 concentrations. If

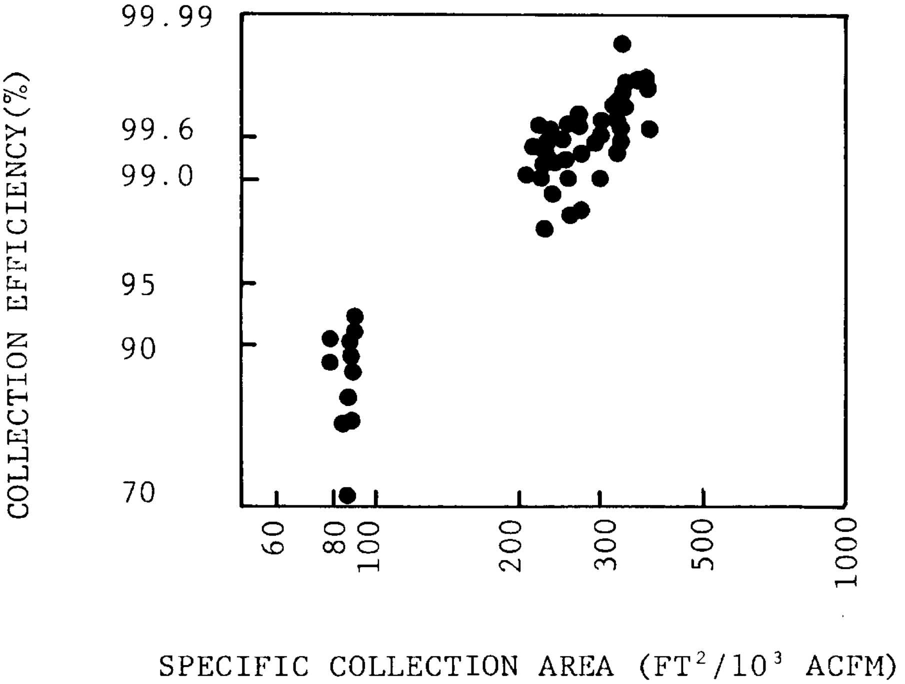


FIGURE 10-7. ACTUAL PERFORMANCE OF HOT-SIDE ELECTROSTATIC PRECIPITATORS AS REPORTED BY WALKER, ET AL. (WA-215)

these data are known, a "hot-side" ESP can be designed to give the desired outlet particulate loading. It should be emphasized that due to the high temperatures, the ESP materials of construction must be thermally compatible and that the required collection area will be approximately twice as great as for an ESP operating at 300°F.

A "cold-side" ESP operates at temperatures around 300°F. One of the main design concerns associated with these ESP's is the reliability of maintaining the specified outlet particulate loading. As discussed earlier, the ash resistivity can vary significantly at these temperatures. Therefore, ash resistivity becomes a significant design issue. For example, the ESP collection area required for removing an ash with a resistivity of 10^{11} ohm-cm would be approximately three times greater than the area required for collecting an ash with a resistivity of 10^{10} ohm-cm (SO-005). As in "hot-side" ESP design, the gas leakage and the gas velocity distribution in the ESP sections, along with the gas flow rate and composition, will be design parameters for "cold-side" ESP's.

The design of "hot-side" and cold-side" electrostatic precipitators can be achieved with current technology. "Hot-side" ESP's have been shown to be capable of removing 99.9 percent of the entering particulates. It should be emphasized that the outlet ESP particulate loading has a significant effect on the Cat-Ox Processes' operation (MO-179), and the ESP needs to be extremely relaible and designed to meet the outlet loading specifications of 0.005 gr/scf.

Catalytic Oxidation of Sulfur Dioxide

The catalytic converter section of the Cat-Ox FGD

Processes is used to oxidize SO_2 to SO_3 over a vanadium pentoxide catalyst. The oxidation step can be considered established technology because it has been used for over 50 years in sulfuric acid production. Conversion efficiencies between 95-99.9 percent have been readily obtained by carrying out the reaction in several stages with intermediate cooling. The cooling has been required to eliminate the high temperature limitation on the equilibrium conversion of this exothermic reaction.

When the catalyst is used in a flue gas environment, several differences from standard sulfuric acid production must be considered. These differences include:

- lower SO_2 and O_2 concentrations in the gas,
- possible catalyst poisons in the flue gas such as H_2O, HF, or HCl,
- particulates in the flue gas, and
- temperature and composition variations during steady-state operation and load swings.

Due to the low reactant concentrations (0.22 percent SO_2 and 4.86 percent O_2) in the flue gas, the temperature rise in the catalytic converter will be only 10°F for complete oxidation of the SO_2. This indicates that the approximation of isothermal converter operation is valid and that there is no need for intermediate cooling.

The catalytic converter performance for the base case operating conditions and for variations from the base case are summarized in Table 10-3. These performance estimates were based on Equation 10-1 in the Environmental Considerations Section. The amount of catalyst is given in the conventional units used in industry, liters of catalyst/ton H_2SO_4 per day. The SO_2 conversion fraction, 0.94, obtained for the base case operating parameters was selected as both a typical design parameter and one representing conversions obtained at Wood River (MA-481). From Table 10-3, the effect variations in the operating parameters would have on the conversion fraction strongly depends on the safety factor included in the catalyst volume in the converter. As shown in Case 3, the volume of catalyst used at Wood River (MA-481), should give complete conversion under most operating conditions. If the amount of catalyst computed from Equation 10-1 is used, the SO_2 conversion would drop to 75 percent for a 35°K decrease in temperature as indicated by Case 1 and Case 5. Case 6 shows that 50 percent decrease in flue gas flow rate. All of the cases in Table 10-3 for SO_2 conversion need considerably more catalyst than used in the sulfuric acid industry as indicated by Case 9. This is due to the large differences in flue gas reactant concentrations. Cases 7 and 8 indicate a considerable lowering of SO_2 conversion with low excess air, even for the high levels of catalyst specified for the Cat-Ox Process at Wood River.

The effects that variations in the operating parameters have on the catalytic converter are listed in Table 10-4. These effects can also be presented in terms of the change in the left-hand side (LHS) of Equation 10-1 which is given in Table 10-4. The SO_2 conversion can be directly obtained from the change in the LHS of Equation 10-1 and equilibrium conversion data (EV-022, PH-029).

TABLE 10-3

CATALYTIC CONVERTER PERFORMANCE FOR VARIOUS OPERATING PARAMETERS

Case No.	Case Description	Catalyst Volume (ℓ/ton H_2SO_4/day)	Temperature (°K)	Equilibrium Conversion (%)	Kinetic Conversion (%)
1	Base case operating parameters	832	750	95.0	94.0
2	Base case with 90% conversion	658	750	95.0	90.0
3	Base case with the volume of catalysts specified at Wood River	1883	750	95.0	94.9^+
4	Case No. 3 with a 34°K decrease in temperature	1883	716	97.5	97.0
5	Case No. 4 with the catalyst volume specified in Case No. 1	832	716	97.5	75.0
6	Case No. 5 with a 50% decrease in flue gas flow	832	716	97.5	97.0
7	Base case with 10% excess air	832	750	91.3	50.0
8	Case No. 3 with 10% excess air	1883	750	91.3	86.0
9	Industry "rule of thumb" (BR-272)	180	-	-	-

TABLE 10-4

CHANGES IN THE LHS OF EQUATION 10-1 FOR VARIOUS OPERATING PARAMETERS

Operating Parameters Variation	Factor Change in the LHS of Equation 10-1*
10% Excess Air	LHS x 1/2.8
3.3 Vol. % Oxygen (Minimum specified by Monsanto)	LHS x 1/1.5
45% Excess Air	LHS x 2.3
62°F Temperature Decrease	LHS x 1/2.2
5% Coal Sulfur Content	LHS x 1/1.2
2% Coal Surfur Content	LHS x 1.35
50% of Full Load	LHS x 2.00

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*

$$\mathrm{LHS} = \frac{P^{\frac{1}{2}}[k_f y_{O_2} + k_r (y_{O_2})^{\frac{1}{2}}]W}{Fg(Y^\circ_{SO_2})^{\frac{1}{2}}}$$

From kinetic and equilibrium considerations, the two changes that could cause SO_2 conversion problems are a decrease in the converter temperature and a decrease in flue gas oxygen content. The conversion problem caused by a temperature drop can be handled by using twice as much catalyst as is specified by Equation 10-1. According to Evarett, et al. (EV-022), a large temperature rise would also limit the SO_2 conversion and could not be tolerated. The activation energy in this reaction mechanism is very critical to the estimation of these temperature effects. The 31 kcal/g-mole activation energy reported by Calderbank, et al. (CA-268), is believed to be an upper limit for commercial catalyst. If interparticle diffusion were considered, the temperature would have a smaller effect on the SO_2 conversion due to the decrease in the corresponding activation energy.

The use of 10 percent excess air, as used by some oil-fired power units, would appear to require three times more catalyst compared to the amount of catalyst calculated from the kinetic expression. Decreases in flue gas oxygen concentration could cause conversion problems unless they were compensated by air leaks in the power unit equipment.

Thermodynamic calculations of the gas phase composition in equilibrium with the catalyst were performed to evaluate the effect of possible poisons contained in the flue gas. It is known in the sulfuric acid industry that fluorine poisons the catalyst (BR-272), with a "rule of thumb" upper fluorine limit of 0.36 vol. ppm.

Only the thermodynamic properties of pure components were used to estimate the flue gas composition in equilibrium with the catalyst. Other compounds or solution phases which may be formed would be expected to be more thermodynamically stable, that is, to have a lower overall flue energy. In light of this, the gas phase compositions computed from the pure-phase approximations to the overall condensed phase should reflect an upper limit for the vapor pressures of possible volatile catalytic constituents. The most abundant gaseous catalyst species, VOF_3, accounted for only 0.01 of the available flourine. All other possible gaseous species were found to be in negligible concentrations. This indicates that catalyst deactivation by flue gas constituents such as HF, HCl, or H_2O occurs, it is by formation of a new inactive solid phase or as a volatilization product by an unknown mechanism.

It is possible to gauge the dynamic effect of flue gas temperature changes by estimating how long it would take a step change in temperature to propagate through the catalyst bed. Based upon the assumption that the catalyst consists mainly of SiO_2, the volumetric heat capacity of the catalyst bed would be 202 cal/liter °K. For the amount of catalyst used at Wood River, the time required for the converter to equilibrate with a temperature change of 62°F would be approximately 12 minutes. In light of this, temperature fluctuations on the order of a few minutes should not affect the converter performance. However, temperature changes of longer duration will. These effects are illustrated in Tables 10-3 and 10-4.

The major criteria to be considered in designing the catalytic converter include the use of an excessive amount of catalyst to insure good SO_2 oxidation for variations in the flue gas composition, temperature, and flow rate. Phase equilibria calculations indicated that the constituents in the flue gas should not poison the catalyst. However, further work is needed to validate these calculations. The thermal inertia of the catalyst bed is approximately 12 minutes. Therefore, longer flue gas temperature variations could affect the converter's performance.

Flue Gas Reheat

In the Reheat Cat-Ox FGD Process, a reheater is used to elevate the flue gas temperature to 454-477°C (850-890°F) before the gas enters the catalytic converter. In evaluating the reheater performance in the Reheat Process, the following items were considered:

- Various types of reheater fuels,
- Amount of particulates introduced into the flue gas by the reheater, and
- Various types of reheaters.

The types of fuel that were considered in evaluating the reheater performance included natural gas, low-Btu gas, and No. 2 fuel oil. Natural gas would be the best choice of fuel since there would essentially be no particulates emitted into the flue gas and a 99.9^+ percent combustion efficiency could be obtained (VO-049). The use of low-Btu gas would be another good choice since it would not produce particulates during combustion. It should be noted that a different burner design would be required to burn this gas. The next best fuel candidate would be No. 2 fuel oil which is the fuel used for the Cat-Ox Demonstration Unit at Wood River. A possible problem with burning No. 2 fuel oil is the amount of particulates that would be introduced into the flue gas. This particulate emission is not only a function of how the oil is combusted, it is also a function of the type of reheater. There are two basic types of reheaters, an external register burner and a duct burner. The external register burner, which is the burner currently installed at Wood River, is specified to emit 0.01 pounds of particulates per million Btu of heat (VO-049). This would correspond to 0.0002 grains/scf particulate loading in the flue gas which is only 4 percent of the required particulate loading, 0.005 gr/scf, to the catalytic converter. A duct burner, which was initially installed at Wood River, could only achieve a particulate loading of 0.1 lb/MM Btu (0.002 gr/scf) (VO-049). This is 40 percent of the grain loading specified to the converter.

Because of the decreasing availability of natural gas, No. 2 fuel oil probably would be selected as the principal reheater fuel. The type of reheater used in the Reheat Process should be an external register burner in order to reduce the particulates emitted from the reheater. If this type of reheater is properly operated, there should be no detrimental effect on the performance of the Reheat Cat-Ox Process.

10.5 Status of Development

Research on the Cat-Ox FGD Processes was started in 1961 as a joint project of Monsanto Company, Pennsylvania Electric Company, Air Preheater Company, and Research-Cottrell, Inc., at the Seward Station of Pennsylvania Electric. Later, Monsanto assumed principal interest and with cooperation from Metropolitan Edison built a 15 Mw prototype at their Portland, Pennsylvania, station. This unit was completed and placed onstream in the fall of 1967. Approximately 63,000 acfm of stack gas taken from the 250 Mw No. 2 boiler at Portland was passed through the prototype.

Fly ash removal was particularly critical to protect the oxidation catalyst. The high-temperature, high-efficiency precipitator installed was found to be very effective for this service. After about a year's operation, the project was pronounced successful in late 1968 and ready for sale to utilities. The process was the first to be ready for demonstration.

In 1970, EPA agreed to partly finance a full-scale demonstration of a Reheat Cat-Ox system on an existing 110 Mw coal-fired unit of Illinois Power at the Wood River Station near East Alton, Illinois. Illinois Power agreed to furnish \$3.8 million and EPA \$3.5 million for the project. Monsanto's Enviro-Chem Systems, Inc., provided the technology for the installation on No. 4 boiler. The detailed engineering was started in November 1970 and on-site construction started January 1971. The unit was ready for operation by mid-1973; however, a limit on the natural gas supply for reheating the stack gas from 310 to 850°F required a delay for modification of the reheat burner system.

SO_2 conversion to SO_3 was expected to be 90 percent or better. However, leakage across seals of the heat exchangers allowed about 5 percent of the gas to by-pass the converter resulting in an overall system efficiency of about 85 percent. Due to the high efficiency electrostatic precipitator, the screening effect of the converter bed, and the efficiency absorbing tower and mist eliminator, particulate emission was virtually negligible.

An extended test program is planned by EPA for the demonstration unit. The MITRE Corporation has been contracted to carry out the test and evaluation program.

Currently, the Cat-Ox Process at Wood River needs refurbishment before it can be operational. Illinois Power Company (IP) indicated that they would operate and maintain the Cat-Ox Process if necessary process and equipment changes were made. IP also stated that they would not invest any more money for refurbishment costs.

10.6 Scale-Up Considerations

According to McGlamery, et al. (MC-136), and Enviro-Chem Systems, Inc. (TE-223), the Cat-Ox Processes for a 500 Mw power unit would consist of four (4), 125-Mw modules. Since the demonstration Cat-Ox Process at Wood River is tied into a 110 Mw power unit, no significant scale-up considerations should be required.

10.7 Utility Applicability

The applicability of the Cat-Ox FGD Processes to the utility industry was assessed using three criteria. These criteria included the following:

- the marketability of the sulfuric acid produced by the Cat-Ox Processes,
- location criteria, and
- raw material availability and fuel requirements.

Cat-Ox Sulfuric Acid Marketability

The potential market for the sulfuric acid produced by the Cat-Ox FGD Processes differs from the total abatement acid market. The marketability of the Cat-Ox acid is restricted to fertilizer production due to the Cat-Ox acid concentration (77.7% H_2SO_4)(MO-179) and the acid impurities. The increase in transportation costs is also a limiting factor for Cat-Ox acid marketability.

According to TVA (BU-132, WA-219, MC-187), the fertilizer industry consumes approximately 54 percent of the total annual sulfuric acid production. This would mean that in 1975, 20 million tons of sulfuric acid will be consumed for fertilizer production. Since fertilizer production requires acid concentrations ranging from 62 to 78 percent H_2SO_4 and does not require a very pure acid (BU-132, WA-219), the sulfuric acid produced by the Cat-Ox FGD Processes (77.7 percent H_2SO_4) would be acceptable for fertilizer production. It should also be realized that many fertilizer manufacturers produce their own sulfuric acid and are concerned with the problems facing sulfuric acid plants. These problems include the need for replacing or extending plant capacity, adding pollution abatement facilities, and increasing sulfur prices.

The effect Cat-Ox acid impurities would have on the acid marketability is uncertain. According to McGlamery (MC-187), the trace elements in the Cat-Ox acid have not been proven to be toxic to the soil or plants. McGlamery did, however, feel that there would be a need for further research on the possible toxicity of these trace elements.

The sulfuric acid produced by the Cat-Ox Process at Enviro-Chem's pilot plant and the Wood River Steam Station has been sold to the following fertilizer manufacturers: a) Kerr McGee, Philadelphia, Pennyslvania; b) Smith Douglas, Streater, Illinois; and c) International Minerals and Chemical Corporation, Spartanburg, South Carolina. The acid produced by the Cat-Ox Process at Wood River was sold for $15 per ton which is approximately twice the selling cost ($7.75 per ton) previously estimated by Waitzman, et al (WA-219).

The differences in transportation costs for Cat-Ox acid versus other abatement sulfuric acid are primarily due to the differences in acid concentrations. According to Bucy (BU-132), the additional costs of transporting 78 percent sulfuric acid versus 98 percent acid would be approximately $1 per ton. It should be emphasized that this $1 per ton difference was based on barge transportation. The differences in rail or truck transportation costs would be greater. This would indicate that a power unit utilizing the Cat-Ox Process for flue gas desulfurization should be located on a waterway capable of handling barge transportation or near a sulfuric acid market.

According to McGlamery (MC-187), there is currently a market for the sulfuric acid produced by the Cat-Ox FGD Processes. This market is limited to superphosphate and fertilizer producers due to the acid's concentration and impurities. The fertilizer manufacturers who have purchased Cat-Ox acid found the acid concentration and impurity levels acceptable.

Location Criteria for the Cat-Ox FGD Processes

The location criteria for a power plant using the Cat-Ox FGD Processes are a function of three items. These items include: 1) land requirements for the Cat-Ox Processes, 2) the operation of the power unit using the Cat-Ox Processes, and 3) the Cat-Ox acid transportation costs.

According to McGlamery (MC-136), the land requirement for the Cat-Ox process installed on a 500 Mw power unit is 7.4 acres. It should be noted that these requirements do not include the land required for fly ash disposal. This land requirement is low and could be a significant factor in choosing a process for flue gas desulfurization.

Power production units can be classified into two general categories, "base-load" plants and "swing-load" plants. "Base-load" units are operated continuously except for maintenance, and "swing-load" plants are operated intermittently or at times of peak power demand. the "base-load" plants are the newer, larger, and more efficient plants. The "swing-load" plants are the smaller and less efficient plants. The power production units that would have the greatest potential for installing a Cat-Ox FGD Process would be the "base-load" plants that use high-sulfur coal or oil (BU-132, WA-219). This is based on: a) the indication that sulfuric acid-producing processes would be less competitive in intermittent service than "throwaway processes" (MC-187), b) the Cat-Ox Processes were designed to operate at steady-state conditions, and c) the current 8-10 hour start-up time required for the Cat-Ox Process (MA-481).

The location criteria for a power plant using a Cat-Ox FGD Process will also be affected by acid transportation costs. According to Waitzman, et al. (WA-219), the increase in barge transportation costs for Cat-Ox acid would be approximately $1 per ton more than the transportation costs of 98 percent sulfuric acid. TVA (BU-132, WA-219) indicated that the optimum locations for a power plant using a Cat-Ox FGD Process would either be near a fertilizer manufacturer who would use the Cat-Ox acid or have access to a waterway capable of handling barges.

Before a power plant installs a Cat-Ox FGD Process, the power plant's land availability, type of operation, and geographical location must be considered. The Cat-Ox FGD Process requires 7.4 acres; it should be installed on a "base-load" plant; and it should be located near a fertilizer manufacturer or on a navigable waterway.

Raw Material Availability and Fuel Requirements

The raw material used by the Integrated and Reheat Cat-Ox FGD Processes is the vanadium pentoxide catalyst used for oxidizing sulfur dioxide to sulfur trioxide. Currently, there is no problem in the avialability of this catalyst (BR-272, MO-179). The current cost of this catalyst is $1.65 per liter.

The fuel requirements for the Cat-Ox Processes include steam and No. 2 fuel oil. For an Integrated Process installed on a new 500 Mw power unit, the annual steam requirements would be 13,500,000 lb of turbine extraction steam. For the Reheat Cat-Ox Process, the annual No. 2 fuel oil requirements would be 7,760,000 gallons.

10.8 Economic Assessment

The economic assessment of the Integrated and the Reheat Cat-Ox Processes indicate that both processes are capital investment intensive and the Reheat Process is also energy intensive.

This assessment was based on Cat-Ox Processes installed on a 500 MW, coal-fired boiler subject to the base case conditions presented earlier.

A study on the economics of advanced flue gas desulfurization processes, (MC-136) indicated that the processing areas in the Integrated Cat-Ox Process where most of the capital investment cost arise are in the acid absorption and particulate removal. These two areas include approximately 70 percent of the total capital investment required for the Integrated Process. For the Reheat Process, the particulate removal, flue gas reheat, and acid absorption are the capital intensive areas and include approximately 60 percent of the total capital investment (MC-136).

The annual raw material and utility costs were estimated for the Integrated and the Reheat Cat-Ox Processes. These costs for the Integrated and Reheat Processes are summarized in Tables 10-5 and 10-6, respectively. From Table 10-5, the raw material and utility cost for the Integrated Process is 0.48 mills/kwhr. The process areas where the majority of these costs are incurred are in fan operation and particulate removal. The combined costs for these process areas would include approximately 95 percent of the total cost. It should be emphasized that a heat credit is incorporated for the Integrated Process which significantly reduces its costs.

From Table 10-6, the total utility and material cost for a Reheat Cat-Ox Process would be 1.40 mills/kwhr. The major difference between the costs of the Integrated and the Reheat Processes is in flue gas reheat and heat recovery. For the Reheat Process, flue gas reheat would have a cost of 0.89 mills/kwhr which is greater than the total cost for the

TABLE 10-5

ANNUAL RAW MATERIAL AND UTILITY COSTS FOR THE INTEGRATED CAT-OX PROCESS (500 MW PLANT)

Process Area*	Chemical and Energy Consumption		Costs (10^3 \$/yr)
Particulate Removal	Power (3917.1 kw)		412.0
		Subtotal	412.0
Catalytic Oxidation	Catalyst (78,900 ℓ)		129.8
	Power (38.6 kw)		4.0
		Subtotal	133.8
Heat Recovery Loop	Power (495.7 kw)		52.2
	Steam (25,600 lb/hr)		134.5
	Heat Credit (141/MM Btu/hr)		(-370.8
		Subtotal	(-184.1)
Fans	Power (7548.6 kw)		794.2
		Subtotal	794.2
Acid Absorption	Power (821.4 kw)		86.4
	Process Water (742.9 gpm)		18.8
		Subtotal	105.2

TOTAL Raw Material and Utility Costs: \$1,261,100/yr

Annualized Raw Material and Utility Costs: 0.48 mills/kwhr

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[*] Does not include acid storage and shipping, utilities or services.

TABLE 10-6

ANNUAL RAW MATERIAL AND UTILITY COSTS FOR THE REHEAT CAT-OX PROCESS (500 MW PLANT)

Process Area*	Chemical and Energy Consumption		Costs (10^3 $/yr)
Particulate Removal	Power (500.0 kw)		52.6
		Subtotal	52.6
Catalytic Oxidation	Catalyst (80,500 ℓ)		132.7
	Power (38.6 kw)		4.0
		Subtotal	136.7
Flue Gas Reheat	No. 2 Fuel Oil (24.6 gpm)		2,328.7
	Power (20.0)		2.2
		Subtotal	2,330.9
Fans	Power (9542.9 kw)		1,004.0
		Subtotal	1,004.0
Acid Absorption	Process Water (19,000 gpm)		119.6
	Power (454.3 kw)		47.8
		Subtotal	167.4

TOTAL Raw Material and Utility Costs: $3,691,600/yr

Annualized Raw Material and Utility Costs: 1.40 mills/kwhr

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[*] Does not include acid storage and shipping, utilities, or services.

Integrated Process. The flue gas reheat costs also include 63 percent of the total annual costs associated with the Reheat Process. From these cost estimations, the Reheat Cat-Ox Process is both capital and energy intensive where the Integrated Process is only capital intensive.

The selling price of the sulfuric acid produced by the Cat-Ox Processes will affect the annual costs. Figure 10-8 illustrates the effect sulfuric acid price has on the Integrated and the Reheat Processes' annual costs. This figure indicates that a six-dollar per ton increase in acid selling price results in a reduced annual cost of approximately 0.19 mills/kwhr.

10.9 Process Summary

The Integrated and the Reheat Cat-Ox FGD Processes utilize catalytic oxidation of the flue gas SO_2 to produce SO_3 and combine this SO_3 with water to produce a 77.7 percent H_2SO_4 product. The critical design features which are common to both Processes include: a) the need for "hot-side" and "cold-side" electrostatic precipitators to remove 99.9 percent of the flue gas particulates, b) the need for converting 90 percent of the SO_2 to SO_3 in the catalytic converter, and c) the need for absorbing at least 98 percent of the acid formed by the combination of SO_3 and water. The additional design features which are critical for the Reheat Cat-Ox Process include: a) flue gas reheat and b) leakage in the flue gas heat exchanger. Both of the Cat-Ox Processes are technically feasible and have favorable economics. They should be viable candidates for flue gas desulfurization.

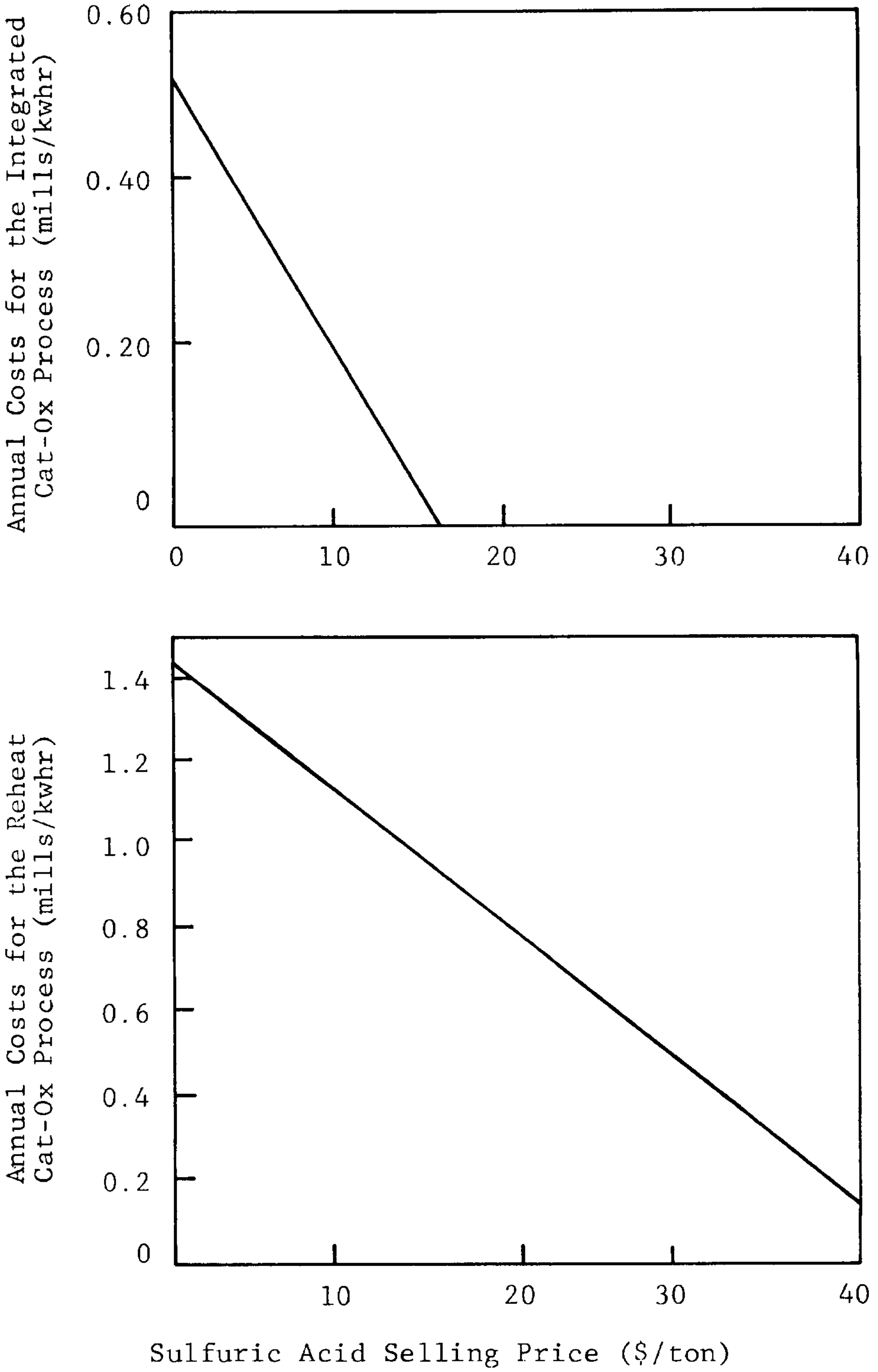

FIGURE 10-8. EFFECT OF SULFURIC ACID SELLING PRICE ON THE ANNUAL COSTS OF THE CAT-OX FGD PROCESSES INSTALLED ON THE BASE CASE 500 MW COAL-FIRED BOILER

11.0 MAGNESIA SLURRY ABSORPTION PROCESS

The magnesia Slurry Absorption Process uses magnesium oxide to absorb SO_2 in a wet scrubber. Magnesium sulfite is the predominant species formed by the reaction with SO_2 in the scrubber according to Equation 11-1.

$$Mg(OH)_2 + SO_2 \rightarrow MgSO_3 + H_2O \qquad (11\text{-}1)$$

The aqueous slurry is centrifuged and the cake is then dried with fuel oil combustion gas to remove free and bound moisture. The magnesium oxide is regenerated in a calciner by thermal decomposition of magnesium sulfite according to Equation 11-2.

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (11\text{-}2)$$

Hot gases from combustion of a heavy fuel oil are again used to heat the magnesium sulfite in the calciner and to remove the SO_2. The SO_2 rich gas stream can be used to produce sulfuric acid or elemental sulfur.

11.1 Process Description

The basic process design of the magnesia scrubbing process can be divided into four major sections:

1) SO_2 Absorption,
2) $MgSO_3/MgSO_4$ Separation and Drying,
3) MgO Regeneration and SO_2 Recovery, and
4) Sulfur Production.

Figure 11-1 is a simplified flow diagram for the process.

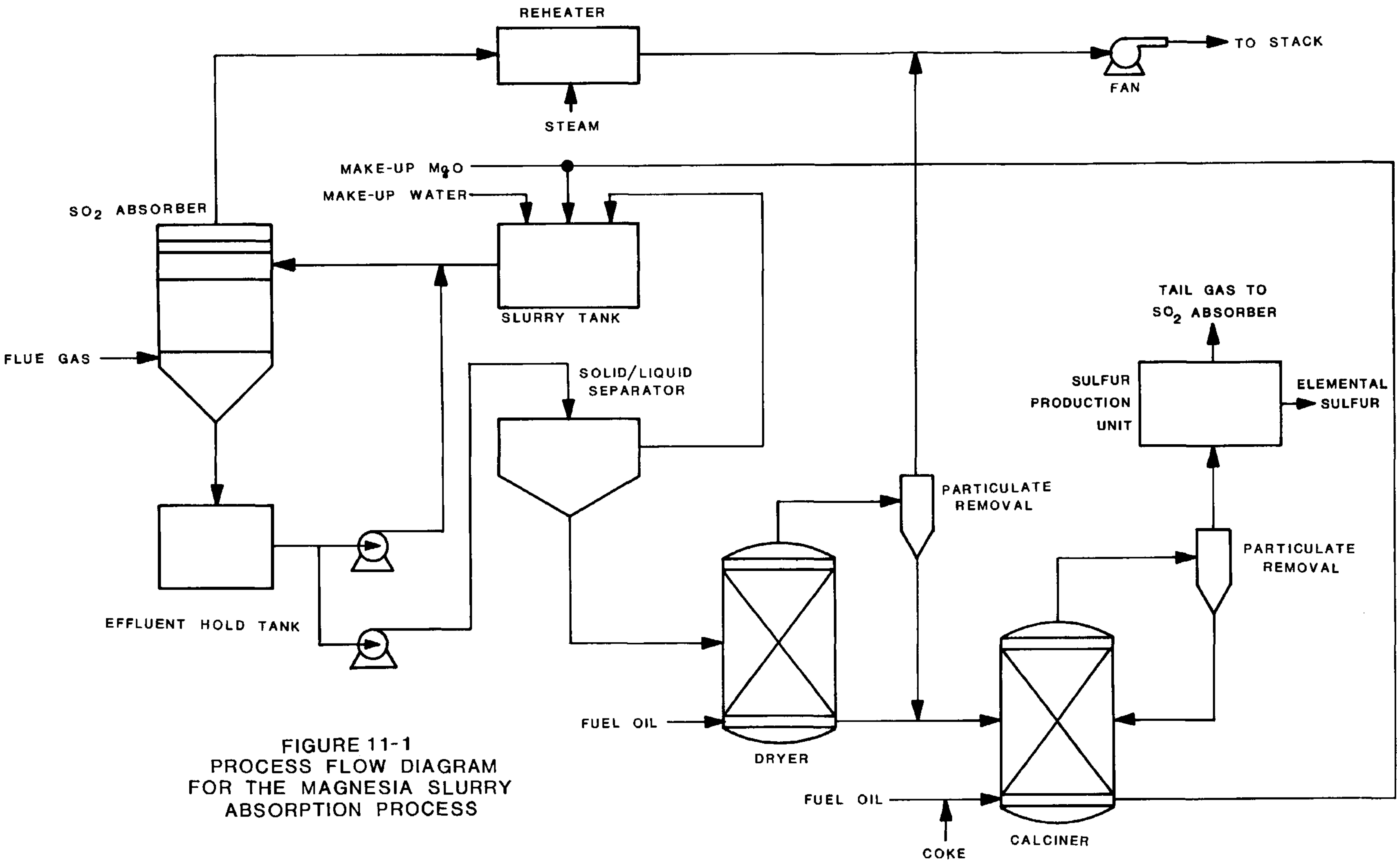

FIGURE 11-1
PROCESS FLOW DIAGRAM
FOR THE MAGNESIA SLURRY
ABSORPTION PROCESS

SO_2 Absorption

Absorption of SO_2 takes place after the flue gas is treated for particulate removal in a wet scrubber or electrostatic precipitator. A separate system ahead of the SO_2 scrubber is used for particulate removal for two reasons. It eliminates some components of the fly ash such as vanadium and iron compounds which can catalyze the oxidation of $MgSO_3$ to $MgSO_4$. Also, there is no easy way to remove fly ash from the circulating scrubbing slurry. A venturi prescrubber for particulate removal is preferred in coal-fired applications because it removes chlorides which are contained in the coal and saturates and cools the flue gas from 310°F to about 125°F.

In a 500 Mw plant, four 125 Mw scrubber trains are used so that the scrubbers will be of reasonable size. Also, this enables the plant to run at a 375 Mw capacity while repairs are made on one scrubber train.

Upon entering the SO_2 absorber a recycle MgO slurry absorbs SO_2 forming $MgSO_3$ crystals. A bleed stream is sent to a centrifuge as a first step for MgO recovery. Make-up water, recycle MgO, and make-up MgO are added to the recycle slurry to maintain a constant slurry composition.

Development work on the magnesia scrubbing process has followed at least three major technical routes since the early 1930's. The use of magnesium sulfite/magnesium oxide slurries having a basic pH, the use of manganese dioxide as an absorbent activator with the slurry, and the use of magnesium sulfite in acidic solution (clear liquor process) are variations of the magnesia slurry process that have been developed.

The presence of manganese promotes the desulfurization, oxidation of magnesium sulfite into sulfate, and also the decomposition of magnesium sulfate by roasting. The use of magnesium sulfite in an acidic solution (pH less than 6.0) produces a clear liquor which can be used on coal-fired systems where one scrubber is used to remove both the particulates and SO_2. A clear solution is used so that the ash can be filtered out. The process is restricted by a lower SO_2 removal efficiency than the basic slurry process because the vapor pressure of the scrubbing solution is higher.

The basic slurry process is the most advanced system and, therefore, will be evaluated in this study. An aqueous slurry of magnesium hydroxide and magnesium sulfite (pH range 6.5 to 8.5) is used to absorb the SO_2 according to Equations 11-1 and 11-3.

$$Mg(OH)_2 + SO_2 \rightarrow MgSO_3 + H_2O \qquad (11\text{-}1)$$

$$MgSO_3 + H_2O + SO_2 \rightarrow Mg(HSO_3)_2 \qquad (11\text{-}3)$$

Sulfite oxidation gives rise to sulfates in the system by the following reaction.

$$MgSO_3 + \tfrac{1}{2}O_2 \rightarrow MgSO_4 \qquad (11\text{-}4)$$

The test facility at Boston Edison reported sulfate concentration to be in the 15-20 weight percent range for solids shipped to the regeneration facility. The sulfite and sulfate solids precipitate as hydrated crystals as illustrated in the following equations.

$$MgSO_3 + 6H_2O \rightarrow MgSO_3 \cdot 6H_2O \qquad (11\text{-}5)$$

$$MgSO_3 + 3H_2O \rightarrow MgSO_3 \cdot 3H_2O \qquad (11\text{-}6)$$

$$MgSO_4 + 7H_2O \rightarrow MgSO_4 \cdot 7H_2O \qquad (11\text{-}7)$$

The bisulfite in the spent scrubbing liquor is reacted with magnesium hydroxide which is formed by slaking the fresh and recycle magnesium oxide.

$$Mg(HSO_3)_2 + Mg(OH)_2 + 4H_2O \rightarrow 2(MgSO_3 \cdot 3H_2O) \qquad (11\text{-}8)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (11\text{-}9)$$

$MgSO_3$/$MgSO_4$ Separation and Drying

After absorption of SO_2 in the scrubber, a portion of the slurry from the main scrubber circulation loop is removed as a 10-15 weight percent slurry and sent to a thickener. The thickener is an optional piece of equipment that has the potential for increasing the surge capacity in the recovery portion of the plant and for improved centrifuge operation.

A stainless steel, solid bowl centrifuge has been used to recover a wet cake of $MgSO_3$/$MgSO_4$ hydrate crystals. The centrifuge has been shown to be capable of separating 50 percent of the incoming solids in the recycle slurry. Satisfactory centrifuge operation is necessary so that solids are removed at a sufficient rate to maintain control of recycle solids concentration. The wet crystals are discharged from the centrifuge through a vertical chute into a screw feeder which provides a seal and a continuous flow of wet solids into a rotary or fluid-bed dryer. The rotary kiln type dryer is presently used in the three U.S. magnesia scrubbing demonstration units. Combustion gases from an oil burner, which can be tempered by a sidestream of stack gas, are used to dry the crystals. The dried $MgSO_3/MgSO_4$ is discharged from the dryer and conveyed to the calciner for MgO regeneration and SO_2 recovery.

MgO Regeneration and SO_2 Recovery

The dried $MgSO_3/MgSO_4$ solids are heated in an oil-fired rotary kiln or fluidized-bed reactor to decomposition. The main decomposition reaction was shown in Equation 11-2.

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (11\text{-}2)$$

The $MgSO_4$ is also reduced in the calciner using carbon as a reducing agent.

$$MgSO_4 + \tfrac{1}{2}C \rightarrow MgO + SO_2 + \tfrac{1}{2}CO_2 \qquad (11\text{-}10)$$

Two installations have used a rotary kiln to regenerate the MgO. High dust losses in the rotary kiln require the use of a hot cyclone and venturi scrubber to recover all of the MgO. If a fluidized-bed reactor were used most of the MgO formed would go overhead with the SO_2 and combustion gases and separation equipment would also be required.

The optimum calcining temperature in the reactor is set by the fact that it must be high enough to decompose all of the $MgSO_3/MgSO_4$ solids without "dead burning" the MgO. "Dead burned" MgO is chemically unreactive and not effective for further SO_2 removal. Operating temperatures in the 1500°F range have been used in the rotary calciner.

Sulfur Production

After dust removal, the sulfur dioxide-rich gas from the calciner is piped to either a sulfur or sulfuric acid production unit. The on-site production of both sulfur and sulfuric acid were evaluated as methods for SO_2 processing in this report. Section 14 describes various methods of sulfur and sulfuric acid production. After cleaning, the gas stream from the calciner is well suited for sulfuric acid production as it is at approximately 100°F, is saturated with water, and contains about 8-10 percent SO_2.

11.2 Environmental Considerations

The process has consistently shown SO_2 removal efficiencies of 90 percent or greater using regenerated magnesium oxide. There have been no reports of NO_x removal by magnesia slurry scrubbing during the operation of the demonstration units at Boston Edison and Potomac Electric. The results of a pilot plant study by Babcock and Wilcox completed in 1970 reported that the absorption of nitrogen oxides was negligible under all conditions tested using either a venturi or packed column absorber.

Two types of system losses can be identified: (1) purge treatment of the magnesia slurry stream when needed, and (2) magnesia losses in the process. The first identifiable system loss is a magnesia slurry stream that is sent to purge treatment. This stream has not been quantitatively identified. It is produced only when the slurry requires the removal of impurities. It depends upon such factors as magnesia quality, make-up water quality, fly ash and impurities from calciner coke addition. Magnesia losses in the system have occurred in different parts of the process. The test data from the Boston

Edison demonstration unit have been extrapolated to predict the magnesia losses in a 500 Mw coal-fired power plant. The total MgO losses measured during a 13-day test at the Boston Edison station amounted to 3.5 percent of MgO consumption. Large magnesia losses also occurred during regeneration at Essex Chemical's sulfuric acid plant. It was concluded that almost all of the losses at the acid plant could be reclaimed by improved design at new regeneration facilities. From the Boston Edison test data it was decided to base the material requirements for the Radian base case in this study on a 3.5 percent magnesia loss (521 lb/hr). Actual MgO losses will probably depend on the equipment and operation of specific Mag-Ox scrubbing units.

11.3 Material and Energy Balances

Radian's material and energy balance calculations for the base case were checked for consistency with those previously performed by TVA as part of a conceptual design study for magnesia scrubbing. A venturi scrubber was used in these calculations as a gas-liquid contactor for SO_2 removal (MC-136). The energy consumption and raw material requirements for the process with both sulfur and sulfuric acid production are shown in Tables 11-1 and 11-2.

The largest electric power requirement for the process is for the flue gas fans which consume 4.6 Mw or 50 percent of the power required for the process. This large amount of power is needed to overcome the pressure drop caused by the FGD system. The fan requirement can be higher or lower depending on the type of scrubber that is used, since the packed-bed type scrubbers (e.g., marble bed and TCA contactors) give a higher pressure drop than the open configuration type scrubbers (e.g., spray towers). The remaining areas of electric power consumption for the process mostly represent pumping, magnesium

TABLE 11-1

MAGNESIA SLURRY RAW MATERIAL AND UTILITY REQUIREMENTS WITH SULFUR PRODUCTION

Basis: 500 Mw Capacity, 3.5% Sulfur Coal,
5260 hrs/yr Operation at Full Load

Process Section	Magnesium Oxide (lb/hr)	Coke (lb/hr)	Process Water (M gal/hr)	No. 6 Fuel Oil (MM Btu/hr)	Coal Gasification Reducing Gas (MM Btu/hr)	High Pressure Steam (MM Btu/hr)	Electricity (Mw)
SO_2 Absorption	521	---	25	--	---	77	6.7
$MgSO_3/MgSO_4$ Separation and Drying	---	---	--	70	---	--	0.8
MgO Regeneration and SO_2 Recovery	---	342	--	60	---	--	0.4
Sulfur Production	---	---	--	--	145.1	--	--
TOTAL	521	342	25	130	145.1	77	7.9

TABLE 11-2

MAGNESIA SLURRY RAW MATERIAL AND UTILITY REQUIREMENTS WITH SULFURIC ACID PRODUCTION

Basis: 500 Mw Capacity, 3.5% Sulfur Coal,
5260 hrs/yr Operation at Full Load

Process Section	Magnesium Oxide (lb/hr)	Coke (lb/hr)	Sulfuric Acid Catalyst (liter/hr)	Process Water (M gal/hr)	Cooling Water (M gal/hr)	No. 6 Fuel Oil (MM Btu/hr)	High Pressure Steam (MM Btu/hr)	Electricity (Mw)
SO_2 Absorption	521	---	---	25	---	--	77	6.7
$MgSO_3$/$MgSO_4$ Separation and Drying	---	---	---	--	---	70	--	0.8
MgO Regeneration and SO_2 Recovery	---	342	---	---	---	60	--	0.4
Sulfuric Acid Production	---	---	0.26	---	285	--	--	1.3
TOTAL	521	342	0.26	25	285	130	77	9.2

solids processing, and sulfur or sulfuric acid production.

Reheat of the cleaned gas to 175°F requires 77 MM Btu/hr, which is the largest single heat requirement in the process. The amount of steam used for reheat should be nearly the same for all wet scrubbing processes which saturate the flue gas.

The 130 MM Btu/hr of fuel oil required for MgO regeneration is about equally divided between $MgSO_3$ drying and calcining. A fluid-bed dryer and calciner used in these operations is probably the most thermally efficient type of equipment that could be used for these applications. The excellent gas-solid contact and heat transfer characteristics of the fluid-bed reactor can also produce a thoroughly dried or calcined mixture if staging is used.

The 145.1 MM Btu/hr of reducing gas required to produce sulfur is used to reduce the SO_2 and O_2 in the calciner off-gas. A typical composition for a Mag-Ox calciner off-gas would include about 9 volume percent SO_2 and 5 volume percent O_2. The oxygen is introduced into the gas by the excess air used for the combustion of fuel oil in the calciner. The oxygen consumes an equal amount of reducing gas as the SO_2 on a molar basis. This makes the SO_2 stream equivalent to a stream containing 14 volume percent SO_2 for purposes of calculating reducing gas requirements. If a method could be devised to eliminate the oxygen in the calciner off-gas the reducing gas requirement would be reduced by 36 percent to 93.3 MM Btu/hr.

The water required for the process is used for SO_2 scrubbing and sulfuric acid production. Water is evaporated in the scrubbing system to saturate and cool the flue gas. The sulfuric acid plant requires a large amount of cooling water to cool the sulfuric acid after reaction in the converter.

The magnesium oxide required represents a 3.5 percent loss in the process. Tests at Boston Edison showed that proper equipment and system operation could probably keep the MgO losses down to this amount.

Coke is consumed in the calcination reaction to reduce the $MgSO_4$ to $MgSO_3$, requiring one-half mole of carbon per mole of $MgSO_4$. Coke with a low ash content (less than 10 percent) is required in the process to prevent excessive contamination of the recycle MgO. The amount of sulfate determines the coke required in the calciner so that some systems with low oxidation of sulfite to sulfate will require less coke. Also, it was found during the operation of the Boston Edison test program that carbon in the fuel oil fly ash removed in the scrubber helped to reduce $MgSO_4$ in the calciner. The coke requirement calculation in this section is based on the experience at Boston Edison.

11.4 Design Considerations

The flow rate and sulfur content of the flue gas are the major parameters to be considered in the magnesia slurry scrubbing system design. The amount of SO_2 in the gas primarily affects the L/G ratio in the scrubber and the size of the processing equipment, particularly in the regeneration and sulfuric acid production sections of the process.

Venturi scrubbers have been used exclusively in this country on the demonstration scale for magnesia scrubbing, but there is no reason that other types of scrubbers such as the TCA, marble-bed, grid tower, and spray tower contactors could not be successfully used. A discussion of scrubber types and their operating characteristics is given in Section 12.4 - Design Considerations of Lime/Limestone Wet Scrubbing.

The process sequence for magnesia slurry scrubbing has been fairly standard for the U.S. installations that have already been operated. The centrifuge and rotary dryer have been used in all three of the demonstration size installations. Two of the installations used a rotary calciner while Philadelphia Electric used a fluidized bed unit to calcine the $MgSO_3/MgSO_4$ product. A thickener is an optional piece of equipment that has been used to concentrate the slurry prior to the centrifuge. The use of a thickener gives the prospect for improved centrifuge operation.

Generally, high SO_2 removals are achievable due to the relatively high solubility of magnesium sulfite. The amount of soluble alkalinity available in magnesia scrubbing systems is more than that available in lime/limestone systems but less than for sodium-based scrubbing systems. Therefore, magnesia systems can operate at a lower L/G than lime/limestone systems but at a higher L/G than sodium-based systems. An L/G of 33 gal/1000 acf was used at the Boston Edison facility using a venturi scrubber.

The major design variables that can be used to regulate the scrubbing operation are the recycle pH and percent solids. A higher pH gives a higher SO_2 recovery. The pH can be controlled by MgO addition while the amount of solids in the slurry can be controlled by adjusting the rate of bleed from the recycle slurry. For more than 90 percent SO_2 removal the pH of the final suspension should be above 7.

Particulate control is carried out separately from the SO_2 scrubbing system. High dust removal efficiencies are required to minimize the amount of contaminants that enter the system. Small amounts of fly ash will still enter the circulating slurry system since particulate control devices are not 100 percent effective in removing fly ash.

Contaminant control is required to reduce the amount of impurities that will accumulate in closed-loop operation. Both soluble and insoluble impurities are of concern. Insoluble impurities come primarily from the fly ash in the flue gas and coke used in the calciner. These insoluble impurities are controlled by high efficiency particulate removal equipment prior to the SO_2 absorber and by using coke with a low ash content.

Soluble contaminants enter the system from the make-up water, make-up MgO, fly ash, and calciner coke. These soluble species must be purged from the system. Chloride attack of scrubber internals can occur when carbon steel or stainless steel are used as absorber construction materials. Glass reinforced polyester resins have been successfully used to prevent corrosion in the scrubber.

Heat recovery from the dryer and calciner off-gas is desirable but is complicated by the entrainment of $MgSO_3$ or MgO fines in the combustion gases. The dryer off-gas at 400°F and the calciner off-gas at 1600°F afford a useful source of energy savings in the process. Particulate collection equipment could be used in each stream to recover the fines before recovering the heat from the gas. Particulate removal of greater than 99.5 percent must be obtained before the calciner off-gas can be used as acid plant feed.

Commercial magnesia scrubbing installations have used fuel oil to fire the calciners. Coal might also be used as a calciner fuel if the coal ash could be readily separated from the MgO product, and would probably be advantageous in areas where low priced coal is available.

The majority of the problems experienced in the oil-fired Boston Edison power plant installation were closely related to the solids-handling system. The production of magnesium sulfite hexahydrate crystals from the scrubber operation was expected from pilot plant experience. Instead, the much finer trihydrate was produced which is less easily dewatered. This unexpected occurrence resulted in crystal properties different from those used in the design of the solids handling system and the dryer. From operating experience to date, it appears that the trihydrate crystals are produced from oil-fired furnaces and the hexahydrate from coal-fired applications. Magnesia scrubbing experience in Japan treating an off-gas produced from a copper smelter and a sulfuric acid plant has resulted in the production of the larger hexahydrate crystals. Proper design of the system based on the expected hydrate will solve the solids handling and dryer operation problem. For material balance purposes, the drying operation is based on production of $MgSO_3$ hexahydrate crystals.

Both commercial installations of the Chemico magnesia slurry scrubbing systems have had problems slaking the magnesium oxide to magnesium hydroxide. This has been found to be a problem particularly when recycle magnesium oxide is used. Experience has shown that successful operation can be achieved when steam heat is used to promote magnesium oxide slaking.

11.5 Status of Development

The magnesia slurry scrubbing process has been shown to be feasible on a full-scale size. Three retrofit units in the U.S. of the 95-150 Mw size have demonstrated 90 percent SO_2 recovery on both oil-fired and coal-fired systems. A list of the operating and planned magnesia scrubbing units is shown in Table 11-3.

The magnesia scrubbing process has been used on a commercial scale at three locations in Japan. A summary of the status of the three Japanese installations is shown in Table 11-4. An SO_2 recovery of over 90 percent has been demonstrated for the Japanese units. The Mitsui unit uses a special cross-flow type absorber which they have developed. The scrubber consists of an empty chamber with two rotating shafts with many spoons. The scrubber has little possibility of scaling because of the simple structure, but the size of the scrubber is limited to the treatment of no more than 60,000 scfm (about 29 Mw).

The SO_2 recovery system at Boston Edison has been able to demonstrate 80 percent availability during sustained operation. The Potomac Electric Dickerson station was only able to operate at 64 percent availability for their SO_2 recovery system during their best month. This indicates that magnesia scrubbing reliability needs improvement.

Scaling or plugging in the scrubber has not been a problem in magnesia slurry scrubbing systems. Venturi scrubbers have been employed on all U.S. plants so far, and SO_2 removal efficiencies of over 90 percent have consistenly been obtained.

TABLE 11-3

OPERATING AND PLANNED MAGNESIA SCRUBBING UNITS ON U.S. POWER PLANTS AS OF DECEMBER, 1975

Utility Company, Power Station	New or Retrofit	Size of FGD Unit (Mw)	Process Vendor	Fuel, Sulfur Content (%)	SO_2 Recovery (%)	Start-up date, Status
Boston Edison Mystic No. 6	Retrofit	150	Chemico	Oil, 2.5	90	Start-up in April, 1972; Test program completed in June, 1974. Not currently operational.
Potomac Electric and Power, Dickerson No. 3	Retrofit	95	Chemico	Coal, 2.0	90	Start-up in September, 1973; Test program completed in September, 1975. Not currently operational.
Philadelphia Electric Co., Eddystone No. 1A	Retrofit	120	United Engineers	Coal, 2.5		Start-up in September, 1975; Not currently operational.
Philadelphia Electric Co., Eddystone No. 1B	Retrofit	240	United Engineers	Coal, 2.5		Start-up due in October, 1978; Letter of intent signed.
Philadelphia Electric Co., Eddystone No. 2	Retrofit	336	United Engineers	Coal, 2.4		Start-up due in October, 1978; Considering FGD system.
Philadelphia Electric Co., Cromby	Retrofit	150	United Engineers			Start-up due in October, 1978; Considering FGD system.

TABLE 11-4

OPERATING MAGNESIA SCRUBBING UNITS ON JAPANESE POWER PLANTS AS OF DECEMBER, 1975

Company Location	Type of Plant	Size of FGD Unit (Mw)	Process Vendor	Flue Gas SO_2 Content (ppm)	SO_2 Recovery (%)	By-Product (tons/day)	Start-up date, Status
Onahama Smelter Onahama, Japan	Copper Smelter	28	Onahama-Tsukishima	15,000-25,000	99.5	H_2SO_4- 240	Start-up in December, 1972; Currently operational.
Mitsui Mining Hibi, Japan	H_2SO_4	24	Mitsui-Mining	1,500- 2,000	90	H_2SO_4- 18	Start-up in October, 1971; Currently operational.
Idemitsu Kosan Chiba, Japan	Claus Unit and Boiler	162	Chemico-Mitsui	- -	95	Sulfur- 70	Start-up in 1974; Currently operational.

Numerous operating problems occurred early in the program at Boston Edison. Most of the problems were of a materials handling nature resulting from the characteristics of the solids generated in the scrubber loop. It was found that trihydrate crystals with an average size of 10-15 microns were formed in the absorber instead of the larger hexahydrate which had been formed in the pilot plant. As a result, the centrifuge cake contained as much as 25 percent unbound moisture. This led to problems of solids adhesion to the dryer drum.

These problems were solved by several operating and design modifications. Among these modifications were changing the dryer to function as a granulator and adding hammers to loosen any material which tended to adhere to the dryer shell. The granulator material discharge was screened and sent through lump breakers to eliminate oversize agglomerated granules of the magnesium sulfite. The dryer off-gas was sent to the SO_2 absorber to prevent high dust losses. This subsequently caused the loss of 15°F of reheat of the saturated flue gas expected from the dryer off-gas.

Other process problems occurred in the calcining system. A rotary kiln has been used for these operations. The formation of the very fine trihydrate crystals in the oil-fired power plant application also resulted in dusting problems in the rotary calciner. The facility at Essex Chemical resolved the dusting problem in the calciner by the use of a cyclone followed by a venturi scrubber to remove all of the MgO fines from the gas. Leakage of air into the calciner was a problem since the reduction of $MgSO_4$ requires a reducing atmosphere. Installation of new seals on the rotary calciner corrected the problem.

"Dead-burning" of the MgO, causing unreactivity of the product for reuse in the scrubber, was due to high temperature operation in the calciner. High reactivity magnesia is favored by low calciner temperature and by increased amounts of carbon in the calciner feed. Recycle MgO reactivity was improved by the correct calciner operating conditions, by pulverizing the calcined MgO, and by heating the MgO slurry tank. More recent tests indicate that continuous stable operations are possible with high SO_2 removal efficiencies and that continuous use of recycle MgO has only a slight effect on the system.

The chemical and mechanical performance of the scrubber was excellent at Boston Edison. No internal plugging was encountered and the polyester lining of the scrubber was in sound condition after two years of intermittent operation.

Erosion and corrosion were experienced in the carbon steel recirculating slurry piping. The use of rubber-lined pumps, valves, and piping in certain areas of the system is considered to be a practical solution to this problem. The slurry recirculating pumps in the system have withstood corrosion using 316 stainless steel impellers.

In Japanese scrubbing experience, the large hexahydrate crystals were obtained at both the Onahama and Mitsui installations. These installations had no problem in the filtration and drying steps which were a problem at Boston Edison. The oxidation of sulfite to sulfate in the absorber at Mitsui was only 7-10 percent or half as much as reported at Boston Edison. The Onahama smelter gas that is treated contains high concentrations of SO_2 (15,000 - 25,000 ppm SO_2) and a low oxygen concentration.

11.6 Scale-up Problems

Few, if any scale-up problems exist for the magnesia slurry scrubbing process since all of the necessary process equipment has been demonstrated at the Boston Edison and Potomac Electric installations. Work still remains to be done, however, in defining the reasons for trihydrate and hexahydrate formation. An undefined area remains in the application of a fluidized bed to the drying and calcining operations. Both of these installations presently use rotary kilns in these process steps. Magnesium sulfite and sulfate crystals are extremely small after drying (on the order of 10 microns) which is on the lower limit of particle size used in fluidized beds.

The system scrubbing and regeneration facilities have up to this time been operated at separate locations. Operation of an on-site regeneration and sulfur or sulfuric acid plant would result in two design differences in the process. First, $MgSO_3$ crystals exiting from the dryer would be at approximately 400°F and would be sent to the calciner close to this temperature instead of at ambient temperature. Secondly, the absorption tower outlet gas from the sulfuric acid plant or the outlet gas from the sulfur plant tail gas incinerator would be mixed with the stack gas prior to the SO_2 absorber. This is to prevent the need for additional gas cleaning equipment to treat the outlet gas stream from the sulfur or sulfuric acid plant.

The effect of contaminant buildup in the system during continuous operation has not been conclusively determined in this country. No information was found on the contaminant buildup in the two Japanese systems that have been operating since 1972.

11.7 Utility Applicability

The land requirement for the scrubbing area of the magnesia slurry scrubbing process (between the stack and the boiler house) is essentially the same as for the lime/limestone scrubbing section. This comes to 22,500 square feet for the base case. The total process land requirement is about 76,000 square feet.

The plant location is an important consideration for this process. The by-product sulfuric acid produced from this process must be sold to other industries or neutralized. The largest end use of sulfuric acid is the production of phosphate fertilizers. A plant located in an area of fertilizer manufacture or usage (mid-West United States) could therefore operate more economically than a plant located elsewhere. Also, location on a navigable river would permit shipping the sulfuric acid by barge to fertilizer plants not located near the power plant.

In the case of a "central-processing concept", where several power plants are serviced by one MgO regeneration site, many sources of SO_2 emissions must be located relatively close to each other. Transportation costs would also become significant. The annual cost to truck the required $MgSO_3$ and regenerated MgO between the "base case" 500 Mw plant and a regeneration facility 50 miles away would be about $900,000 at $0.25/100 lbs.

Sulfuric acid market conditions and storage facilities for the by-product sulfuric acid are both important in the design of a magnesia scrubbing unit. Since the sulfuric acid is an intermediate product, the largest part of the storage burden is passed on to the industrial consumer. However, the phosphate fertilizer market is cyclic. Thus, 30 days' storage capacity for the sulfuric acid is suggested.

A minimum storage for $MgSO_3$ and recycled MgO of one day's supply will provide flexibility to the operation if in-plant calcination is practiced. However, for a central processing arrangement, more storage would be required because of possible transportation delays.

11.8 Economic Assessment

The utility and raw material requirements for the magnesia scrubbing process with both sulfur and sulfuric acid production are given in Tables 11-5 and 11-6. Annual raw material and utility costs for this process are 2.3 mills/kwhr with sulfur production and 1.2 mills/kwhr with sulfuric acid production. The major areas of expense are for the stack gas reheat, stack gas fan, liquid pumping, $MgSO_3$ drying, $MgSO_3$ calcining, make-up MgO, and for reducing gas when sulfur is produced. The fuel oil used in the drying and calcining operations represents 48 percent of the annual operating cost when acid is produced and 26 percent of the annual operating cost when sulfur is produced. Efficient operation of the dryer and calciner is needed to prevent the use of excess fuel oil.

A potential savings exists by lowering the amount of make-up MgO needed for the process. The amount of make-up MgO required represents a 3.5 percent loss in the process cycle. Depending on the need for a purge stream to remove impurities in the system, MgO consumption could possibly be lowered by efficient design and operation of the magnesia scrubbing facility. If the losses could be reduced to 2.5 percent of MgO consumption, a savings of about $60,000 would result.

TABLE 11-4

UTILITY AND RAW MATERIAL REQUIREMENTS FOR MAGNESIA SLURRY SCRUBBING WITH SULFUR PRODUCTION

Basis: 500 Mw, 3.5 wt % S Coal,
90% SO_2 Removal, 5260 hr/hr

	Quantity	Unit Price	Annual Cost
SO_2 Absorption:			
Magnesium Oxide	1370 tons/hr	\$155/ton	\$ 212,000
Steam (Flue Gas Reheat)	77 MM Btu/hr	\$1.00/MM Btu	405,000
Process Water	25.0 M-gal/yr	\$0.08/M-gal	11,000
Electricity			
Flue Gas Fans	4600 kw	\$0.02/kwhr	484,000
Other	2100 kw	\$0.02/kwhr	221,000
			\$1,333,000
Percent of Total Cost - 22%			
$MgSO_3/MgSO_4$ Separation and Drying:			
No. 6 Fuel Oil	70 MMBtu/hr	\$2.30/MM Btu	\$ 847,000
Electricity	800 kw	\$0.02/kwhr	84,000
			\$ 931,000
Percent of Total Cost - 15%			
MgO Regeneration and SO_2 Recovery:			
No. 6 Fuel Oil	60 MM Btu/hr	\$2.30/MM Btu	\$ 726,000
Coke	900 tons/yr	\$45/ton	41,000
Electricity	400 kw	\$0.02/kwhr	42,000
			\$ 809,000
Percent of Total Cost - 13%			
Sulfur Production:			
Coal Gasification Reducing Gas	145.1 MM Btu/hr	\$4.00/MM Btu	\$3,053,000
Percent of Total Cost - 50%			
		TOTAL	\$6,126,000

Annualized Utility and Raw Material Cost - 2.3 mills/kwhr

TABLE 11-5

UTILITY AND RAW MATERIAL REQUIREMENTS FOR MAGNESIA SLURRY SCRUBBING WITH SULFURIC ACID PRODUCTION

Basis: 500 Mw, 3.5 wt % S Coal,
90% SO_2 Removal, 5260 hr/yr

	Quantity	Unit Price	Annual Cost
SO_2 Absorption:			
Magnesium Oxide	1370 tons/yr	$155/ton	$ 212,000
Steam (Flue Gas Reheat)	77 MM Btu/yr	$1.00/MM Btu	405,000
Process Water	25.0 M-gal/yr	$0.08/M-gal	11,000
Electricity			
Flue Gas Fans	4600 kw	$0.02/kwhr	484,000
Other	2100 kw	$0.02/kwhr	221,000
			$1,333,000
	Percent of Total Cost - 41%		
$MgSO_3/MgSO_4$ Separation and Drying:			
No. 6 Fuel Oil	70 MM Btu/hr	$2.30/MM Btu	$ 847,000
Electricity	800 kw	$0.02/kwhr	84,000
			$ 931,000
	Percent of Total Cost - 28%		
MgO Regeneration and SO_2 Recovery:			
No. 6 Fuel Oil	60 MM Btu/hr	$2.30/MM Btu	$ 726,000
Coke	900 tons/yr	$45/ton	41,000
Electricity	400 kw	$0.02/kwhr	42,000
			$ 809,000
	Percent of Total Cost - 25%		
Sulfuric Acid Production:			
Cooling and Process Water	285 M-gal/hr	$0.03/M-gal	$ 45,000
Electricity	1300 kw	$0.02/kwhr	137,000
			$ 182,000
	Percent of Total Cost - 6%		
		TOTAL	$3,255,000

Annualized Utility and Raw Material Cost - 1.2 mills/kwhr

11.9 Process Summary

The magnesia slurry scrubbing process uses magnesium oxide to absorb SO_2 in a wet scrubber. The resulting magnesium sulfite/sulfate solution is dewatered, dried, and regenerated back to magnesium oxide. The concentrated SO_2 stream produced from the process is normally sent to a sulfuric acid plant but can also be used as the feed stream for a sulfur production facility.

The outstanding feature of the process is the high degree of development that has been undertaken to make it successful. Operating problems still exist with the formation of different $MgSO_3$ crystalline forms under different scrubber operating conditions and with the solids handling in the dryer and calciner operations. But, the technology to solve these problems is well proven so that magnesia scrubbing should become a technically sound process. The raw material and utility cost for the magnesia scrubbing process is competitive with the costs for other FGD processes.

12.0 LIME/LIMESTONE WET SCRUBBING PROCESS

The lime/limestone flue gas desulfurization process uses a slurry of calcium oxide or calcium carbonate to absorb SO_2 in a wet scrubber. This process is commonly referred to as a "throwaway" process because the calcium sulfite and sulfate formed in the system are disposed of as waste solids. The principal reactions in the scrubber are as follows:

For lime systems:

$$SO_{2\,(g)} + CaO_{(s)} + \tfrac{1}{2}H_2O \rightarrow CaSO_3 \cdot \tfrac{1}{2}H_2O_{(s)} \qquad (12\text{-}1)$$

For limestone systems:

$$SO_{2\,(g)} + CaCO_{3\,(s)} + \tfrac{1}{2}H_2O \rightarrow CaSO_3 \cdot \tfrac{1}{2}H_2O_{(s)} + CO_{2\,(g)} \qquad (12\text{-}2)$$

Some oxygen will also be absorbed from the flue gas or surrounding atmosphere and will cause oxidation of absorbed SO_2 and formation of calcium sulfate. The calcium sulfite and sulfate crystals are precipitated in a hold tank and then sent to a solid/liquid separator where the solids are removed. The waste solids are generally disposed of by ponding or landfill.

12.1 Process Description

The basic design of a lime or limestone scrubbing system can be divided into the following process areas:

1) SO_2 Absorption,
2) Solids Separation, and
3) Solids Disposal.

Figure 12-1 shows a generalized process flow diagram for the lime/limestone slurry scrubbing processes.

SO_2 Absorption

Absorption of SO_2 takes place in a wet scrubber using lime or limestone in a circulating slurry. Carbide sludge, an impure slaked lime that is a byproduct of acetylene manufacture, has also been used successfully at two installations. Particulates can be removed in the SO_2 absorber or ahead of the absorber by an electrostatic precipitator or particulate scrubber. The selection of a method for removal of particulates is based on economics and operational reliability. Removing particulates in the SO_2 absorber increases the solids load in the SO_2 scrubbing system. It is also believed that some components of the fly ash catalyze the oxidation of sulfite to sulfate which increases the potential for sulfate scaling.

The absorption of SO_2 from the flue gases by a lime or limestone slurry constitutes a multiphase system involving gas, liquid, and several solids. The overall reaction of gaseous SO_2 with the alkaline slurry yielding $CaSO_3\text{-}\frac{1}{2}H_2O$ is shown in Equations 12-1 and 12-2.

$$SO_{2(g)} + CaO_{(s)} + \tfrac{1}{2}H_2O \rightarrow CaSO_3\cdot\tfrac{1}{2}H_2O_{(s)} \qquad (12\text{-}1)$$

For limestone systems:

$$SO_{2(g)} + CaCO_{3(s)} + \tfrac{1}{2}H_2O \rightarrow CaSO_3\cdot\tfrac{1}{2}H_2O_{(s)} + CO_{2\,(g)} \qquad (12\text{-}2)$$

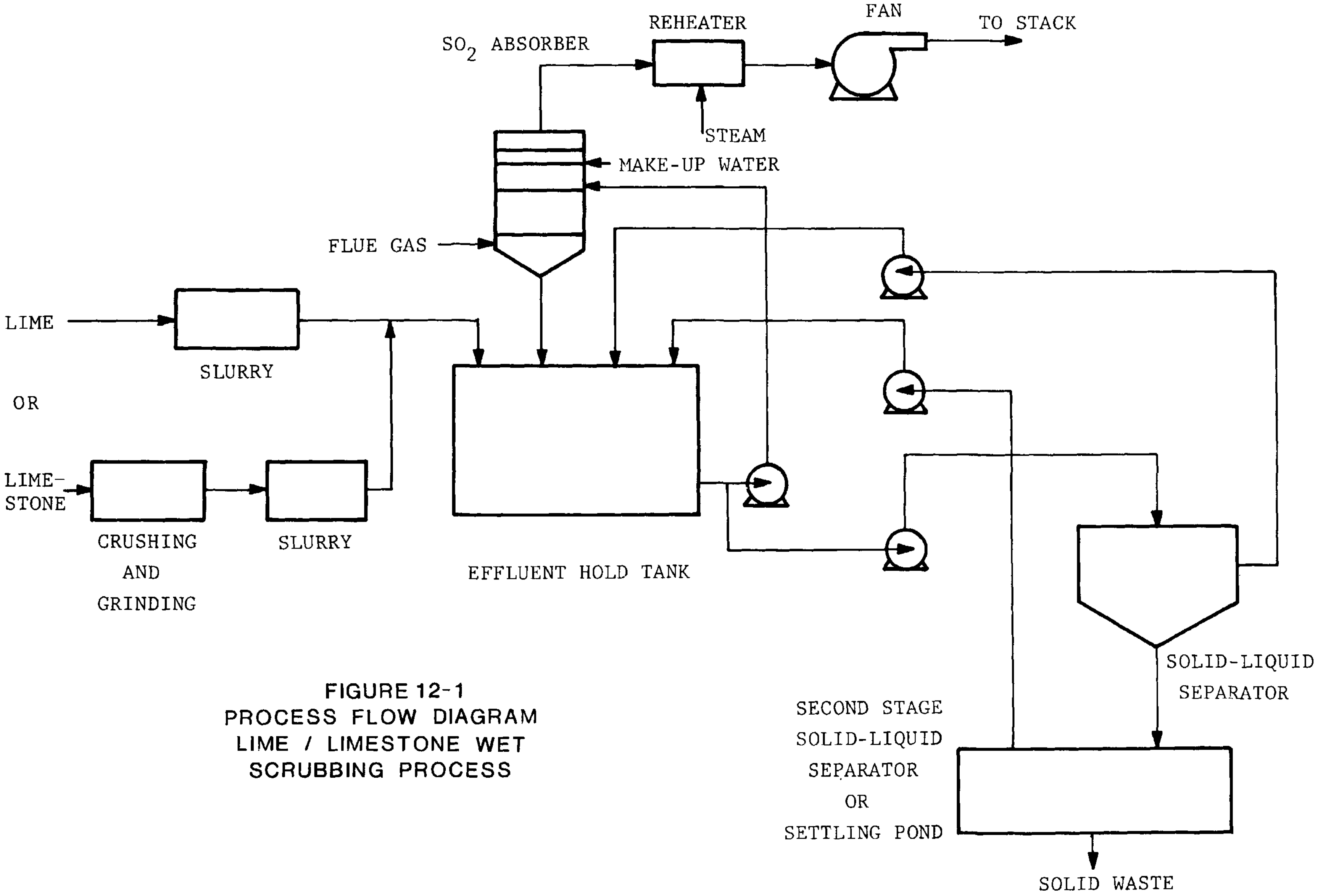

FIGURE 12-1
PROCESS FLOW DIAGRAM
LIME / LIMESTONE WET
SCRUBBING PROCESS

The solid sulfite is only very slightly soluble in the scrubbing liquor and thus will precipitate to form an inert solid for disposal. In the lime system some CO_2 may also be absorbed from the flue gas and will react in a similar fashion to form solid calcium carbonate.

In most cases some oxygen will also be absorbed from the flue gas or surrounding atmosphere. This leads to oxidation of absorbed SO_2 and precipitation of solid $CaSO_4 \cdot 2H_2O$. The overall reaction for this step is as follows:

For lime systems:

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} + CaO_{(s)} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O_{(s)} \qquad (12\text{-}3)$$

For limestone systems:

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} + CaCO_{3(s)} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O_{(s)} + CO_{2(g)} \qquad (12\text{-}4)$$

The extent of oxidation can vary considerably, normally ranging anywhere from almost zero to 40 percent. In some systems treating dilute SO_2 flue gas streams, sulfite oxidations as high as 90 percent have been observed. The actual mechanism for sulfite oxidation is not completely understood. The rate is known to be a strong function of oxygen concentration in the flue gas and liquor pH. It may also be increased by trace quantities of catalysts in fly ash entering the system.

Various types of gas-liquid contactors can be used as the SO_2 absorber. These differ in SO_2 removal efficiency as well as operating reliability. Four general types of contactors are usually used for SO_2 removal:

- venturi scrubbers,
- spray towers (horizontal and vertical),
- grid towers, and
- mobile bed absorbers (such as marble bed and turbulent contact absorber (TCA)).

The liquid to gas ratio (L/G) generally ranges between 35-110 gal/1000 scf depending upon the type of contactor. A discussion of contactor types is found in Section 12.4, Design Considerations. Simple impingement devices are placed downstream from the absorber to remove mist entrained in the flue gas.

The effluent hold tank receives the lime or limestone feed slurry and absorber effluent. In addition, settling pond water and clarifier overflow can be sent to the hold tank. The tank is equipped with an agitator for uniform composition. The volume of the hold tank is sized to allow residence time for adequate calcium sulfite and sulfate precipitation. Reaction time outside the scrubber is needed to allow the supersaturation caused by SO_2 sorption in the sorber to dissipate and to permit dissolution of absorbent. Too little residence time in the hold tank can cause nucleation of calcium sulfite and sulfate solids in the scrubber, resulting in scaling.

The feed material for a lime scrubbing process is usually produced by calcining limestone. Feed for a limestone process generally comes directly from the quarry, and is then reduced in size by crushing and grinding. The lime or limestone is mixed with water to make a 25-60 percent solids slurry.

Solids Separation

A continuous stream of slurry of 10-15 percent solids is recycled to the absorber from the effluent hold tank. In addition, a bleed stream is taken off to be dewatered. The dewatering step, which is needed to minimize the area needed for sludge disposal varies depending on the application and type of disposal. The waste sludge contains some unreacted lime or limestone. This depends upon system design (additive stoichiometry). Generally, more excess additive is required in limestone systems than in lime systems.

For systems with on-site pond disposal, solids may be pumped directly from the effluent hold tank to the pond area. Clean overflow liquor from the pond would then be returned to the system. Depending on the physical properties of the solids produced in the system, a thickening device such as a clarifier or centrifuge can be used to increase the solids content to a maximum of about 40 weight percent. Additional dewatering to 60-70 percent solids can sometimes be achieved by vacuum filtration.

Solids Disposal

Sludge disposal is one of the main disadvantages of lime/limestone FGD systems in comparison to recovery processes. The quantity of sludge produced is large in both weight and volume, and requires a large waste pond or landfill area for disposal.

On-site disposal is usually performed by sending the waste solids to a large pond. Settling of the solids occurs and pond water is recycled back to the process hold tank for re-use. "Stabilization" methods are currently under development to convert the sludge to structurally-stable, leach-resistant, landfill material. These methods could be used when on-site disposal is not possible. The stabilized material can then be trucked to an off-site area for landfill.

At least four companies are developing sludge fixation processes. A fixation process is currently employed to dispose of the sludge generated by a limestone wet scrubbing system installed on a 163 Mw unit at Commonwealth Edison's Will County Station. The annual cost for sludge fixation is likely to be about $2.00 to $2.50 per ton of 3.5 percent sulfur coal burned. This is equivalent to $2-$2.5 million dollars for the base case conditions.

12.2 Environmental Considerations

The ability of lime/limestone scrubbing systems to remove over 90 percent of the flue gas SO_2 has been successfully demonstrated at full-scale commercial installations. The SO_2 removal efficiency at Louisville Gas and Electric Company's Paddy's Run No. 6 is normally greater than 90 percent when burning coal containing 3.7 percent sulfur. The unit uses carbide sludge lime to remove SO_2.

The removal of NO_x species in the scrubbing system was believed to be up to 10-20 percent in early stages of lime/limestone process development. According to Radian pilot plant experience, NO_x removal was found to be negligible and the build-up of nitrites and nitrates in the system was not a problem.

High particulate removal has been obtained without major operational problems. Wet scrubbing of flue gas can obtain an outlet grain loading of 0.038 gr/scf (99 percent removal) at liquid-to-gas ratios of 7-35 gal/1000 scf. Many system designers feel that greater system reliability can be obtained by removing particulates ahead of the SO_2 scrubber. When particulates are removed with the SO_2 the dust increases the solids load in the scrubber system, and may increase sulfite oxidation.

Removal of SO_2 is a function of scrubber design and operating conditions. Scrubbers, such as marble bed and TCA contactors, give high contact area per cubic foot of volume and yield higher removal efficiencies for a given liquid flow rate. Operating conditions which affect SO_2 removal are the L/G (liquid to gas ratio), gas velocity, liquid and gas distribution in the scrubber, liquor pH, and scrubbing slurry composition. Higher alkalinity in the liquor gives a greater driving force for mass transfer of SO_2 to the liquid.

The major drawback to lime/limestone wet scrubbing is the waste stream which is produced. The waste stream consists of the calcium solids bled off after reaction in the effluent hold tank. The stream is usually drawn off the process hold tank and dewatered before final disposal. For a 500 Mw station burning 3.5 percent sulfur coal (Radian's base case conditions), a limestone scrubbing system would produce a waste stream of about 61 tons/hr after concentration to 50 wt. percent solids. This disposal rate assumes a system design based upon a 79 percent limestone utilization. For a 5260 hr/yr load factor, the waste stream would be 320,336 tons/year. The waste stream from a lime system under the same conditions (50 wt. percent solids) would be produced at a rate of 54 tons/hr. This disposal rate assumes a lime utilization of 86 percent. For a plant operating at a 5260 hr/yr load factor, 283,496 tons per year of waste could be produced. These waste streams consist of $CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$, unreacted CaO, $Ca(OH)_2$, $CaCO_3$, inerts, and fly ash. It is usually disposed of in waste ponds or used as landfill after adequate dewatering.

12.3 Material and Energy Balances

Heat and material balance calculations were performed by TVA for a limestone system using a base case similar to the one defined for this study. These calculations were compared with Radian's as a check for consistency and reproducibility. The system consisted of a mobile bed SO_2 absorber for lime and limestone scrubbing. The L/G ratio was about 83 gal/1000 scf for both systems.

The lime and limestone scrubbing systems are characterized by large raw material requirements. Since it is a throwaway process, no reducing gas is needed. The pumping energy to move the lime or limestone slurry through the process equipment is the major energy requirement on the liquid side. Steam for stack gas reheat and electric power for flue gas booster blowers are the major energy requirements on the gas side. The energy required to produce lime by calcining limestone, from 4-10 MM Btu/ton CaO, has not been included in the material and energy balance calculations. It has been assumed for this study that lime can be purchased in a form suitable for SO_2 absorption. The system raw material and energy requirements are shown in Tables 12-1 and 12-2.

TABLE 12-1

RAW MATERIAL AND ENERGY CONSUMPTION FOR LIMESTONE SCRUBBING

Basis: 500 Mw, 3.5 Percent Sulfur Coal, 5,260 hr/yr

Process Area	Limestone tons/hr	Steam MM Btu/hr	Water M gal/hr	Electricity Mw
SO_2 Absorption	25	77	25	10.1
Solids Separation	-	-	-	0.1
Solids Disposal	-	-	11	0.1
TOTAL	25	77	36	10.3

TABLE 12-2

RAW MATERIAL AND ENERGY CONSUMPTION FOR LIME SCRUBBING

Basis: 500 Mw, 3.5 Percent Sulfur Coal, 5,260 hr/yr

Process Area	Lime tons/hr	Steam MM Btu/hr	Water M gal/hr	Electricity kw
SO_2 Absorption	11.6	77	25	9.5
Solids Separation	-	-	-	0.1
Solids Disposal	-	-	10	0.1
TOTAL	11.6	77	35	9.7

The pumping of the lime or limestone slurry through the mobile bed absorber system accounts for 3.2 Mw of the electric power requirement. The fan power requirement that is needed to overcome the total FGD system pressure drop is 6.2 Mw. Scrubbers with an open configuration are characterized by higher liquid flow rates and lower gas-side pressure drops. Generally, the sum of the liquid-side energy requirement for pumping and the gas-side energy requirement for the flue gas blowers tends to remain fairly constant for most systems. For example, consider the power requirements for a system using a spray tower versus a system using a mobile bed absorber. Table 12-3 shows the operating parameters and total power requirements for each system. The total power requirement for both systems is about the same.

The large quantity of calcium oxide or calcium carbonate required for scrubbing the SO_2 and the large volume of sludge produced for subsequent disposal are the major considerations for the process. The limestone requirement is generally 5-20 percent higher because it is less reactive than lime in the scrubbing system. Lime systems generally operate at higher utilizations (moles reacted/moles fed) and less reactant is lost in the waste sludge effluent. Typical compositions and quantities of waste sludge produced for lime/limestone systems under the base case assumption are shown in Table 12-4. As can be seen, the unreacted species represent 11 percent of the lime sludge and 15 percent of the limestone sludge. It should be noted that limestone systems can be designed for higher utilizations. In these cases, the waste product would be similar to that shown for lime systems in Table 12-4. However, this decreased waste product rate would be accomplished at the expense of increased processing, such as limestone grinding, in the FGD system. Pumping requirements for transporting the waste sludge

TABLE 12-3

ENERGY REQUIREMENTS FOR A SPRAY TOWER AND MOBILE BED ABSORBER

Bais: 500 Mw, 3.5 Weight Percent
Sulfur Coal

	Spray Tower	Mobile Bed Absorber
L/G (gal/1000 scf)	105	83
ΔP Across Scrubber (in H_2O)	2	10
Total Scrubber System ΔP (in H_2O)	18	26
G (SCFM)	1,160,000	1,160,000
L (GPM)	121,800	96,280
Power for Pumping Liquid (Mw)	4.8	3.2
Fan Power Requirement for Total System (Mw)	4.3	6.2
Total Power Requirement (Mw)	9.1	9.4

TABLE 12-4

TYPICAL COMPOSITIONS AND QUANTITIES OF WASTE PRODUCT FROM LIME/LIMESTONE FGD SYSTEMS

Lime Waste (dry)	Weight Percent	Production (tons/yr)	Assumed Packing Volume (ft^3/ton of waste)	Approximate Volume Required For Storage in 30 Years (acre-feet)
$CaSO_3 \cdot \frac{1}{2}H_2O$	60	85,741		
$CaSO_4 \cdot 2H_2O$	27	38,099		
$CaCO_3$	11	14,857		
Inerts	2	3,051		
TOTAL	100	141,748	22	2,148
Lime Waste Sludge (wet, 50% solids)		283,496	45	4,393
Limestone Waste (dry)				
$CaSO_3 \cdot \frac{1}{2}H_2O$	53	85,741		
$CaSO_4 \cdot 2H_2O$	24	38,099		
$CaSO_3$	15	23,835		
Inerts	8	12,493		
TOTAL	100	160,168	22	2,427
Limestone Waste Sludge (wet, 50% solids)		320,336	45	4,964

Assumptions:
Coal: 3.5% S
Plant: 500 Mw, 5,260 hr/yr, 375,000 lb/hr coal
Scrubber: 90% SO_2 removal
86% utilization of CaO
79% utilization of $CaCO_3$

from the scrubber area to the disposal area are generally low since very little increase in elevation over the pumping distance would probably be encountered and the pumping distance is relatively short.

12.4 Design Considerations

The flow rate and sulfur content of the flue gas are the major parameters to be considered in the lime or limestone scrubbing system design. The quantities of lime or limestone consumed and waste solids produced are roughly proportional to the amount of sulfur in the gas. The tendency for scale formation in the system is also directly related to the amount of SO_2 removed from the gas. Since all of the SO_2 removed must precipitate from solution before leaving the system, increased crystal seed must be provided in proportion to the amount of SO_2 removed. The scrubber liquid to gas ratio would have to be increased for removal of high SO_2 concentrations and to avoid exceeding the scaling limits in the scrubber effluent liquor.

Gas-Liquid Contactors

The different types of gas-liquid contactors can be separated into two categories; those having an open configuration and those having a closed (packed) configuration. These gas-liquid contactors differ in their gas velocity, L/G ratio, gas-side pressure drop, and resistance to plugging. These characteristics will be discussed in detail for the different scrubber types.

Depending on the scrubber type, SO_2 removal efficiency may be increased by:

1) increasing the number of scrubber stages,
2) increasing the contacting area per stage (usually increases gas-side pressure drop),
3) increasing scrubber liquid to gas ratio, and
4) increasing lime or limestone utilization.

Some of these design measures not only affect SO_2 removal but also affect the scaling tendency of the system.

The most frequently used contactors for SO_2 removal are:

- venturi scrubbers,
- spray towers (horizontal and vertical),
- grid towers, and
- mobile bed absorbers (marble bed, TCA packed column).

The performance characteristics of each of these types of scrubbers are listed in Table 12-5.

Any of these scrubbers could be applied for both gas absorption and particulate removal, however packed columns show a much greater tendency for solids plugging. Resistance to plugging is an important parameter in scrubber selection. The open configurations of the grid tower and the spray tower give a lower gas-side pressure drop and make them less susceptible to plugging when compared to the closed configuration of the marble bed and TCA scrubbers.

TABLE 12-5

COMPARISON OF SCRUBBER TYPES FOR A LIMESTONE WET SCRUBBING SYSTEM

	Scrubber Type				
Parameter	Marble Bed	TCA	Venturi	Grid Tower	Spray Tower
SO_2 Removal Efficiency	Good	Good	Fair	Good	Good
Particulate Removal Efficiency	Good	Good	Excellent	Good	Fair
Typical L/G (gal/1000 scf) for SO_2 Removal	40-70	50-85	20-50	50-100	70-110
Gas Side Pressure Drop (in H_2O) for L/G Above	8-12	6-12	8-20	1-7	1-3
Gas Velocity (ft/sec)	3-8	6-11	125-300	6-11	5-25
Dissolution of Solids	Good	Fair	Poor	Fair	Poor
Resistance to Solids Plugging	Fair	Good	Excellent	Fair	Excellent

The volume of flue gas to be treated normally determines the physical size of the scrubbing device. The minimum and maximum velocities selected vary widely among the scrubber types but generally fall in a range of 5-25 ft/sec. The highest gas velocities occur when using a venturi due to the small diameter of the venturi throat. The high gas velocity in the venturi must, however, be reduced for mist eliminator considerations. Because of equipment limitations, several scrubber modules are necessary to treat the total flue gas flow from a 500 Mw power plant.

The amount of slurry circulated is critical. If the liquid to gas ratio is too low, the slurry will absorb too much SO_2 per volume and critical supersaturation will occur. Crystallization will then take place in the scrubber rather than in the reaction tank. The minimum L/G generally ranges between 35 and 110 gal/1000 scf, depending on inlet SO_2 concentration, type of scrubber, and lime or limestone reactivity. The lowest L/G's are used for venturi scrubbers and mobile bed absorbers such as marble beds. High L/G's are common in spray columns while TCA's generally use mid-range values. In general, L/G ratios are higher for limestone systems than they are for lime systems due to limestone's lower reactivity.

In some applications, especially in retrofit situations, it is desirable to design a system with a low gas-side pressure drop to reduce the capital and operating cost for additional fans. Pressure drop through the scrubbers is a function of gas velocity, liquid to gas ratio, and scrubber design and size.

Both calcium sulfite and calcium sulfate form scales. Calcium sulfate can form supersaturated solutions in the system. The rate of scaling is sensitive to the supersaturation of calcium sulfate. Test results from the TVA Shawnee test facility have shown that scrubber internals can be kept relatively free of scale if the sulfate (gypsum) saturation of the scrubber liquor is kept below about 135 percent (at 50 °C). If supersaturation is unchecked, calcium sulfate dihydrate starts to crystallize on solid surfaces, forming a scale. The supersaturation can be controlled by seeding the liquid with calcium sulfate dihydrate crystals, which provide a large surface area on which the dissolved salts preferentially deposit.

Evidence has also been encountered that coprecipitation of calcium sulfite and sulfate may occur. This phenomenon may enable operation of the process in a mode where calcium sulfate concentration will not reach its normal saturation level and thus will not form sulfate scale. Operation in this mode seems to depend on the level of oxidation occurring in the system.

Changes in liquor pH can also cause scaling. The solubility of calcium sulfite decreases with increasing pH. If the pH is allowed to fall below 5, comparatively soluble calcium bisulfite is formed. With a subsequent increase in pH value, the bisulfite is converted to calcium sulfite which, being less soluble, crystallizes out and forms scale.

The pH of a fresh prepared limestone slurry is usually between 8 and 9. On contact with the SO_2 in the flue gas, the pH rapidly falls below 7, but below pH 6 the decrease in pH is slow until the slurry is exhausted. The efficiency of SO_2 removal is not appreciably affected until the pH drops below about 5.2. The effect appears to be independent of the type of limestone. Limestone scrubbers usually operate with an inlet and outlet pH range between 5.2-6.4. The scrubber pH can be changed by varying the limestone feed.

For a scale-free scrubbing system the following factors should be considered.

1) The pH should not fall below 5 in a one-stage scrubbing system.
2) A sufficient quantity of seed crystal of calcium sulfate and sulfite should recirculate in the slurry.
3) After the addition of fresh limestone, sufficient residence time in the hold tank should be allowed for crystalization to occur. This will help to ensure that the liquid entering the scrubber is not supersaturated with calcium sulfate.
4) The liquid-to-gas ratio should be adjusted so that calcium sulfur salts do not form highly supersaturated solutions.

Mist eliminator operation is a major trouble spot in lime/limestone scrubbing. All wet scrubbers introduce mist droplets into the gas, some more than others. The mist must be collected and separated to prevent corrosion and solid deposits on downstream equipment and to avoid high energy consumption in evaporating the mist in the gas reheater. Since the drops are relatively large, usually 40 microns and larger, they can be removed effectively by simple impingement devices, such as zig-zag baffles (chevrons) or cyclonic demisters. Practically all designers have used chevrons with the major exception being Detroit Edison, where a cyclonic vane-type eliminator was installed.

Chevrons have had trouble with both inefficient mist removal and with plugging by soft deposits and scale. Almost complete mist elimination by chevrons has been achieved by mounting them in a slanted or vertical position instead of the usual horizontal position, so that the liquor can drain off. This prevents re-entrainment of the liquor in the gas. Plugging and scaling of mist eliminators can be prevented by washing with fresh water. Intermittent washing with a high pressure soot-blower type spray has been more successful than a lower pressure continuous wash. Wash trays and wet electrostatic precipitators have also been used as part of the mist elimination system. A wash tray is placed under a horizontal chevron to remove solids in the entrained mist and to collect wash liquor flowing off the chevron. Wet electrostatic precipitators remove both mist and residual dust in the flue gas.

Sludge Dewatering

The sludge dewatering process step is used to concentrate the solids for ease of handling and disposal, and to lower transportation costs. The clear liquor is usually recycled back to the process for re-use. Methods available for dewatering sludges from nonregenerable FGD systems are summarized in Table 12-6. They consist of clarification, bed drying, centrifugation, vacuum filtration, and thermal drying. In addition to these methods, interim ponding is sometimes used as a dewatering procedure. The settling characteristics of the sludge determine the effectiveness of this technique.

Clarifiers are presently used in SO_2 removal systems as a primary dewatering device when the solids content of the sludge is low. Limestone scrubber sludges containing unreacted

TABLE 12-6

SUMMARY OF SLUDGE DEWATERING TECHNIQUES

Source: RA-200

METHOD	APPLICATION	SLUDGE	RESULTS	COMMENTS
Clarification	Currently used as primary dewatering device on full-scale systems.	Various lime and limestone scrubbing system sludges.	Limestone sludges thicken "better" than lime because of coarse unreacted additive present.	
	Bench-scale column	Limestone system sludge.	∿20% solids achieved	
Bed Drying	Bench-scale column studies.	Shawnee Limestone system sludge.	Steady state drainage rate was 0.046 cm^3/min. Sludge with "relatively" high sulfate content settled to 50% solids with underdrainage. High sulfite sludges settled only to 35% solids under similar conditions.	Air-dried sludge exposed to water regained original moisture (51.7%).
	Demonstration program, Hollywood, Penn.	Acid mine drainage (AMD) neutralization sludge.	Results not available at time of report.	
Centrifugation	Bench-scale tests.	Various lime-scrubbing system sludges	47-57% final solids content (original: 19-44%).	Fly ash was present in the samples.
	Bench-scale tests (short-term).	Limestone scrubbing system sludge	53-64% solids achieved (feed was 10-29% solids).	
	Full-scale	Chiyoda process sludge (high sulfate/sulfite ratio).	85-90% solids achieved.	

TABLE 12-6 - SUMMARY OF SLUDGE DEWATERING TECHNIQUES (Cont.d)

METHOD	APPLICATION	SLUDGE	RESULTS	COMMENTS
Centrifugation (Cont.d)	Comparative laboratory-scale.	Various limestone system sludges	Shawnee sludge: solids content increased from 20 to 56%. Western plant's sludge: >65% solids achieved.	Although original water content of sludges were similar, better results obtained with Western plant sludge were believed to be due to its lower water content at maximum density.
Vacuum Filtration	Bench-scale	Limestone Scrubbing system sludges.	∿65% solids achieved.	
	Bench-scale	AMD neutralization sludge.	Solids content increased from 0.6 to 23%	Problems with cake blocking filter were experienced.
	Bench-scale	Pilot plant limestone scrubbing system samples.	55-60% solids content was achieved.	Compare to 38% solids with settling alone. Thixotropic nature of sludge caused filter cake to rewater upon release. cake cracking in early stages. prohibited further dewatering. Removal of cake from filter was difficult.
	Pilot-scale; in conjunction with clarification.	Double-alkali system (General Motors).	70% solids achieved.	
	Full-scale; in conjunction with clarification.	Carbide sludge system (Louisville Gas and Electric).	50% solids was achieved.	
Thermal Drying	Commercial for other applications	SO_2/fly ash removal process.	90-05% of original water content (70%) removed; i.e., achievement of 90-95% solids is claimed.	

additive are reported to thicken well compared to lime sludges because of the limestone present. Limestone processes sometimes produce a turbid supernatant liquor.

Because of the physical nature of sulfate crystals as opposed to sulfite, dewatering is improved by a higher sulfate/ sulfite ratio. Therefore, good results (85-90 percent solids) have been reported for a sample obtained from the Chiyoda process, which produces a sludge with an extremely high sulfate to sulfite ratio.

One engineering company currently markets an SO_2/fly ash control process using a sludge dehydration operation after an alkali scrubbing system. Clarifier underflow at 30 percent solids concentration is raised to 90-95 percent solids by passing the slurry through a dehydrator co-current with the hot flue gases (300°F).

Fly Ash and Chlorides

The fly ash content of the flue gas affects the scrubbing system design. When little or no upstream particulate removal is used, the fly ash content of the scrubbing slurry will be a significant portion of the total solids. For the base case system at 99.5 percent particulate removal, about 17 tons/hr of fly ash would be removed. This is equivalent in weight to about 28 percent of the total calcium solids (at 50 weight percent water) that are sent to disposal for a limestone system.

Since the maximum slurry solids content that can be conveniently handled in a typical system is fixed at about

15 weight percent, fly ash replaces a portion of the solids that would otherwise consist of sulfite and sulfate seed crystals. For a given system, longer residence time in the hold tanks would thus be required to prevent scaling.

Systems with high fly ash contents have experienced more severe erosion than those with more efficient upstream particulate removal. The dust also increases the solids load in the scrubber system, and thus can aggravate sticking of solids to scrubber surfaces and increase sulfite oxidation.

Chlorine is contained in the coal and is present in the flue gas as chlorides. Chlorides enter the SO_2 scrubbing operation unless a pre-scrubber for particulate removal is used, and always present a potential problem with corrosion and system chemistry. Chlorides have not been a real problem with lime/limestone wet scrubbing because it is a throwaway process. The large waste stream of calcium solids remove a sufficient amount of chlorides from the system to prevent buildup to any significant level.

12.5 Status of Development

Lime/limestone scrubbing was first used to control SO_2 emissions on commercial boiler pilot plants in England about 40 years ago. This led to full-scale gas washing plants which proved successful in removing SO_2 and dust from stack gas. The lime/limestone process was also the first SO_2 stack-gas scrubbing technology used in this country, mainly due to the fact that there was more experience behind the process and no product had to be marketed. The trend to using lime/limestone scrubbing for SO_2 removal is strong today due to rapid progress in coping with the many process problems and a clearer economic position.

At the present time about 25,000 Mw in the U.S. have been committed to lime/limestone scrubbing. The operating and planned lime/limestone scrubbing units on U.S. power plants are shown in Tables 12-7, 12-8, and 12-9.

Operating problems that have been commonly encountered in the scrubbing process can be summarized into the following areas:

- scrubber and pipe plugging,
- chemical scaling,
- corrosion and erosion,
- demister/reheater operating problems, and
- solids disposal.

Most of the problems in these areas are a result of basic process and mechanical design deficiencies common to the early versions of lime/limestone scrubbing processes.

In general, plugging problems in the slurry handling system have been avoided by proper equipment design. Plugging problems in the scrubber area have been solved by using scrubber types with uncomplicated internals. To avoid plugging in process piping, slurry velocities must be sufficient to keep solids from settling out. Also pipe bends,

TABLE 12-7

SUMMARY OF OPERATIONAL LIME/LIMESTONE FGD SYSTEMS AS OF OCTOBER 1975

Utility Company Power Station	New Or Retrofit	Size of FGD Unit (Mw)	Process/Vendor	Fuel Characteristics	Start-up Date Mo/Yr
Arizona Public Service Cholla No. 1	R	115	Research Cottrell Limestone Scrubbing	Coal 0.44-1 percent sulfur	10/73
Commonwealth Edison Will County No. 1	R	167	Babcock & Wilcox Limestone Scrubbing	Coal 9463 Btu. 2.1% sulfur	2/72
Dairyland Power Coop. Alma Station	R	80	Foster Wheeler Lime Injection	Coal 3.0-3.5 percent sulfur	6/71
Duquesne Light Elrama	R	510	Chemico Lime Scrubbing	Coal 1.0-2.8 percent sulfur	10/75
Duquesne Light Phillips	R	410	Chemico Lime Scrubbing	Coal 1.0-2.8 percent sulfur	7/73
Kansas City Power & Light Hawthorn No. 3	R	140	Combustion Engineering Limestone Injection & Wet Scrub	Coal 0.6-3.0 percent sulfur	11/72
Kansas City Power & Light La Cygne No. 1	N	820	Babcock & Wilcox Limestone Scrubbing	Coal 5.2 percent sulfur	2/73
Kansas City Power & Light Hawthorn No. 4	R	100	Combustion Engineering Limestone Injection & Wet Scrub	Coal 0.6-3.0 percent sulfur	8/72
Kansas Power & Light Lawrence No. 4	R	125	Combustion Engineering Limestone Injection & Wet Scrub	Coal 3.5 percent sulfur	12/68

TABLE 12-7 - SUMMARY OF OPERATIONAL LIME/LIMESTONE FGD SYSTEMS AS OF OCTOBER 1975 (Cont'd)

Utility Company Power Station	New Or Retrofit	Size of FGD Unit (Mw)	Process/Vendor	Fuel Characteristics	Start-up Date Mo/Yr
Kansas Power & Light Lawrence No. 5	N	400	Combustion Engineering Limestone Injection & Wet Scrub	Coal 0.5 percent sulfur	11/71
Kentucky Utilities Green River Units 1 & 2	R	64	American Air Filter Lime Scrubbing	Coal 3.8 percent sulfur	10/75
Key West Utility Board Stock Island Plant	N	37	Zurn Air Systems Limestone Scrubbing	Oil 2.4 percent sulfur	10/72
Louisville Gas & Electric Paddy's Run No. 6	R	65	Combustion Engineering Lime Scrubbing	Coal 3.5-4.0 percent sulfur	4/73
Montana Power Co. Colstrip No. 1	N	360	Combustion Equip. Associates Lime Scrubbing	Coal 0.8 percent sulfur	10/75
Pennsylvania Power Co. Bruce Mansfield No. 1	N	835	Chemico Lime Scrubbing	Coal 4.3 percent sulfur	10/75
Public Service Co. of Colorado Valmont No. 5	R	50	Universal Oil Products Limestone Scrubbing	Coal 0.72 percent sulfur	1/75
Southern California Edison Mohave No. 1A	R	170	Universal Oil Products Limestone Scrubbing	Coal 0.5-0.8 percent sulfur	11/74
Tennessee Valley Authority Shawnee No. 10	R	30	Tennessee Valley Authority Lime/Limestone Scrubbing	Coal 2.9 percent sulfur	4/72

Source: PE-178

TABLE 12-8

SUMMARY OF LIME/LIMESTONE FGD SYSTEMS UNDER CONSTRUCTION AS OF OCTOBER 1975

Utility Company Power Station	New Or Retrofit	Size of FGD Unit (Mw)	Process/Vendor	Fuel Characteristics	Start-up Date Mo/Yr
Arizona Public Service Four Corners No. 5A	R	160	SCE Lime Scrubbing	Coal 0.7-0.75 sulfur (avg.)	11/75
Central Illinois Light Co. Duck Creek No. 1	N	100	Riley Stoker/Environeering Limestone Scrubbing	Coal 2.5-3.0 percent sulfur	4/76
Columbus & Southern Ohio Elec. Conesville No. 5	N	400	Universal Oil Products Lime Scrubbing	Coal 4.5-4.9 percent sulfur	6/76
Detroit Edison St. Clair No. 6	R	180	Peabody Engineering Limestone Scrubbing	Coal 3.7 percent sulfur	11/75
Indianapolis Power & Light Co. Petersburg No. 3	N	530	Universal Oil Products Limestone Scrubbing	Coal 3.0-3.5 percent sulfur	4/77
Louisville Gas & Electric Cane Run No. 4	R	178	American Air Filter Lime Scrubbing	Coal 3.5-4.05 percent sulfur	6/76
Louisville Gas & Electric Cane Run No. 5	R	183	Combustion Engineering Lime Scrubbing	Coal 3.5-4.05 percent sulfur	11/76
Louisville Gas & Electric Mill Creek No. 3	N	425	American Air Filter Lime Scrubbing	Coal 3.5-4.0 percent sulfur	6/77
Minnkota Power Cooperative Milton R. Young No. 2	N	450	Combustion Equip. Associates Lime Scrubbing	Lignite 6.500 Btu 0.7% S	0/77
Montana Power Co. Colstrip No. 2	N	360	Combustion Equip. Associates Lime Scrubbing	Coal 0.8 percent sulfur	7/76
Northern States Power Co. Sherburne No. 1	N	680	Combustion Engineering Limestone Scrubbing	Coal 0.8 percent sulfur	5/76
Northern States Power Co. Sherburne No. 2	N	680	Combustion Engineering Limestone Scrubbing	Coal 0.8 percent sulfur	5/77
Pennsylvania Power Co. Bruce Mansfield No. 2	N	835	Chemico Lime Scrubbing	Coal 4.3 percent sulfur	4/77

TABLE 12-8 - SUMMARY OF LIME/LIMESTONE FGD SYSTEMS UNDER CONSTRUCTION AS OF OCTOBER 1975 (Cont'd)

Utility Company Power Station	New Or Retrofit	Size of FGD Unit (Mw)	Process/Vendor	Fuel Characteristics	Start-up Date Mo/Yr
Rickenbacker AFB Rickenbacker	R	20	Research Cottrell Lime Scrubbing	Coal 5.0 percent sulfur	2/76
Springfield City Utilities Southwest No. 1	N	200	Universal Oil Products Limestone Scrubbing	Coal 3.5 percent sulfur	6/76
Tennessee Valley Authority Widows Creek No. 8	R	550	Tennessee Valley Authority Limestone Scrubbing	Coal 3.7 percent sulfur	2/77

Source: PE-178

TABLE 12-9

SUMMARY OF LIME/LIMESTONE PLANNED FGD SYSTEMS AS OF OCTOBER 1975

Utility Company Power Station	New Or Retrofit	Size of FGD Unit (Mw)	Process/Vendor	Fuel Characteristics	Start-up Date Mo/Yr
Columbus & Southern Ohio Elec. Conesville No. 6	N	400	Universal Oil Products Lime Scrubbing	Coal 4.5-4.9 percent sulfur	1/78
Arizona Public Service Cholla No. 2	N	250	Research Cottrell Limestone Scrubbing	Coal 0.44-1 percent sulfur	6/77
Alabama Electric Coop. Tombigbee No. 2	N	225	Peabody Engineering Limestone Scrubbing	Coal 0.8-1.5 percent sulfur	3/78
Alabama Electric Coop. Tombigbee No. 3	N	225	Peabody Engineering Limestone Scrubbing	Coal 0.8-1.5 percent sulfur	3/79
Texas Utilities Co. Martin Lake No. 1	N	793	Research Cottrell Limestone Scrubbing	Coal 1.0 percent sulfur	9/76
S. Mississippi Elec. Pwr. Assoc. R. D. Morrow No. 2	N	180	Riley Stoker/Environeering Limestone Scrubbing	Coal 1 percent sulfur	6/78
S. Mississippi Elec. Pwr. Assoc. R. D. Morrow No. 1	N	180	Riley Stoker/Environeering Limestone Scrubbing	Coal 1 percent sulfur	11/77
Texas Utilities Co. Martin Lake No. 2	N	793	Research Cottrell Limestone Scrubbing	Coal 1.0 percent sulfur	6/77
LETTER OF INTENT SIGNED					
Arizona Electric Power Coop. Apache No. 2	N	200	Research Cottrell Limestone Scrubbing	Coal 0.5-0.8 percent sulfur	6/79
Arizona Electric Power Coop. Apache No. 3	N	205	Research Cottrell Limestone Scrubbing	Coal 0.5-0.8 percent sulfur	6/79

TABLE 12-9 - SUMMARY OF LIME/LIMESTONE PLANNED FGD SYSTEMS AS OF OCTOBER 1975 (Cont'd)

Utility Company Power Station	New Or Retrofit	Size of FGD Unit (Mw)	Process/Vendor	Fuel Characteristics	Start-up Date Mo/Yr
Utah Power & Light Co. Huntington No. 1	N	415	Chemico Lime Scrubbing	Coal 0.5 percent sulfur	6/77
S. Carolina Pub. Serv. Authority Winyah No. 2	N	140	Babcock & Wilcox Limestone Scrubbing	Coal 1.0 percent sulfur	5/77
REQUESTING/EVALUATING BIDS					
Kansas Power & Light Jeffery No. 2	N	700	Combustion Engineering Limestone Scrubbing	Coal	6/79
Kansas Power & Light Jeffery No. 1	N	700	Combustion Engineering Limestone Scrubbing	Coal	6/78
Cincinnati Gas & Electric Co. Miami Fort No. 8	N	300	Not Selected Lime/Limestone Scrubbing	Coal 1.3 percent sulfur	1/78
Louisville Gas & Electric Cane Run No. 6	R	277	Not Selected Lime Scrubbing	Coal 3.5-4.0 percent sulfur	6/77
CONSIDERING FGD SYSTEM					
Louisville Gas & Electric Cane Run No. 1	R	110	Not Selected Lime Scrubbing	Coal 3.5-4.0 percent sulfur	6/80
Louisville Gas & Electric Cane Run No. 2	R	107	Not Selected Lime Scrubbing	Coal 3.5-4.0 percent sulfur	6/80
Louisville Gas & Electric Cane Run No. 3	R	137	Not Selected Lime Scrubbing	Coal 3.5-4.0 percent sulfur	6/80
Louisville Gas & Electric Mill Creek No. 1	R	330	Not Selected Lime Scrubbing	Coal 3.5-4.0 percent sulfur	6/81
Louisville Gas & Electric Mill Creek No. 4	N	425	Not Selected Lime Scrubbing	Coal 3.5-4.0 percent sulfur	6/79
Louisville Gas & Electric Mill Creek No. 2	R	330	Not Selected Lime Scrubbing	Coal 3.5-4.0 percent sulfur	6/82

TABLE 12-9 - SUMMARY OF PLANNED LIME/LIMESTONE FGD SYSTEMS AS OF OCTOBER 1975 (Cont'd)

Utility Company Power Station	New Or Retrofit	Size of FGD Unit (Mw)	Process/Vendor	Fuel Characteristics	Start-up Date Mo/Yr
Central Illinois Light Co. Duck Creek No. 2	N	400	Not Selected Limestone Scrubbing	Coal 2.5-3.0 percent sulfur	1/81
Southern California Edison Kaiparowits No. 2	N	750	Not Selected Lime Scrubbing	Coal 10,800 Btu 0.5% S	0/82
Southern California Edison Kaiparowits No. 4	N	750	Not Selected Lime Scrubbing	Coal 10,800 Btu 0.5% S	0/84
Southern California Edison Mohave No. 2	R	790	Not Selected Lime/Limestone Scrubbing	Coal 0.5 to 0.8% sulfur	6/77
Southern California Edison Kaiparowits No. 1	N	750	Not Selected Lime Scrubbing	Coal 10,800 Btu 0.5% S	0/81
Southern California Edison Kaiparowits No. 3	N	750	Not Selected Lime Scrubbing	Coal 10,800 Btu 0.5% S	0/83
Southern California Edison Mohave No. 18	R	620	Not Selected Lime/Limestone Scrubbing	Coal 0.5-0.8 percent sulfur	6/77
Salt River Project Navajo No. 1	R	750	Not Selected Lime/Limestone Scrubbing	Coal 0.45 percent sulfur	11/77
Salt River Project Navajo No. 3	R	750	Not Selected Lime/Limestone Scrubbing	Coal 0.45 percent sulfur	11/77
Salt River Project Navajo No. 2	R	750	Not Selected Lime/Limestone Scrubbing	Coal 0.45 percent sulfur	11/77

Source: PE-178

valves other than gate valves, and obstacles in the flow path should be avoided. With the exception of mist eliminator problems, plugging is no longer considered a serious obstacle to process reliability.

Much development and design effort has been spent on scale prevention. Scaling was found to be primarily a chemical problem and neither special materials nor periodic in-service washing was found successful in preventing scale. High solids concentration in the circulating slurry (up to 15 percent), increased L/G ratios, and increased delay times in the scrubber hold tank have helped to alleviate scale problems. The Chemico unit at Mitsui Aluminum Company in Japan and the Combustion Engineering unit at Louisville Gas and Electric's Paddy's Run Station have both demonstrated scale-free service during continuous operation.

Surfaces in the wet scrubbing system that come in contact with wet SO_2 gas or acid scrubber liquor should be constructed of acid resistant materials to minimize corrosion. Materials now being used for scrubber shells and internals are usually stainless steel or lined carbon steels. Glass flake epoxy type materials are also used to line the scrubber shell.

Surfaces that come in contact with slurry solids should be constructed of abrasion-resistant materials to minimize erosion. Experience with equipment erosion in lime/limestone scrubbing systems is not as well defined as is corrosion experience. One of the disadvantages of using high solids concentration to avoid scaling is the abrasive effect of the solids on spray nozzles, pumps, and piping. The trend for spray nozzle use is to ceramic (SIC). Soft rubber or neoprene lined carbon steel can be effective for pump and piping material under abrasive conditions up to 175°F in temperature. Erosion also occurs of the glass marbles and plastic spheres in marble beds and TCA scrubbers. Significant weight loss has been observed in both the spheres and marbles. Some of the plastic spheres at the TVA pilot plant installation at the Colbert Station have lost mechanical strength resulting in wall collapse.

Three of the previously mentioned design and operating problems - plugging, scaling, and corrosion - have often occurred in connection with demister maintenance by lowering the amount of slurry carryover from the scrubber. Increased distance between the scrubber and demister is also desirable. Placing the demister in a horizontal or sloped position so that wash water can effectively drain from the area also contributes to improve system reliability.

Reheat is a design problem that is unique to each installation. In the cases where heat exchangers are placed in the duct, any material passing through the demister may plug, scale, or corrode the reheater surfaces. Efficient mist removal in the demister and the proper choice of materials will help to control the problem. Direct fired reheat using a clean fuel has suffered from poor combustion but improved design has made the reheat system operable.

Disposal of solid wastes generated by lime/limestone wet scrubbing processes has received increased attention as the problems more critical to system reliability are solved. Sludge can be handled and disposed of without undue environmental effects. Waste sludge is currently being stored in waste ponds or stabilized and used as a landfill material. The large land requirement reasonably close to the point of waste sludge generation is a problem for some existing power plants.

12.6 Scale-up Problems

Lime/limestone wet scrubbing has been successfully demonstrated on a full-scale system to be a reliable FGD process for the utility industry. The system components have been fully integrated and successfully operated. Design data exist for all process areas. Disposal of the waste sludge from the process is the major area where technology is still being developed. Methods of waste disposal are discussed in Section 12.4 - Design Considerations. Further work should be done to develop more economical methods of stabilizing the waste sludge for landfill material.

12.7 Utility Applicability

The limiting factor of applying lime/limestone wet scrubbing to a new power plant is the land requirement for sludge disposal. For the base case chosen there is a land requirement of 120 acres for limestone sludge disposal over a 30 year period if the sludge is deposited in ponds 40 feet deep. Power plants built in highly industrialized areas such as on the east coast might be required to pay high costs for the necessary land around the plant or high transportation costs for off-site disposal. This is also a major limiting factor for retrofit applications.

Another major concern for retrofitting the SO_2 removal system onto existing plants is the space required for the scrubbing section of the process. Process equipment outside of the scrubber area is of less concern to the retrofit problem since it can be located on the peripheral areas of the plant. The total ground space requirements for the scrubbing section of a 500 Mw lime/limestone unit with four scrubbers and four hold tanks is 22,500 square feet. The area of the scrubbing section can be reduced by placing the hold tanks at some peripheral area instead of between the powerhouse and the stack. The total area required for the scrubbing would then be about 12,000 square feet.

Limestone is a readily available material as is reflected by its low price of approximately $4/ton. Production of limestone in the United States was approximately 630 million tons in 1970. It is mined in many areas of the U.S. so that close proximity to many power plants is possible.

Lime is produced by calcining high calcium limestone in kilns at about 1800-2300°F to drive off CO_2 and form CaO. The heat of reaction required to convert $CaCO_3$ to CaO is about 2.8 MM Btu/ton of CaO. In practice, heat input may vary from 4 to 10 MM Btu/ton of lime. Total lime consumption by the United States in 1971 (including limes processed within captive facilities) was 19.63 million tons. Over 80 percent of the lime used in the United States is by the chemical and related industries, mostly as quicklime. Since limestone is used to make lime and is readily available, lime also can be obtained fairly easily. The cost of lime is presently about $22/ton. There are no fuel requirements for producing a reducing gas since the process is of the nonregenerable "throwaway type."

12.8 Economic Assessment

Full scale lime/limestone scrubbing systems have already been installed on utility boilers so that operating costs calculated for the base case chosen should be fairly accurate. The annual operating costs for lime and limestone systems are shown in Tables 12-10 and 12-11. Costs are reported for both on-site and off-site solid waste disposal.

The lime or limestone requirement is one of the single largest cost items for both scrubbing systems. The cost for limestone is 26 percent of the operating cost while lime makes up 48 percent of the operating cost. The higher cost for lime causes the scrubbing operating cost to be higher when it is used as the SO_2 absorbent. The lime utilization was taken to be 86 percent and the limestone utilization to be 79 percent. Higher values for limestone utilization are possible by grinding the limestone feed, but this would subsequently cause an increase in the limestone processsing cost.

The other large cost items are for liquid pumping and feed preparation, electric fans, and stack gas reheat. Liquid pumping and feed preparation amount to 21 percent of the limestone system operating cost. This energy requirement is somewhat lower for the lime system because the crushing and grinding operation necessary to prepare the raw limestone for feed is not necessary with lime. It is assumed that lime is received in a pebble form which can be slaked without pretreatment. The fan used to overcome the limestone scrubber system pressure drop consumes electric power amounting to 32 percent of the operating cost and represents the largest energy requirement for this system.

TABLE 12-10

LIMESTONE UTILITY AND RAW MATERIAL COSTS

Basis: 500 Mw, 3.5 Percent Sulfur Coal, 5,260 hr/yr

	Quantity	Unit Price	Annual Cost	Percent of Total Cost
On-site Disposal:				
Limestone	131,500 tons	$4/ton	$ 526,000	26
Electric Power:				
1) Flue Gas Fan	6,200 kw	.02/kwhr	652,000	32
2) Liquid Pumping and Feed Preparation	4,100 kw	.02/kwhr	431,000	21
Steam (Flue Gas Reheat)	77 MM Btu/hr	1.00/MM Btu	405,000	20
Process Water	36 M gal/hr	.08/M gal	15,000	1
		TOTAL	$2,029,000	100

Equivalent to 0.8 mills/kwhr

	Annual Cost
Off-site Disposal:	
Reduce Process Water by 4M/gal/hr	$ -2,000
Increase Electric Power by 26 kw	+3,000
Trucking and Off-site Disposal of Calcium Solids @$4/ton 320,336 tons	+1,281,000
	$1,282,000
Total Cost of Scrubbing with Off-Site Disposal	$3,311,000

Equivalent to 1.3 mills/kwhr

TABLE 12-11

LIME UTILITY AND RAW MATERIAL COSTS

Basis: 500 Mw, 3.5 Weight Percent Sulfur Coal, 5,260 hr/yr

	Quantity	Unit Price	Annual Cost	Percent of Total Cost
On-Site Disposal:				
Lime	61,000 tons	$22/ton	$1,342,000	48
Electric Power:				
1) Flue Gas Fan	6,200 kw	.02/kwhr	652,000	23
2) Liquid Pumping and Feed Preparation	3,500 kw	.02/kwhr	368,000	13
Steam (Flue Gas Reheat)	77 MM Btu/hr	1.00/MM Btu	405,000	15
Process Water	35 M gal/hr	.08/M gal	15,000	1
		TOTAL	$2,782,000	

Equivalent to 1.1 mills/kwhr

	Annual Cost
Off-site Disposal:	
Reduce Process Water by 3.0 M gal/hr	$ -1,000
Increase Electric Power by 67 kw	+7,000
Trucking and Off-site Disposal of Calcium Solids @$4/ton 283,496 tons	1,134,000
	$1,140,000
Total Cost of Scrubbing with Off-site Disposal	$3,922,000

Equivalent to 1.5 mills/kwhr

The fan and liquid pumping power requirement was calculated for a mobile bed absorber, using the case illustrated in Table 12-3 in the section on Material and Energy Balances. Steam required for reheating the flue gas represents 20 percent of the total cost for the limestone system. This requirement is essentially a fixed amount for any flue gas wet scrubbing system which saturates the flue gas.

The cost for off-site disposal adds an additional \$1.14-\$1.28 million or 0.4-0.5 mills/kwhr for lime/limestone scrubbing assuming a cost of \$4/ton for trucking and off-site stabilization of the sludge. This cost will vary somewhat depending on the distance between the utility and disposal site, the solids content of the sludge, and the degree of stabilization required.

12.9 Summary

Wet lime/limestone scrubbing is the most widely used process for flue gas desulfurization. The process consists of scrubbing the flue gas with a lime or limestone slurry to remove the SO_2. The resulting calcium sulfite/sulfate sludge is dewatered and disposed of by ponding or landfill. The unique feature of the process is the use of a low-cost SO_2 absorbent which does not require regeneration to make the process economically competitive with other processes. Lime/limestone wet scrubbing has one of the lowest operating costs for FGD processes. Waste disposal is the major problem with the process resulting in large land areas being required to deposit the spent sludge.

13.0 REDUCING GAS PRODUCTION

Several of the FGD systems being evaluated require the use of a hydrogen-rich reducing gas. The following reducing gas production methods have been investigated to determine their development status, quality of product gas, cost of product gas, and utility applicability:

1) Steam-Methane Reforming
2) Steam-Naphtha Reforming
3) Heavy Oil Partial Oxidation
4) Wellman-Galusha Coal Gasification
5) Koppers-Totzek Coal Gasification

Each of these processes is briefly discussed in the following sections.

The amount of reducing gas required for the base case plant was calculated assuming a 90 percent removal of SO_2 in the FGD system. The active reducing agents were taken to be CO and H_2. Many of the FGD systems produce elemental sulfur by reducing an SO_2-rich recovery stream. The theoretical stoichiometry for SO_2 reduction is 2.0 moles of $CO + H_2$ per mole SO_2, i.e.,

$$SO_2 + 2CO \rightarrow 2CO_2 + \tfrac{1}{2}S_2 \qquad (13\text{-}1)$$

$$SO_2 + 2H_2 \rightarrow 2H_2O + \tfrac{1}{2}S_2 \qquad (13\text{-}2)$$

Other FGD processes recover the SO_2 as H_2SO_4, which theoretically requires 3 moles of CO + H_2 per mole SO_2, i.e.,

$$H_2SO_4 + 3CO \rightarrow 3CO_2 + \tfrac{1}{2}S_2 \qquad (13\text{-}3)$$

$$H_2SO_4 + 3H_2 \rightarrow 2H_2O + \tfrac{1}{2}S_2 \qquad (13\text{-}4)$$

The Shell/UOP process produces $CuSO_4$, which theoretically requires 4 moles of CO + H_2 per mole SO_2 for the reduction

$$CuSO_4 + 4CO \rightarrow 4CO_2 + Cu + \tfrac{1}{2}S_2 \qquad (13\text{-}5)$$

$$CuSO_4 + 4H_2 \rightarrow 4H_2O + Cu + \tfrac{1}{2}S_2 \qquad (13\text{-}6)$$

The actual stoichiometry used for each of the FGD processes is, of course, greater than the theoretical stoichiometry. A compromise value of 3.0 moles of CO + H_2 per mole SO_2, or 362,000 scfh, was selected as a design basis. The costs for reducing gas production for each FGD process can be scaled up or down from design basis costs.

Table 13-1 is a summary of the quality and quantity of reducing gas required under the stated conditions for the five reducing gas systems. Table 13-2 summarizes the product gas compositions, raw material and energy requirements, and product gas cost for each of the reducing gas systems. Capital charges of 25 percent of the capital investment cost were included in the product gas costs.

13.1 Steam-Methane and Steam-Naphtha Reforming

This section describes a steam-hydrocarbon reforming process where both methane and naphtha can be used as feedstocks. Simplified flow diagrams for the methane and naphtha processes are shown in Figures 13-1 and 13-2 (BE-155).

TABLE 13-1

COMPARISON OF QUALITY AND QUANTITY OF PRODUCT GAS FROM REDUCING GAS SYSTEMS

				Coal Gasification	
Parameter	Steam Methane Reforming	Steam Naphtha Reforming	Partial Oxidation	Wellman-Galusha	Koppers Totzek
Gross Heating Value (Btu/scf)	323	314	125	158	301
H_2/CO (mole ratio)	5.5	4.2	0.61	0.60	0.58
Total Gas Flow Rate (scfh)	417,000	435,000	950,000	910,000	400,000
$CO+H_2$ Flow Rate (scfh)	362,000	362,000	362,000	362,000	362,000
Total Heat Rate (MM Btu/hr)	135	137	119	144	120
Overall Fuel Efficiency $\left(\frac{\text{Btu Reducing Gas}}{\text{Btu Fuel + Feed}}\right)$	0.78	0.72	0.57	0.63	0.63

TABLE 13-2

COMPARISON OF REDUCING GAS SYSTEMS

COMPARISON CRITERIA	REDUCING GAS SYSTEMS				
				COAL GASIFICATION(1)	
	STEAM METHANE REFORMING	STEAM NAPHTHA REFORMING	PARTIAL OXIDATION	WELLMAN-GALUSHA	KOPPERS-TOTZEK
Product Gas Composition (Dry Basis)					
H_2	73.7	67.3	14.5	14.9	33.3
CO	13.3	16.0	23.6	24.9	57.1
CH_4	4.0	4.3	0.2	2.5	--
H_2S	--	--	<200 ppm	0.7	1.4
N_2	0.3	--	60.0	51.6	1.1
CO_2	8.7	12.2	1.0	5.4	7.1
Raw Material and Utility Requirements and Steam Credits					
Natural Gas (MM Btu/hr)	205	--	--	--	--
Heavy Fuel Oil (MM Btu/hr)	--	86	181	--	--
Naphtha (MM Btu/hr)	--	127	1	--	--
Coal (MM Btu/hr)	--	--	--	250	193
Electricity (kwhr)	100	100	4035	520	1700
Process Water (Mgal/hr)	5.0	5.1	1.7	--	--
Steam Credit (MM Btu/hr)	⟨34⟩	⟨30⟩	⟨16⟩	⟨26⟩	⟨20⟩
Reducing Gas Costs					
\$/MM Btu Fuel Gas	3.05	5.28	6.54	4.00	7.80
\$MM Btu H_2/CO	3.65	6.50	6.65	4.92	8.07

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(1) Raw Material Data and Costs Based on a 2 Gasifier System.

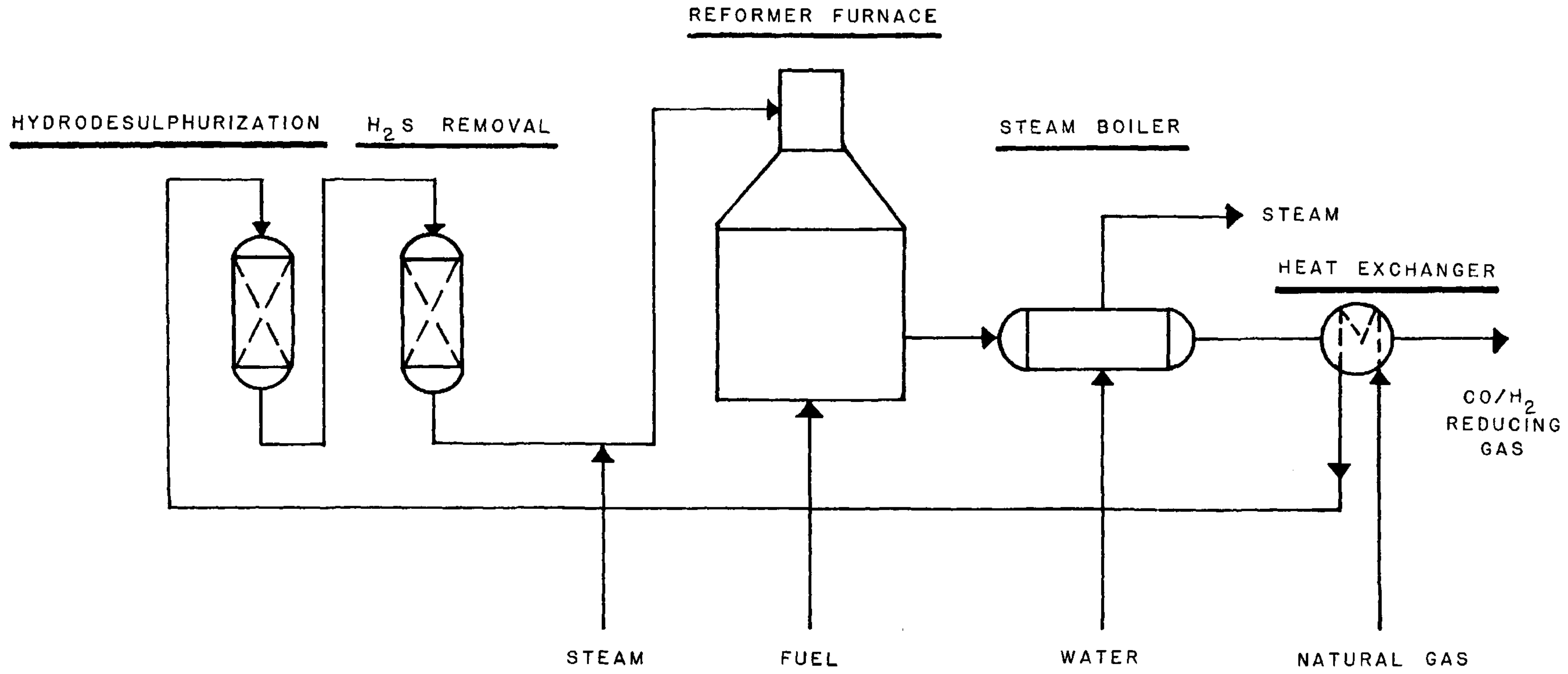

FIGURE 13-1
PROCESS FLOW DIAGRAM
STEAM-METHANE REFORMING

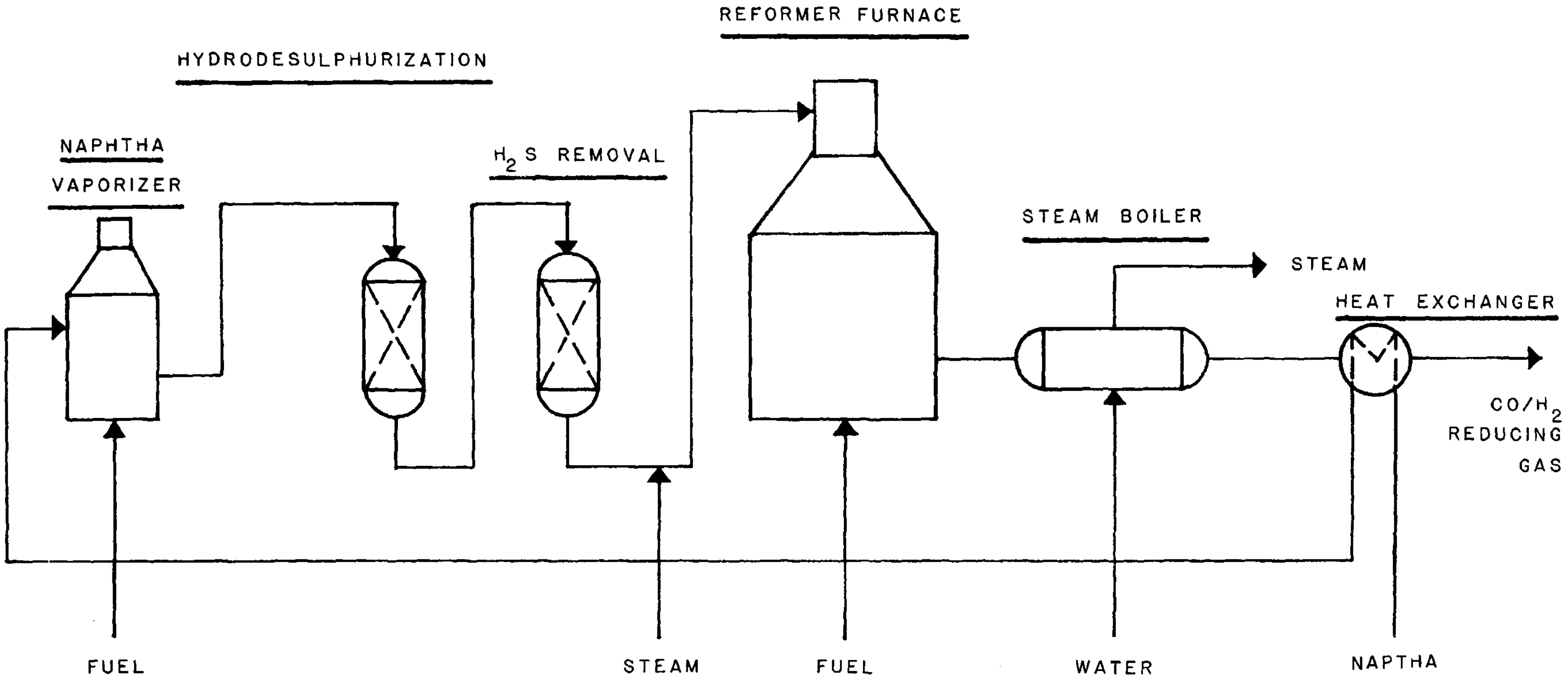

FIGURE 13-2
PROCESS FLOW DIAGRAM
STEAM-NAPHTHA REFORMING

13.1.1 Process Description

The basic steps of the process are desulfurization, reforming, and heat recovery. When a liquid feed such as naphtha is used a naphtha vaporizer must be included prior to the reforming furnace.

Reduction of the sulfur content to less than 0.5 ppm is essential to prevent deactivation or poisoning of the reforming catalyst (SY-017). Depending on the feedstock and the nature of the sulfur contaminants, the desulfurization method can be any of the following:

- ambient temperature adsorption on activated carbon,
- high temperature reaction with zinc oxide, and
- catalytic hydrogenation followed by high temperature reaction with zinc oxide.

For the cases shown in Figures 13-1 and 13-2, the feedstocks are preheated against reformer effluent to a temperature in the range of 550-750°F and passed over a cobalt-molybdenum hydrodesulfurization catalyst to convert various sulfur compounds to hydrogen sulfide. The feed is then contacted with zinc oxide to reduce hydrogen sulfide to low levels.

The sulfur-free feed gas is mixed with superheated steam and reformed at approximately 1400-1600°F in tubes filled with catalyst. A nickel-based catalyst is used for the natural gas type feed. A special catalyst such as a rehnium promoted bimetallic catalyst is used for a naphtha feedstock (PR-103). The reactions that take place are highly endothermic and thus require a reformer furnace to supply process heat.

The reformer can be designed to operate at pressures over 400 psig (BL-078). Since a reducing gas near atmospheric pressure will be used in the FGD process, the reformer will operate from 25-50 psig. Although high line pressure natural gas may be available, operating in a low pressure mode will eliminate the need to compress the vaporized naphtha feed.

The reformed gas stream contains residual methane, hydrogen, carbon monoxide, carbon dioxide, and excess steam. This hot effluent stream is cooled to approximately 600°F after being used to produce steam. The product gas is then used to preheat the process feedstock and leaves the process at 150°F. Condensate can be collected and removed in a condensate knock-out drum.

13.1.2 Development Status

The steam-methane reforming process has been in use for four decades and is a primary source of hydrogen for the petroleum and petrochemical industry. The first commercial continuous steam-methane reformer was installed in 1931 for the Standard Oil Company of New Jersey. Hydrogen is an essential component for ammonia synthesis and for hydrocracking, which are two hydrogen consuming processes that have greatly increased in use in recent years (ZE-024).

A successful process for the continuous catalytic reforming of naphtha was developed in 1962. The basic problem in attempts to steam-reform liquid feedstocks has been carbon formation in the furnace tubes and resultant pressure increase due to tube blockage. New catalyst developments have provided the solution to the problem (BL-078).

Steam-hydrocarbon reforming today is a reliable process with proven technology. Numerous hydrogen plants are in operation, and plants with capacities up to 140 MM scfd have been built.

13.1.3 Gas Quality

The typical gas compositions that can be expected from the steam-methane and steam-naphtha reforming processes are shown in Table 13-3 and Table 13-4 (KI-109). The naphtha feedstock results in higher concentrations of CO and CO_2 because the carbon/hydrogen ratio is larger. For both cases, the product gas leaves the reactor saturated with water. For the natural gas case, the total product stream contains nearly 35 percent water. If required, a hydrogen product purity of 95-99+ percent by volume can be obtained when subsequent shift converters, a CO_2 absorber, and a methanator are added to the process (HY-020).

13.1.4 Economics

The costs were determined for a steam-hydrocarbon reforming plant designed by Selas Corporation producing 10 MM scfd of reducing gas. The capital cost was based on a plant designed to run on either natural gas or naphtha. A naphtha-vaporizer and condensate knock-out to remove the water in the product gas stream were included in the cost. The total capital

TABLE 13-3

STEAM-METHANE REFORMER PRODUCT GAS COMPOSITION, PERCENT (DRY)

Composition	Volume Percent (Dry)
CO	13.3
CO_2	8.7
H_2	73.7
CH_4	4.0
N_2	0.3

TABLE 13-4

STEAM-NAPHTHA REFORMER PRODUCT GAS COMPOSITION, PERCENT (DRY)

Composition	Volume Percent (Dry)
CO	16.0
CO_2	12.2
H_2	67.3
CH_4	4.3
N_2	--

cost (± 20 percent) of a plant built today (Gulf Coast erected including foundations) would be $5,000,000 (KE-109). Naphtha reforming is a process developed by ICI and must be licensed from this company.

The plant operating costs using a typical natural gas feed (CH_4) containing 95.5 percent methane are shown in Table 13-5. The plant operating costs using a naphtha feed (C_7H_{15}) are shown in Table 13-6. The final reducing gas product was taken to be a water-free gas at 150°F (KI-109).

13.1.5 Applicability

The applicability of steam hydrocarbon reforming systems depends largely upon the availability of raw materials. The availability of natural gas is predicted to decrease in the immediate future as well as in the long range forecast. In June, 1975, the Federal Power Commission released statistics estimating that interstate gas pipelines would be 19.4 percent short of the gas they need to meet firm requirements over the next 12 months (April 1975 through March 1976). However, the reserve estimates of gas producers which were used as a basis for the prediction have been disputed by the Federal Trade Commission (NA-246).

The primary role of our remaining recoverable domestic gas resource will be to maintain our current commitments over a reasonably sustained period of time. Any significant future growth of the natural gas industry (in terms of national production rates) must primarily be based on supplemental sources of gas such as SNG from coal or imported gas (PU-088).

Naphtha is the dominant feedstock for petrochemical operations outside the United States. In this country natural gas liquids are the prime feedstock, but use of naphtha is

TABLE 13-5

ECONOMIC SUMMARY FOR THE STEAM-METHANE REFORMING PROCESS

Basis: 417×10^3 scfh Product Gas
Natural Gas Feed
5,260 Hr/Yr Operation

		Cost (10^3 Dollars/yr)
Natural Gas Feed	123 MM Btu/hr	647.0
Process Fuel (Natural Gas)	82 MM Btu/hr	431.0
Process Water	5.0 M gal/hr	2.1
Steam Credit	34 MM Btu/hr	⟨89.4⟩
*Electric Power	100 kw	10.5
Capital, Maintenance, ROI (25% of Capital Cost)		1,250
Total Operating Costs:		2,251
Total as \$/MM Btu Fuel Gas**		3.05
Total as \$/MM Btu H_2/CO		3.65

---

*Rough estimation

**Includes $1/MM Btu credit for CH_4

TABLE 13-6

ECONOMIC SUMMARY FOR THE STEAM-NAPHTHA REFORMING PROCESS

Basis: 435×10^3 scfh Product Gas
Naphtha Feed
5,260 Hr/Yr Operation

		Cost (10^3 Dollars/Yr)
Naphtha Feed	127 MM Btu/hr	1,670
No. 6 Fuel Oil	86 MM Btu/hr	1,040
Process Water	5.1 M gal/hr	2.1
Steam Credit	30 MM Btu/hr	⟨78.9⟩
*Electric Power	100 kw	10.5
Capital, Maintenance, ROI (25% of Capital Cost)		1,250
Total Operating Costs:		3,894
Total as $/MM Btu Fuel Gas:**		5.28
Total as $/MM Btu H_2/CO:		6.5

---

*Rough estimation

**Includes $1/MM Btu credit for CH_4

growing. High prices keep naphtha from being traded as a commodity. A scarcity of naphtha due to a crude run decline was reported in December, 1974. The scarcity was not nearly as bad, however, as existed in late 1973 and early 1974 during the Arab oil embargo (NA-242).

Steam hydrocarbon reforming systems have the ability to operate at 50 percent of feed capacity by adjusting the throughput and the fuel firing rate in the reformer furnace. The turndown is accomplished in small steps over a period of hours to allow for contraction or expansion (KI-109).

13.2 Partial Oxidation of Heavy Fuel Oil

Partial oxidation of heavy fuel oils results in a product gas which is rich in hydrogen and carbon monoxide. The sulfur present in the heavy fuel oil feed is converted to gaseous sulfur compounds, mostly hydrogen sulfide.

The two major systems in use today are the Texaco and Shell processes. Of these, the Shell process is described in this section. As commercially developed and demonstrated, the process is non-catalytic, can use any hydrocarbon feedstock from natural gas to the heaviest residue, and can use either oxygen or air as the oxidizing agent. The description and calculations contained in this section assume the use of heavy residual oil feedstock and air as the oxidizing agent.

13.2.1 Process Description

There are four basic processing areas in the Shell partial oxidation process: heavy oil gasification, waste heat recovery, carbon removal, and soot recovery/recycle. A process flow diagram is provided as Figure 13-3.

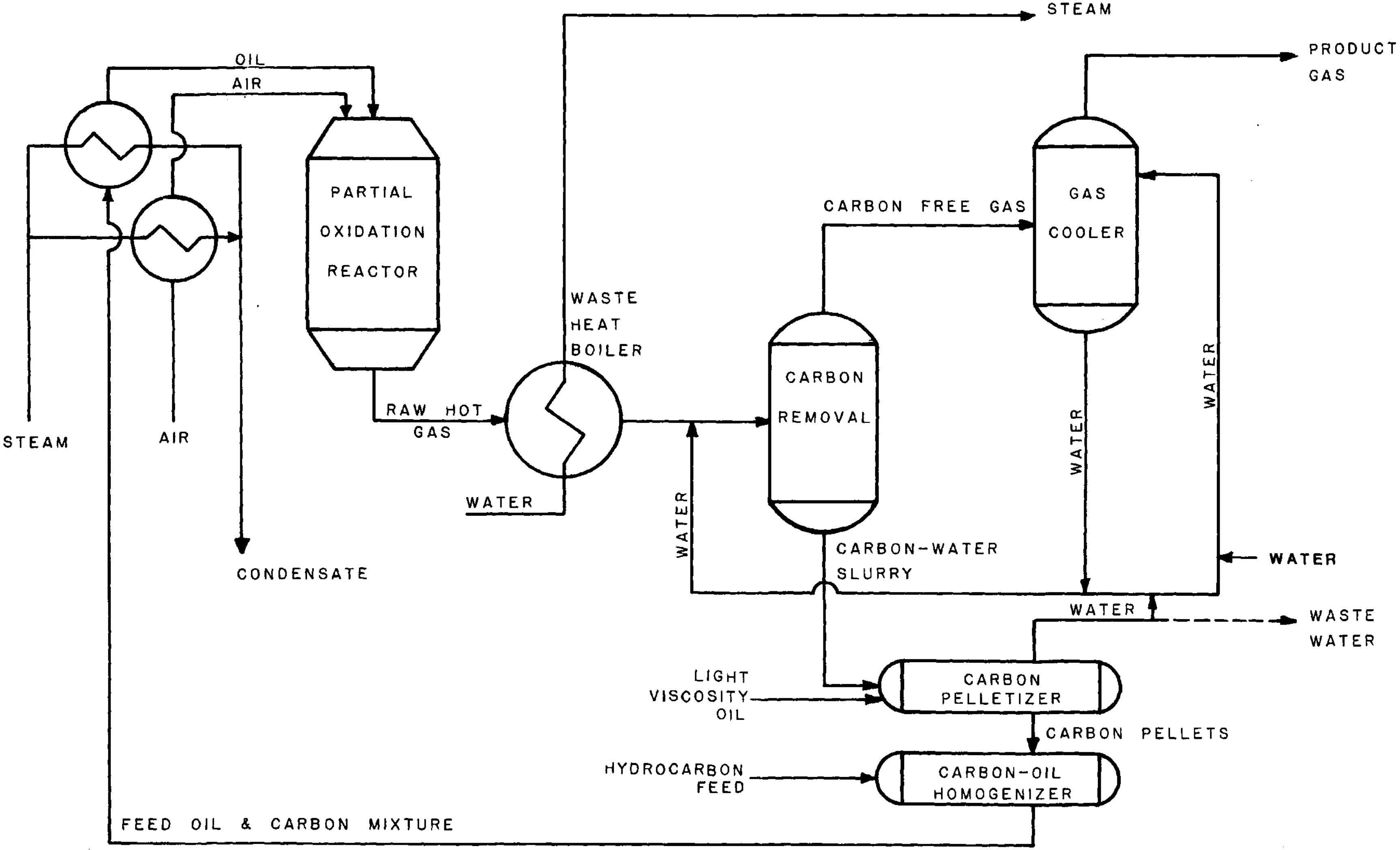

FIGURE 13-3
PROCESS FLOW DIAGRAM
PARTIAL OXIDATION PROCESS

The reactor is a vertical, refractory lined vessel which operates at relatively high temperatures and pressures (about 2300°F and up to 55 atmospheres). Preheated hydrocarbon fuel and air are fed to the reactor under precisely controlled conditions through a nozzle to achieve effective mixing of the fuel and oxidant. The residence time in the reactor is on the order of 5-6 seconds.

The hot reducing gas produced in the reactor passes to a waste heat boiler designed to operate satisfactorily in the presence of soot which is produced during partial oxidation of heavy oils. As much as five weight percent of the feed may result in a solid carbon or soot which could cause problems by depositing and forming "hot spots" on conventional boiler tubes. A specifically designed boiler employing helical tubes has been demonstrated to provide reliable service in this application.

Saturated steam is produced in the boiler at pressures independent of the gas generation pressure and these pressures may be up to 1500 psig. Typically, an excess of about three to four pounds of steam per pound of fuel is produced, some of which is used for feed preheat and the rest exported for credit to the partial oxidation plant.

Gas from the waste heat boiler containing the soot and ash formed in the reactor is first quenched in a spray tower and then water scrubbed to remove carbon and soot to a level of about 1 ppm. A carbon water slurry results which contains about 1.5 percent carbon.

A low viscosity oil is then contacted with the carbon-water slurry in a device called a pelletizer. The oil preferentially wets the soot particles and forms pellets which can be homogenized into the oil feed to the gasification reactor.

13.2.2 Status of Development

Partial oxidation of heavy oil can be considered a well demonstrated and reliable process which is commercially available today. The Shell process was developed in the early 1950's. Since then over 100 reactors have been placed in operation or construction at over 30 different locations throughout the world with a total design capacity of over one billion scfd of hydrogen and carbon monoxide. Stream factors of 0.95 or better have been achieved by this process (KU-063).

13.2.3 Gas Quality

The following gas composition is typical of that produced by this process. Since the reactor operates at 2300°F and 55 atm, the product gas can be delivered at any temperature and pressure below these values by employing proper temperature and pressure reduction techniques.

Reactor Product Gas Composition, Percent (Dry)

Component	Volume Percent (Dry)
H_2	14.5
CO	23.6
CO_2	1.0
H_2S	<200 ppm
CH_4	0.2
N_2	60.7

Several process alternatives are available to produce a higher purity reducing gas. Pure oxygen can be used as the reaction oxidant and its use will eliminate most of the inerts but will result in an increased capital expenditure for an oxygen plant. A process may also employ sulfur removal, water-gas shift reactors, and CO_2 removal facilities to produce an essentially pure H_2 product stream.

13.2.4 Economics

Cost estimates used as a calculation basis were presented in a paper by Shell Development Company at the March, 1974 AIChE Meeting held in Tulsa, Oklahoma. Capital costs, as presented, were for a process some 10-15 times larger than needed for FGD reducing gas production. Standard economic scaling practices were used to roughly estimate the cost of a process sized for FGD application. This calculation resulted in a cpaital cost of about six million dollars for the process. Operating costs are based on production rates reported in this section and are shown in Table 13-7. The high electricity costs are due primarily to the cost of compressing air to 55 atm.

13.2.5 Applicability

The attractiveness of the system for use as a reducing gas producer lies in its relatively simple operation and its ability to use heavy, high sulfur petroleum fractions for fuel. The relatively simple non-catalytic gasification reactor lends itself to a high turndown ability, but care must be taken to make changes in small increments to avoid thermal stresses. Heavy, high-sulfur fuels have historically been an environmentally unacceptable residential, commercial, or industrial fuel but have been demonstrated to provide a reliable feed source for generation of FGD reducing gas.

TABLE 13-7

ECONOMIC SUMMARY FOR SHELL PARTIAL OXIDATION PROCESS

Basis: $950x10^3$ scfh Product Gas
5,260 Hr/Yr Operation

		Cost (10^3 dollars/Yr)
Heavy Fuel Oil	181 MM Btu/hr	2,190
Naphtha	1.1 MM Btu/hr	14.5
Steam Credit	16 MM Btu/hr	⟨42⟩
Power	4,035 kw	424
Process Water	1.7 M gal/hr	0.7
Capital Charges	(25% of Cost)	1,500
	Total Operating Cost:	4,087
	Total as $/MM Btu Fuel Gas:	6.54
	Total as $/MM Btu H_2/CO:	6.65

13.3 Coal Gasification

The quantity of reducing agent required for a typical flue gas desulfurization facility is very small compared to the capacity of the more advanced gasifiers. Therefore little benefit in cost would be expected from the use of the gasifiers under development for SNG and advanced combined cycles. Furthermore, pressurized gas is usually not required, so the atmospheric gasifiers are most applicable. The two systems considered here, Wellman-Galusha and Koppers-Totzek, are available technology at atmospheric conditions. Economic data has been synthesized from a report on low-Btu gasification to EPRI by TVA (WA-199).

13.3.1 Process Description

Wellman-Galusha

The Wellman-Galusha gasifier is typical of several available moving-bed, atmospheric gasifiers. Product gas leaves the gasifier at about 1200°F and contains tars, phenols, light hydrocarbons, and NH_3 as well as H_2/CO. Typically 5 percent of the coal goes to tars and phenols and up to 20 percent of the gas reducing power is present as methane. Air is required for gasification. Steam is supplied from jacket cooling.

Almost all applications would require gas cleaning to remove tars and particulates (see Figure 13-4). The TVA design to accomplish this includes a tar quench scrubber operating at 900 degrees Fahrenheit, gas cooling with heat recovery, and a water scrubber to remove particulate and residual tars. The tars tend to emulsify in water and would require special separation operations. Phenols and NH_3 accumulate in water solution

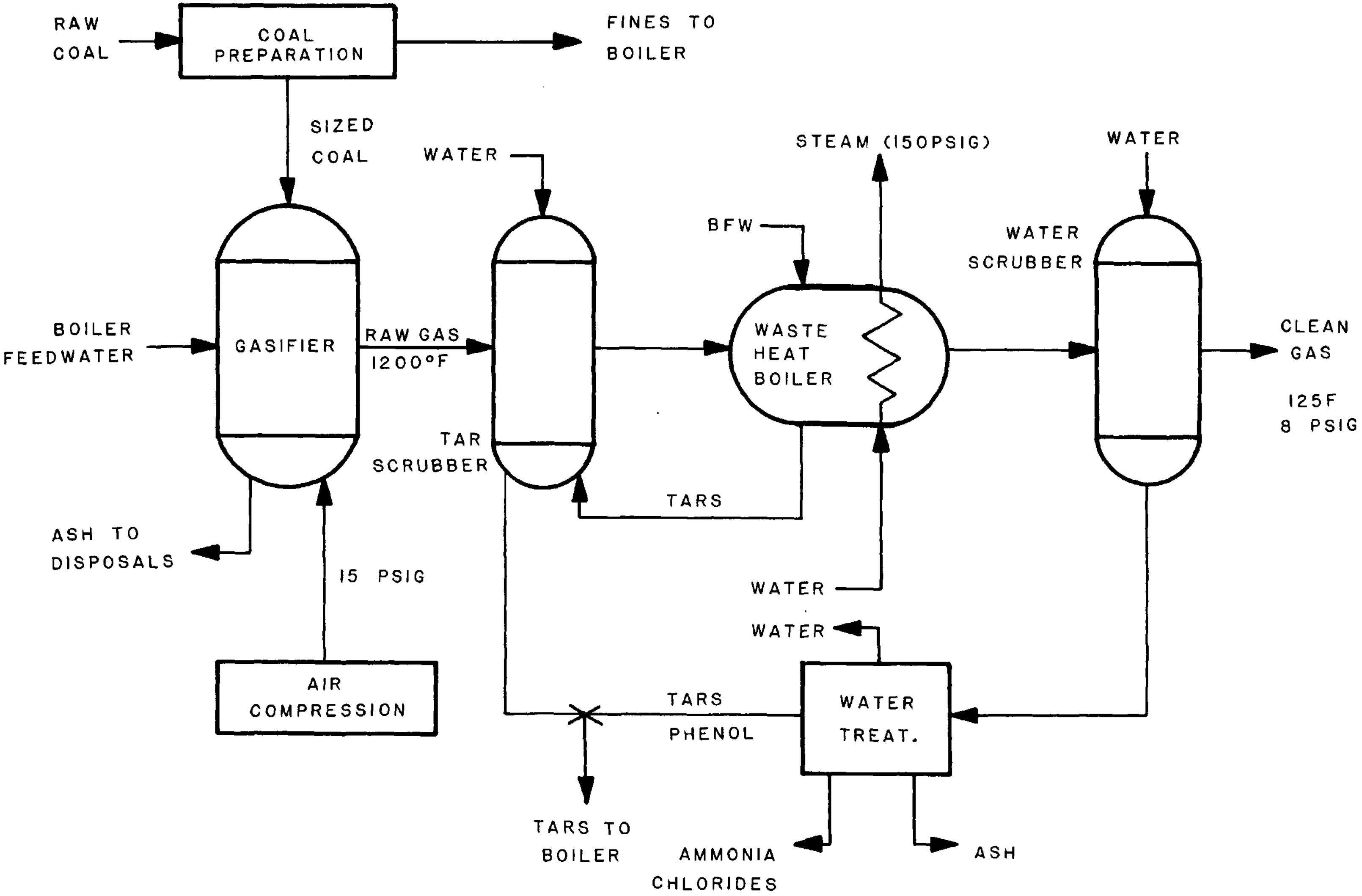

FIGURE 13-4
PROCESS FLOW DIAGRAM
WELLMAN-GALUSHA
COAL GASIFICATION PROCESS

and must be removed by solvent extraction and stripping. Lurgi has proprietary technology for tar/water separation and phenol removal that would be quite expensive applied on a small-scale.

Wastewater treatment could potentially be avoided by total water recycle. However, impurity build-up of compounds such as chlorides would probably require some blowdown and subsequent water treatment. Furthermore, NH_3, phenols, and residual tars might not be removed under such conditions. The alternative technologies are not well-defined and would pose both technical and economic problems. Tars from the system can be disposed of by combustion as supplementary boiler fuel.

Applications that could not utilize methane would be required to use high temperature reforming of the atmospheric, H_2S-containing gas. Alternatively, if CH_4 caused no undesirable effects such as coking, exhaust gas containing unreacted methane could be used as supplementary boiler fuel.

As with most moving bed gasifiers, strongly caking coal cannot be used in the Wellman-Galusha gasifier. A stirring device has been developed and tested to permit the use of slightly caking coals, however, there has not been extensive use on caking coals. Since most Eastern steaming coals are caking, a separate non-caking coal supply may be necessary for the gasification system.

Coal for the gasifier must be sized and screened. Typically about 15% of the coal is rejected as fines. Provision must be made to combine fines production with coal feed to the main pulverized coal boiler.

Koppers-Totzek

The Koppers-Totzek gasifier is a high temperature entrained gasifier. Oxygen and low-pressure steam are required for gasification. The coal feed is pulverized and may be caking or non-caking. The gas product exits at 2200°F and is quenched to 1500°F by water. It contains no tars, phenol, NH_3, or methane and primarily consists of H_2, CO, CO_2, and H_2O. The gas is cooled in a waste heat boiler and scrubbed with water to remove particulate. Since most of the water is recycled, no water treatment unit is required. The system as a whole is less complicated than Wellman-Galusha, but it does require an oxygen plant and a more expensive gasifier. The flow sheet is given in Figure 13-5.

13.3.2 Development Status

The two coal gasification technologies evaluated are fully proven commercial processes. More than 6,000 Wellman-Galusha gasifiers were built in the early 1900's. Currently, there are two U.S. sites with operating gasifiers and several foreign applications. Similar moving bed gasifiers are also offered by Pullman Kellogg and Riley Morgan.

The Koppers-Totzek gasifier has a good foreign commercial record as indicated in Figure 13-6 (WI-106). There are currently no U.S. installations.

13.3.3 Gas Quality

Both processes produce a gas with high hydrogen and carbon monoxide concentrations. The main composition differences result from the presence of inerts in the air blown

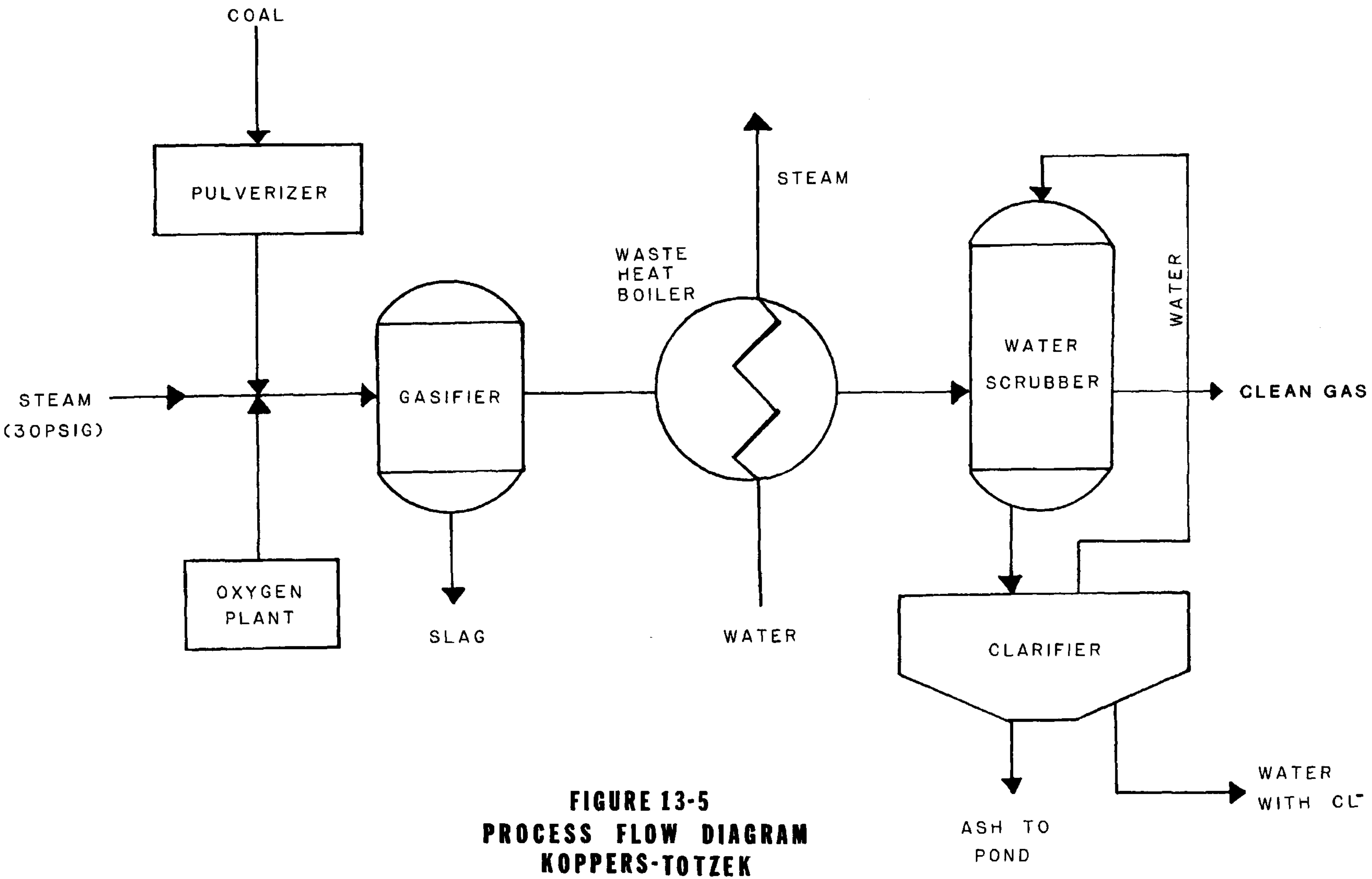

FIGURE 13-5
PROCESS FLOW DIAGRAM
KOPPERS-TOTZEK
COAL GASIFICATION PROCESS

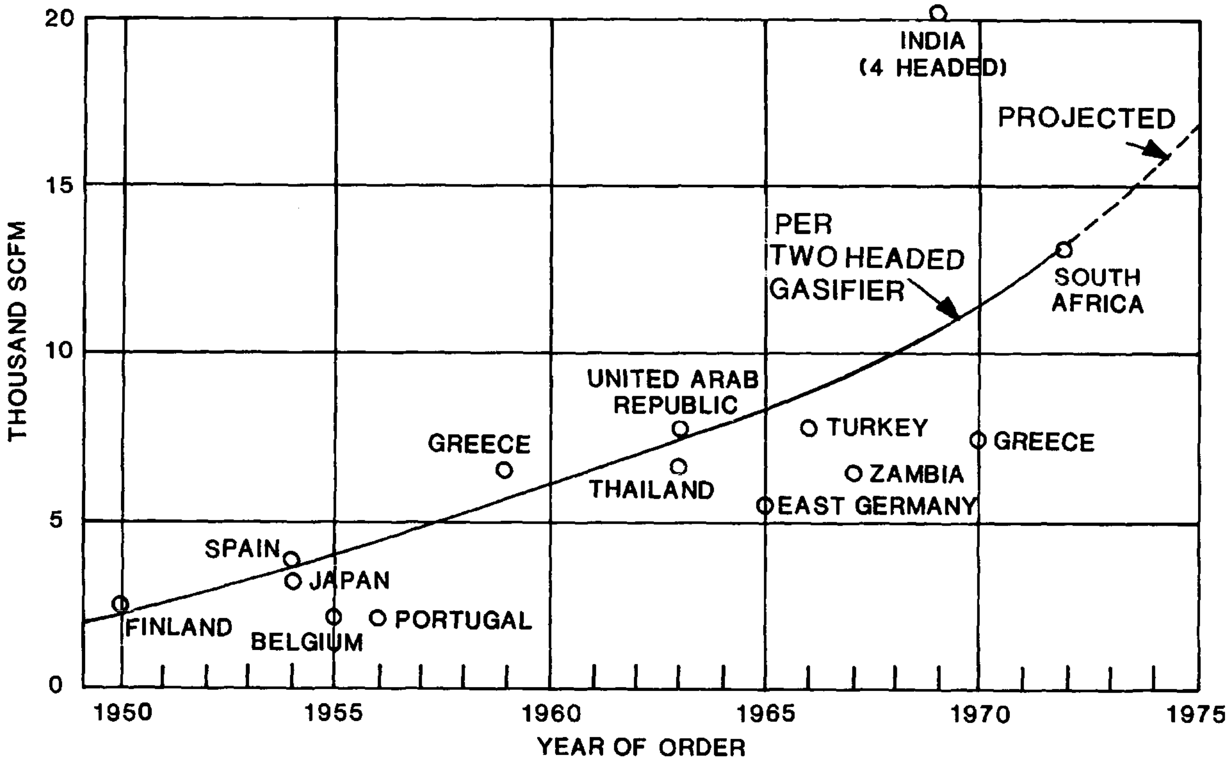

FIGURE 13-6
KOPPERS COAL GASIFICATION PROCESS
DRY GAS PRODUCTION CAPACITY
(CHRONOLOGICAL ORDER)

gasification products. Product gas compositions are shown in the following table:

Gas Component	Composition Percentage	
	Wellman-Galusha	Koppers-Totzek
H_2	14.9	33.3
CO	24.9	57.1
CH_4	2.5	-
H_2S	0.7	1.4
N_2	51.6	1.1
CO_2	5.4	7.1

There are several alternatives affecting reducing gas composition. The air-blown moving bed gasifiers produce gas that contains about 50 percent inerts plus significant quantities of methane. Use of oxygen rather than air will eliminate most of inerts, but not the methane, and will increase the capital cost about 50 percent. The Koppers-Totzek oxygen-blown gasifier will produce gas containing no methane or inerts but at a capital cost about double that of an air-blown moving bed gasifier. If methane cannot be used, but does not adversely affect the system, effluent gas from the user system can be sent to the boiler to recover methane heating value.

Gas containing primarily hydrogen, rather than a mixture of H_2 and CO, can be produced by reheating the gas to about 700°F and adding a water gas shift converter. Reheat would best be accomplished by direct combustion of some of the gas. This would reduce net H_2/CO production by 15 percent for an air-blown gasifier and 5 percent for an oxygen-blown gasifier. Most uses of H_2 require hot gas, so the reheat would be required in any case. Low-temperature (400°F) shift conversion cannot be used because of the presence of H_2S; therefore residual CO would be left in the gas. Low-pressure steam may be required to complete the water-gas shift, depending on operation of the previous water scrubber. Product gas after shift would probably have the following composition:

	Composition Percentage (Dry)	
Gas Component	Wellman-Galusha	Koppers-Totzek
H_2	23.4	54.4
CO	2.1	4.2
CH_4	1.6	-
CO_2	21.0	39.6
H_2S	0.6	0.9
N_2	51.3	0.8

More concentrated hydrogen would be made by cooling and amine scrubbing the gas to remove water and CO_2.

13.3.4 Economics

TVA developed costs of the Wellman-Galusha system for low-Btu gas for a 500 Mw power plant. The system required 57 operating gasifiers. The TVA estimate was scaled down by considering cost detail on a single gasifier without desulfurization and boiler conversion costs. TVA developed costs (WA-199) were also used as a basis for scale down for the Koppers-Totzek system. Results of these evaluations are presented in Tables 13-8 and 13-9.

13.3.5 Applicability

The Koppers gasifier can gasify any pulverized coal. The moving bed gasifiers may have some restrictions on highly caking coals, but otherwise can gasify most steam coals.

TABLE 13-8

ECONOMIC SUMMARY OF WELLMAN-GALUSHA COAL GASIFICATION SYSTEM

Basis: 480,000 scfh Product Gas Per Gasifier
5,260 Hrs/Yr

	1 Gasifier	2 Gasifiers
Capital Costs (10^3 dollars, 1975)		
Coal Conveying/Screening	140	210
Gasification	2,810	4,300
Gas Cleanup/Heat Recovery	400	700
Tar/Phenol Water Processing	1,200	1,500
Service/Construction Facilities and Utilities	550	850
Total (Including Indirects):	5,100	7,560
Annualized Operating Costs (10^3 dollars/yr per gasifier)		
Coal 125 MM Btu/hr	458	1,315
Power 261 kw	27	55
Steam Credit 13 MM Btu/hr	⟨34⟩	⟨69⟩
Capital, Maintenance, ROI (25% of Capital Cost)	1,275	1,890
Total Operating Costs:	1,726	3,191
Total as $/MM Btu Fuel Gas:*		4.00
Total as $/MM Btu H_2/CO:		4.92

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*With $1.00/MM Btu credit for excess CH_4.

TABLE 13-9

ECONOMIC SUMMARY OF KOPPERS-TOTZEK
COAL GASIFICATION SYSTEM

	1 Gasifier	2 Gasifiers
Capital Costs (10^3 dollars)		
Gasification	8,200	10,097
Oxygen Production	5,186	5,186
Total	13,386	15,283
Annualized Operating Costs (10^3 dollars)		
Coal 193 MM Btu/hr	1,015	1,015
Power 1700 kw	180	180
Steam Credit 20 MM Btu/hr	⟨53⟩	⟨53⟩
Capital, Maintenance, ROI (25% of Capital Cost)	3,340	3,820
Total Operating Cost:	4,482	4,962
Total as $/MM Btu Fuel Gas:		7.80
Total as $/MM Btu H_2/CO:		8.07

Turndown of the moving bed gasifiers can be very fast and can be carried to as low as 10 percent of capacity. Turndown is accomplished by simply reducing air rate. Coal flow control is automatic.

Turndown of the Koppers-Totzek system is more complicated, since both O_2 and coal feed rates must be reduced, and slagging must occur under controlled conditions.

13.4 Summary

The steam-hydrocarbon reforming, partial oxidation, and coal gasification processes were considered to be the processes that were most likely to be used to produce a CO/H_2 reducing gas for FGD regeneration systems. These reducing gas production processes were evaluated to determine the cost and suitability of their respective product gases for use in conjunction with an FGD system installed on a utility boiler. The following points summarize the findings of the reducing gas evaluation.

1) All five methods can be considered commerically proven technology. The coal gasification processes will, however, present more operating problems than the reforming or partial oxidation processes. The solids handling requirement and the additional ash and impurities that are not found in liquid and gaseous hydrocarbon feeds require a more sophisticated process arrangement than found in the other reducing gas methods.

2) The partial oxidation and coal gasification processes would probably be run with air instead of oxygen as the use of oxygen raises the cost of the reducing gas to any unacceptable level. These two methods would, therefore, produce a dilute CO/H_2 reducing gas. The reforming process does not require oxygen or air in the feed stream and, therefore, produces a concentrated CO/H_2 reducing gas stream.

   The size of the FGD system's regeneration facility is dependent directly upon the volumetric flow rate of the reducing gas. If a pure SO_2 stream is sent to a regeneration facility to be reduced to sulfur, the use of a reforming gas would require a facility that uses an air-blown partial oxidation gas.

3) One of the main drawbacks of steam-methane and steam-naphtha reforming is the scarcity of the required feedstocks. Natural gas and naphtha will also become very high-priced as U.S. oil and gas reserves continue to dwindle and the fuel economy is switched to coal. The partial oxidation process can use any fluid hydrocarbon as a feedstock. Feeds could include such relatively low-valued materials as high sulfur resid and asphalts.

4) The price differences among the processes are primarily due to the capital cost and feed and fuel requirements. The largest cost item for most of the processes is the capital charge. The reforming processes have the lowest capital charge at $1,250,000/yr, while the Koppers-Totzek gasification system has a very high capital charge at $3,820,000/yr. The high capital charge of the Koppers-Totzek process causes the reducing gas cost to be at an unacceptable level for an FGD regeneration system. About one-third of the capital cost is for the oxygen plant. The type of hydrocarbon used as the feed and fuel also causes a large price difference for the different reducing gases produced. The steam-naphtha reforming and partial oxidation processes use naphtha and heavy fuel oil which are about two and a half times more expensive than the natural gas or coal used in the other processes. Therefore, these two processes produce a more expensive reducing gas than steam-methane reforming and Wellman-Galusha coal gasification. Partial oxidation also consumes a large amount of electricity which is used in compressing the air fed to the process to 55 atmospheres.

5) Reforming is the only method that is catalytic. In order to prevent catalyst poisoning in the reactor, the feedstock

must first be desulfurized. The other two reducing gas production methods do not require fuel cleaning of the process feedstock.

6) All of the processes appear to have a high turndown ability. The turndown is accomplished in steps to allow for expansion and contraction. Turndown of the Koppers-Totzek system is more complicated, since both O_2 and coal feed rates must be reduced, and slagging must occur under controlled conditions.

14.0 SUITABILITY OF THE FGD PROCESSES FOR SULFUR OR SULFURIC ACID PRODUCTION

Many of the FGD processes being evaluated have the ability to produce either sulfur or sulfuric acid as a final product. Most of the calculations in the FGD process evaluations, however, were based on processing schemes resulting in sulfur as a process by-product. During the course of the evaluations, it was suggested that sulfuric acid might be a preferred by-product.

In this section, the technical suitability of the eleven regenerable FGD processes to produce either sulfur or sulfuric acid is evaluated. Various methods of producing sulfur and sulfuric acid are described with special emphasis on their applicability for FGD by-product production. Costs associated with treatment of the FGD unit off gas to produce an acid plant feed have not been included in this evaluation. Only the suitability of preparing an acid plant feed gas was examined. For comparison purposes, the Allied Chemical Sulfur Plant and a single absorption contact sulfuric acid plant are used as the base case sulfur and sulfuric acid production units. Sulfur production costs are calculated for both natural gas and coal gasification reducing gas as the reductant. Both of the units, sulfur and sulfuric acid, would be designed to send the tail gas back to the SO_2 scrubber in the FGD system to prevent SO_2 emissions.

An alternative to treating the tail gas from these units in the FGD system would be to construct a tail gas treatment unit for the sulfur plant or use a Double Contact/Double Absorption Acid Unit (DC/DA). These facilities would result in added costs to the sulfur/acid production units whereas routing the tail gas back through the FGD process would result in increased FGD costs for processing the extra gas. An economic comparison on a site specific basis is needed to determine the best choice. For this evaluation, it is being assumed that the FGD system can handle the relatively small increase (about 5 percent) in load from routing the gases back through the system.

14.1 Process Descriptions

A single absorption contact process has been selected as the sulfuric acid production method. As discussed earlier, a process alternative would be to use a CD/DA process to reduce acid plant emissions. Three different sulfur production processes will be described: The Allied Chemical Process, The RESOX Process, and the BAMAG Process. The Allied Chemical Process was selected for comparison with the acid production unit due to data availability.

Sulfuric Acid Production

Basically, the single absorption contact process oxidizes sulfur dioxide to sulfur trioxide over a vanadium pentoxide catalyst. The sulfur trioxide then combines with water in an absorber where the product acid is formed. Single absorption contact acid plants operate at sulfur dioxide conversion efficiencies of about 97 percent. A typical flow diagram of the process is illustrated in Figure 14-1.

The feed gas to the process should consist of 8.4 to 9.0 volume percent SO_2 and 8.6 to 9.2 volume percent O_2 on a dry basis. This feed gas first passes through a drying tower. The dry gas then passes through a series of heat exchangers to bring the gas temperature to 435°C (815°F). This hot gas passes

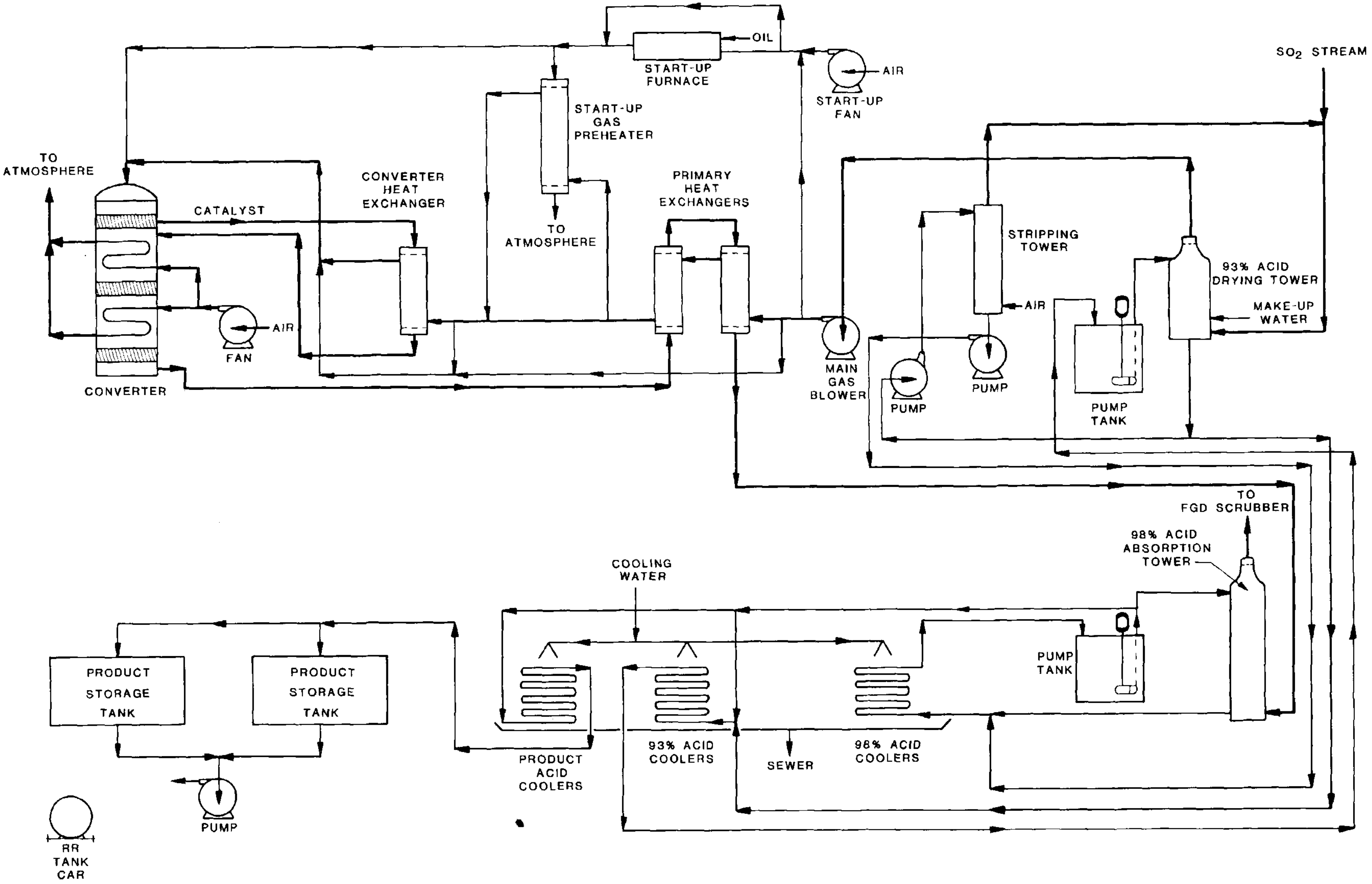


FIGURE 14-1. TYPICAL FLOW DIAGRAM OF A SINGLE ABSORPTION CONTACT SULFURIC ACID PLANT

SOURCE: MC-147

through the first three catalyst beds with intermediate heat exchange to remove the heat generated by the exothermic reaction shown below.

$$SO_2 + \tfrac{1}{2}O_2 \xrightarrow{\text{catalyst}} SO_3 \qquad (14\text{-}1)$$

After the third catalyst bed, the gas is fed to an absorber where the SO_3 combines with the water in the circulating acid. The vapor from the absorber passes through a demister to remove any entrained acid mist before being mixed with the flue gas going to the SO_2 absorber.

Sulfuric acid from the absorption towers flows to the acid pump tank where it is diluted to the required strength for absorption. The acid is pumped through a series of coolers before returning to the absorption towers. The product acid is removed from the absorption tower system through product coolers and sent to storage.

Sulfur Production

Elemental sulfur is currently produced by reacting an SO_2 stream with a reducing agent at elevated temperatures. Three processes have been applied to an SO_2 source from an FGD process: the Allied Chemical Process using natural gas, the RESOX Process using anthracite coal, and the BAMAG Process using a medium Btu town gas. In addition, the Allied Chemical Process using coal gasification reducing gas will be economically evaluated from preliminary data provided by Allied Chemical. Each of these processes will be briefly described in this section. Economics will be discussed for only the Allied Chemical Process as data is lacking on the other processes due to their early stages of development.

Allied Chemical

Allied Chemical Corporation has developed and commercialized a process for direct, catalytic reduction of SO_2 to elemental sulfur using natural gas as a reductant. The first plant to use the process operated successfully for two years using a 12 percent SO_2 stream from a sulfide-ore roasting facility. The plant, located near Sudbury, Ontario, Canada, was shut down because unsatisfactory performance of the matallurgical operations created unfavorable economics for the venture.

The process may be joined to a regenerable FGD process that produces a SO_2-rich gas stream with a low oxygen content. This application will be demonstrated at the D. H. Mitchell Station of Northern Indiana Public Service Co. (NIPSCO) at Gary, Indiana. There, the process will be combined with the Wellman-Lord SO_2 Recovery Process to provide an FGD system for a 115 Mw coal-fired boiler. The system is due to start operations in the first half of 1976.

A process flow diagram for an Allied Chemical Process with an SO_2 feed stream from an FGD system is shown in Figure 14-2. The plant consists of three main sections: (1) gas purification, (2) SO_2 reduction, and (3) sulfur recovery. The gas purification system, which is designed to remove excess water vapor and gaseous and solid impurities, is not required for all of the FGD processes.

The principle function of the catalytic reduction section is to increase the H_2S/SO_2 ratio in the gas stream to approximately the stoichiometric ratio of 2:1 required for the Claus reaction, while achieving maximum formation of elemental

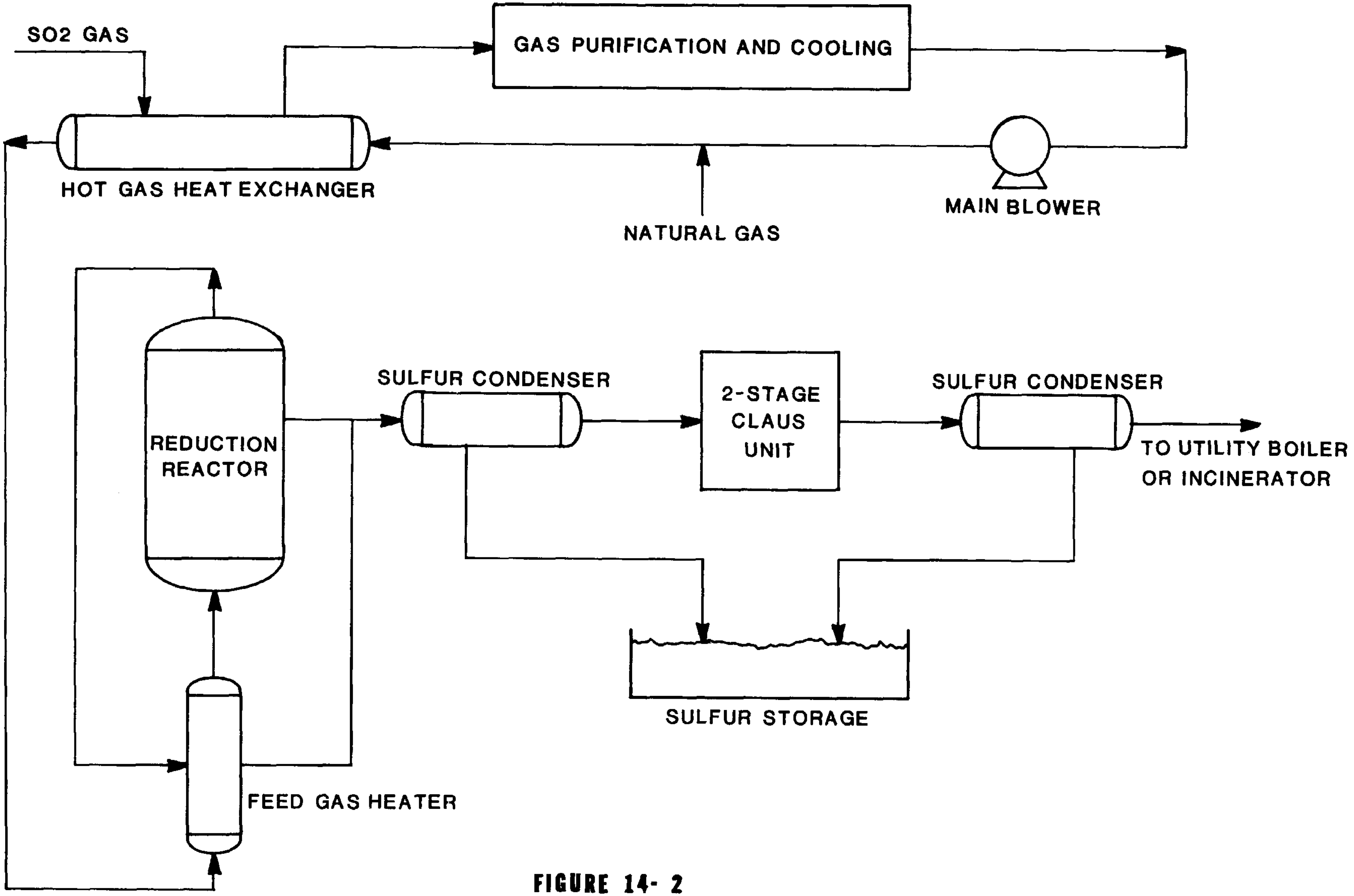


FIGURE 14- 2
TYPICAL PROCESS FLOW DIAGRAM
OF THE ALLIED CHEMICAL SO2 REDUCTION PROCESS

sulfur. The primary reaction system may be summarized in the following equations:

$$CH_4 + 2SO_2 \rightarrow CO_2 + 2H_2O + S_2 \qquad (14\text{-}2)$$

$$4CH_4 + 6SO_2 \rightarrow 4CO_2 + 4H_2O + 4H_2S + S_2 \qquad (14\text{-}3)$$

In the reduction section, the SO_2 stream which has been combined with preheated natural gas first passes through a four-way flow reversing valve and a final preheat reactor. The heated stream then enters the primary reactor where over 40 percent of the total recovered sulfur is formed. The reactor, which uses a catalyst developed by Allied Chemical that is stable up to 2000°F, achieves efficient methane utilization and provides minimum formation of undesirable side products. Careful control of the reaction conditions is necessary to achieve chemical equilibrium in the single reactor.

The gas leaving the reduction reactor passes through a second heat regenerator where it gives up its heat to the packing. Direction of flow through the two heat regenerators is periodically reversed to interchange their functions of heating and cooling.

After condensing sulfur in a steam generator, the gas stream enters a two-stage Claus reactor system where H_2S and SO_2 react to produce elemental sulfur and water. At this point, product sulfur is again removed from the gas by condensation. Residual H_2S in the Claus plant effluent gas is oxidized to SO_2 by recycling the gas stream back to the boiler. The residual SO_2 is then recovered in the absorber of the original FGD recovery process.

According to the developer, this process can be applied directly to SO_2 streams containing as low as four percent SO_2 where the oxygen content is not over five percent. Processing streams with low SO_2 concentrations will, however, be very costly as compared to more concentrated streams. When higher oxygen concentrations are encountered, provisions must be made to dissipate the excess heat produced as a result of methane oxidation. The Canadian plant has demonstrated that this process is capable of converting better than 90 percent of the SO_2 from the entering gas stream. Operation at one-third of design capacity with constant operation efficiency has been established. The major disadvantage of this method of sulfur production is the need for methane as a reductant.

Since the availability of methane in the future is predicted to decrease substantially, a process using a CO/H_2 coal gasification reducing gas appears to be an attractive alternate route to elemental sulfur production. Allied Chemical has made a preliminary evaluation of using a CO/H_2 reducing gas. The primary reactions in such a process would be as follows:

$$2\ CO + SO_2 \longrightarrow 2\ CO_2 + 1/2\ S_2 \qquad (14\text{-}4)$$

$$2\ H_2 + SO_2 \longrightarrow 2\ H_2O + 1/2\ S_2 \qquad (14\text{-}5)$$

The configuration of such a process would probably be very similar to the present Allied Chemical process using methane reductant.

RESOX Process

The RESOX Process is a proprietary process developed by Foster Wheeler Corporation. Anthracite coal is used as a catalyst and reducing agent to convert 90 percent of the inlet

SO_2 to elemental sulfur. A flow diagram for this process is shown in Figure 14-3.

Countercurrent flow of the SO_2 and coal in a single reactor is used to effect the conversion. The overall reaction is:

$$C_{(s)} + SO_{2\,(g)} \xrightarrow[H_2O_{(g)}]{1100\text{-}1500°F} S_{(g)} + CO_{2\,(g)} \qquad (14\text{-}4)$$

The temperature in the reactor ranges from 1100-1500°F at the reaction front depending on the coal used and the composition of the gas feed. The ash and unreacted coal are removed at the bottom of the reactor.

Since roughly 50 percent of the coal is utilized in the reactor, the coal/ash stream leaving the reactor may possibly be combined with the coal feed to the power plant boiler to recover the heating value of the unreacted coal. The gas stream going overhead contains elemental sulfur, unreacted SO_2, steam, CO_2, and N_2. Small amounts of hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), perhaps some hydrogen (H_2), and possibly some carbon monoxide (CO) would also be present in the off-gas, depending on process parameters. A condenser is used to remove the elemental sulfur and the gas stream is then sent to an incinerator or to the power plant boiler to oxidize the various sulfur compounds and combined with the flue gas entering the SO_2 absorber.

BAMAG Process

The BAMAG Process is owned and operated by BAMAG Verfahrenstechnik Gmbh, a subsidiary of Davy International Limited. The process uses a proprietary catalyst to reduce SO_2

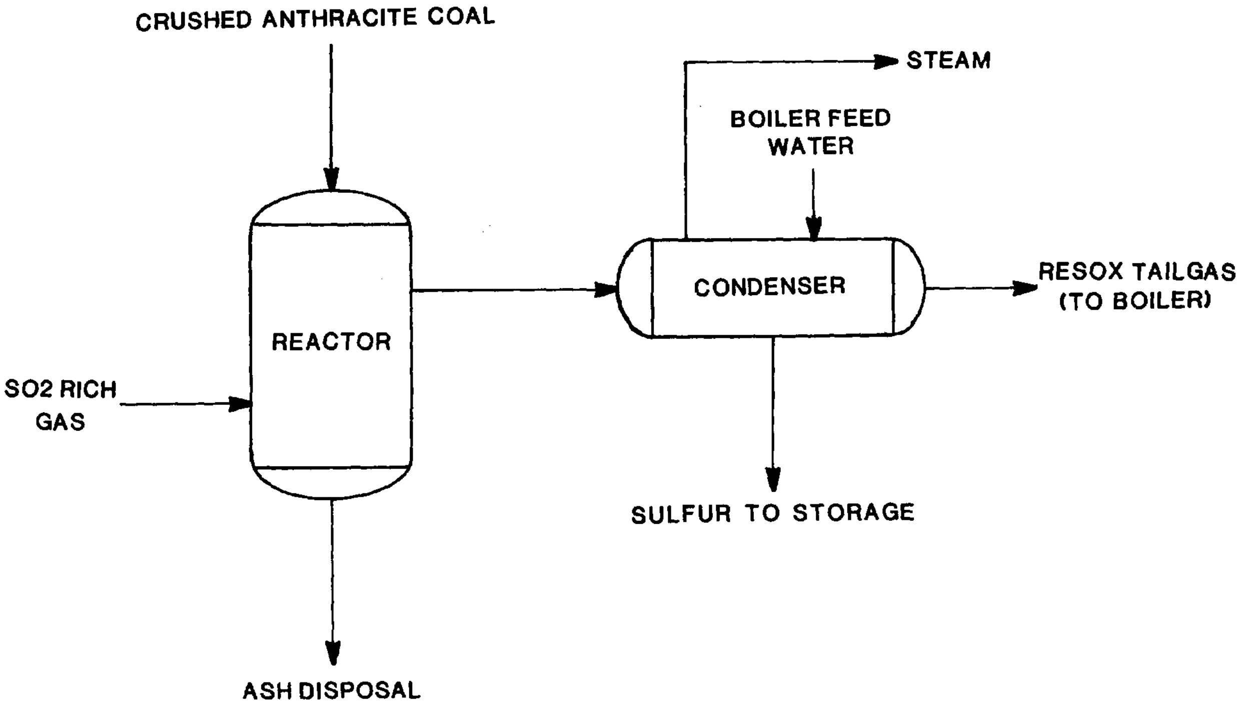


FIGURE 14-3

PROCESS FLOW DIAGRAM FOR THE RESOX PROCESS

to elemental sulfur using a medium Btu town gas. The gas is derived from a coking process and consists primarily of H_2, CH_4, and CO. A 90 percent conversion of SO_2 to sulfur has been demonstrated. The process is currently being used in Lunen, West Germany on the tail end of a 35 Mw capacity Bergbau-Forshung FGD unit on a coal-fired boiler.

14.2 Economics

The economic assessment of the sulfur and sulfuric acid production units included: (1) the initial capital investment, (2) raw material and utility costs, and (3) additional revenue that could be realized for various sulfur and acid selling prices. The economic estimates reported in this section were based on the operating parameters for the base case 500 MW power unit. The following assumptions were also made:

- 90 percent of the sulfur dioxide in the boiler flue gas is removed by the FGD Process.

- No costs for pretreating feed gas are included.

Sulfuric Acid Production

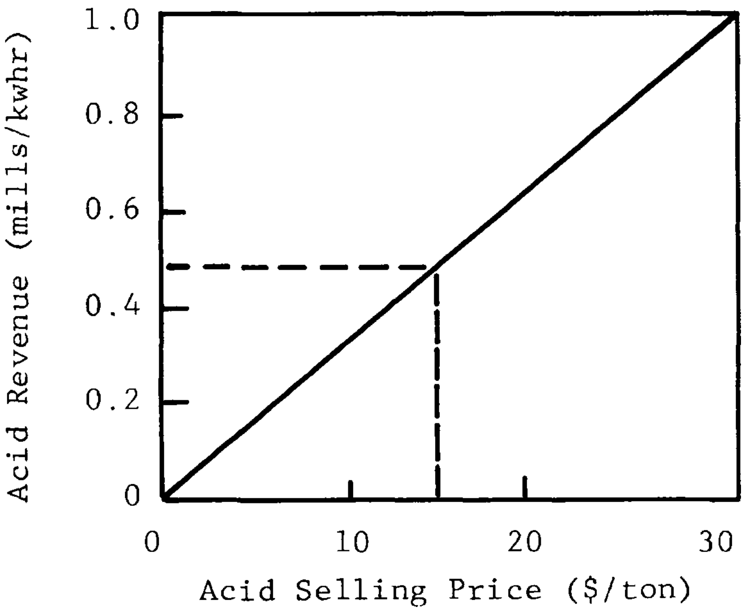
Economic data on sulfuric acid production was obtained from a report by Waitzman, et al. (WA-219). The following assumptions were also made:

- A 1.3 cost index factor, obtained from the CE Plant Cost Index (CH-278), was used to scale up the initial capital investment costs reported by Waitzman, et al. (WA-219) to current costs.

- The sulfur dioxide to sulfuric acid conversion efficiency of the acid plant is 97 percent (BR-283).
- The sulfur dioxide concentration in the feed gas to the acid plant is 9 volume percent.

From the base case operating parameters and the above assumptions, the sulfuric acid production rate was calculated to be 385 tons/day of 98 percent H_2SO . From Waitzman, et al, (WA-219) and the assumed cost index factors, the initial capital investment of an acid plant producing 385 tons/day would be approximately \$6,000,000 (\$11.9/kw). The required amount of catalyst for this acid plant would be 180 liters of catalyst/ton/day or 69,300 liters of catalyst. According to Browder (BR-272), the current cost of the catalyst is \$1.65/liter. Since the catalyst is the only raw material required by the acid plant, the total annual raw material cost would be the catalyst costs of \$114,000 (0.04 mills/kwhr). The acid plant's utility costs were estimated from the data reported by Waitzman, et al. (WA-219) to be 0.05 mills/kwhr. The main portion of the utility costs, approximately 80 percent, is due to electrical requirements. It should be emphasized that these low utility costs result from reduced heat requirements due to the heat recovered from the exothermic oxidation of sulfur dioxide to sulfur trioxide.

The annual revenue that would be realized from variations in sulfuric acid selling price (\$0/ton to \$30/ton) is illustrated in Figure 14-4. For example, if the sulfuric acid selling price is \$15/ton, the annual revenue from the product acid sales would be \$1,266,000/yr (0.48 mills/kwhr).



Basis:
- Base case 500 Mw power unit and acid plant.
- 90 percent removal of sulfur dioxide
- 97 percent acid plant SO_2 - H_2SO_4 efficiency.

FIGURE 14-4. ANNUAL REVENUE FOR VARIOUS SULFURIC ACID SELLING PRICES

Sulfur Production

Data provided from a TVA publication (MC-147) and an Allied Chemical publication (HU-051) were used as a basis for the economic estimates reported in this section. These data were scaled up from mid-1973 to current costs. The following assumptions were also made:

- The feed gas to the sulfur production unit contains 90 volume percent SO_2 and 10 volume percent H_2O.
- The sulfur dioxide to sulfur conversion efficiency of the Allied Chemical plant is 90 percent.

From the base case operating parameters and the above assumptions, the sulfur production rate was calculated to be 116 long tons/day of sulfur. Two different reducing gases were evaluated for use as reductants for the process; natural gas and coal gasification reducing gas. A comparison of the raw material and utility requirements with the associated costs using the two different reducing gases is shown in Table 14-1. As can be seen, the cost of the sulfur production process using a coal gasification reducing gas is about 5 times as expensive as the process using a natural gas reductant.

Raw material and utility costs for sulfur production is predominately governed by the price of the reductants. The price differential between using natural gas and a coal based reducing gas is expected to decrease with an increase in natural gas prices.

The capital cost is dependent upon the gas volume processed and the concentration of SO_2 in the inlet feed stream. Figure 14-5 shows the relationship of the total installed cost

TABLE 14-1

MATERIAL AND ENERGY REQUIREMENTS FOR THE ALLIED CHEMICAL SO_2 REDUCTION PROCESS

Basis: 500 MW, 3.5% S Coal, 90% SO_2 Removal Efficiency, 90% SO_2 In Sulfur Plant Feed Stream

Natural Gas Reductant	Quantity	Annual Cost	Percent of Total Annual Cost
Natural Gas	75 MM Btu/hr	$ 394,500	92
Electricity	322 KW	33,900	8
		428,400	
Heat Credit	12.9 MM Btu/hr	33,900	
		$ 394,500	

ANNUALIZED UTILITY AND RAW MATERIAL COST - 0.15 MILLS/KWHR

Coal Gasification Reducing Gas	Quantity	Annual Cost	Percent of Total Annual Cost
Reducing Gas	91.6 MM Btu/hr	$1,927,300	98
Electricity	322 KW	33,900	2
		1,961,200	
Heat Credit	12.9 MM Btu/hr	33,900	
		$1,927,300	

ANNUALIZED UTILITY AND RAW MATERIAL COST - 0.73 MILLS/KWHR

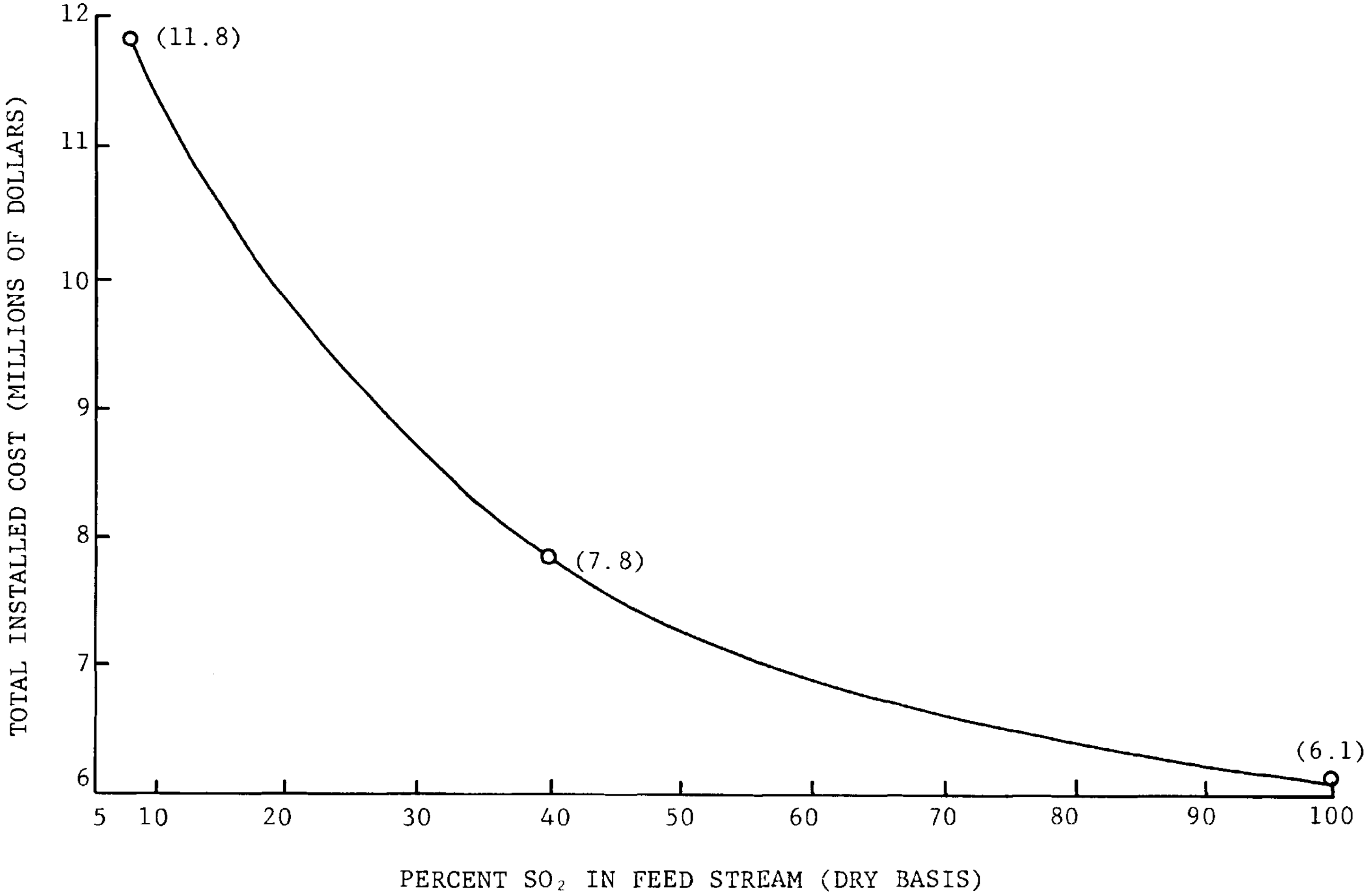


FIGURE 14-5. ALLIED CHEMICAL SO_2 REDUCTION TOTAL INSTALLED COST FOR A 500 MW BASE CASE UNIT (BATTERY LIMITS PLANT)

versus the SO_2 feed concentration for the base case 500 Mw plant. It can be seen that the capital cost increases rapidly when the SO_2 concentration drops below 40-50 percent (dry basis). This gives FGD systems delivering a concentrated SO_2 stream, such as the Wellman-Lord Process, an advantage over FGD systems delivering a low concentration SO_2 stream, such as the magnesia slurry.

The price of sulfur can vary widely and will depend on the price of available fuels and the amount of sulfur produced by FGD systems will tend to lower the price. Figure 14-6 shows the annual revenue obtained for the base case 500 Mw power plant versus the selling price of the sulfur product. High prices have recently been paid for elemental sulfur ($40-60/long ton). These prices would bring in an annual revenue of .39 to .58 mills/kwhr.

14.3 Suitability of the FGD Processes for Sulfuric Acid Production

In this section, the suitability of the eleven regenerable FGD processes for sulfuric acid production will be discussed. The discussion will be limited to acid production as the sulfur production aspects of these processes were discussed in Sections 1-12. The suitability for producing sulfuric acid will be based on the pretreatment steps required to bring the FGD process off-gas to the base case acid plant feed gas composition (9 volume percent SO_2, 9.2 wt percent O_2, and less than 9 volume percent H_2O).

All of the FGD processes can be divided into four categories with regards to sulfur and sulfuric acid processing: (1) processes that are suitable for production of both sulfur and sulfuric acid, (2) processes that are suitable for sulfuric

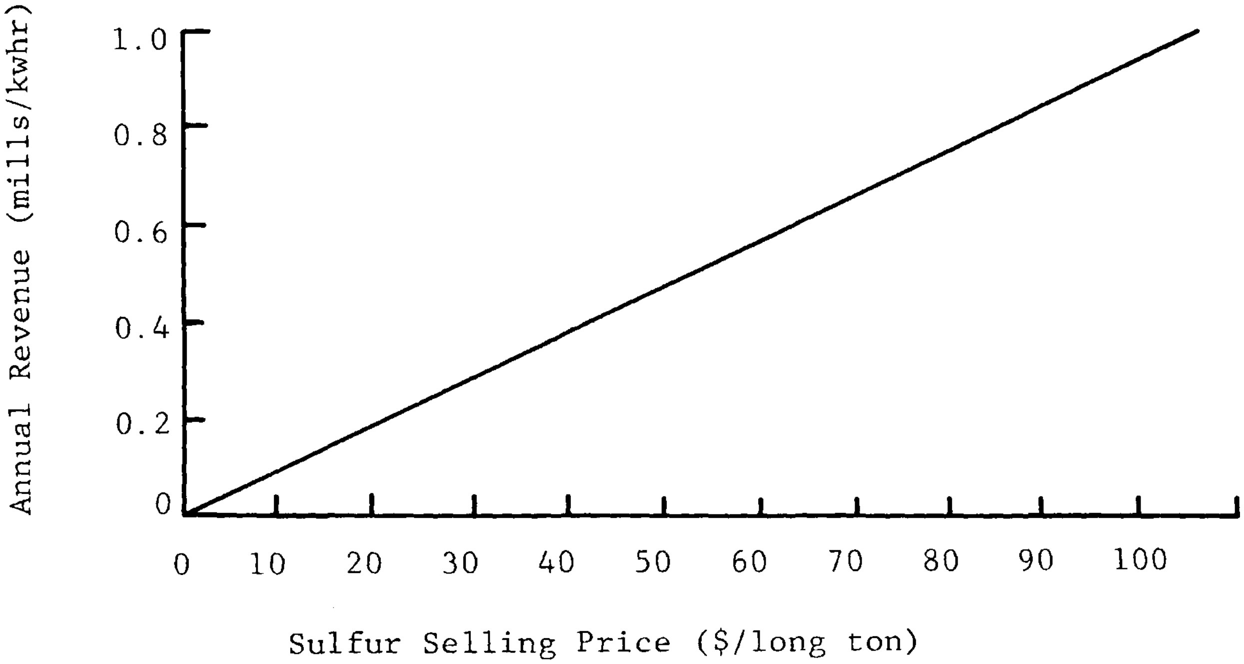


FIGURE 14-6 ANNUAL REVENUE FOR VARIATIONS IN SULFUR SELLING PRICE

acid production only, (3) processes suitable for sulfur production only, and (4) processes unsuitable for either sulfur or sulfuric acid production. Each of these categories will be examined in the following discussion.

14.3.1 Processes Suitable for Both Sulfur and Sulfuric Acid Production

Six of the twelve processes evaluated were found to be suitable for both sulfur and sulfuric acid production. These six processes are as follows:

1) Shell/UOP Copper Oxide Adsorption Process
2) Bergbau-Forschung/Foster Wheeler Dry Adsorption Process
3) TVA Ammonia - ABS Process
4) Ionics Electrolytic Regeneration Process
5) Wellman-Lord Sulfite Scrubbing Process
6) Magnesia Slurry Scrubbing Process

Each of these processes yields an SO_2 stream of varying concentrations, and is considered capable of producing sulfuric acid with a minimum of process modifications.

In addition, the Westvaco Process is potentially able to produce a suitable feed gas for sulfuric acid production by decreasing the amount of reducing gas fed to the process by less than one-half. This step has been piloted by Westvaco and their results indicated it to be a feasible and desirable process alternative. Table 14-2 discusses the FGD process changes and additional equipment needed to produce a sulfuric acid plant feed gas.

TABLE 14-2

FGD PROCESS MODIFICATIONS REQUIRED TO PRODUCE SULFURIC ACID PLANT FEED GAS

FGD Process	Acid Plant Feed Gas Composition Prior to Clean-Up	Feed Gas Cleanup Equipment Required	Comments
1) Shell/UOP Copper Oxide Adsorption Process			
a) Dilute SO_2 Stream	.Temperature = 150°F 6-15% SO_2 Major diluents are N_2, CO_2, H_2O. CO and CH_4 may also be present.	.Water Separator .Addition of air	.CO and CH_4 are reducing agents which could possibly have an undesirable effect upon catalyst performance in the acid plant. Excess air is added to the gas stream to oxidize the species to CO_2 and H_2O at the high temperatures in the acid plant converter.
b) Concentrated SO_2 Stream	.85% SO_2 .15% H_2O CO and CH_4 may be present	.Addition of air	
2) Bergbau-Forshung/ Foster Wheeler Dry Adsorption Process	.20% SO_2 60% H_2O 20% N_2+ CO_2	.Water Separator .Addition of air	
3) TVA Ammonia-ABS Process	.65% SO_2 7% O_2 1% H_2O Remainder - Primarily N_2	.Addition of air	
4) Ionics Electrolytic Regeneration Process	.85-90% SO_2 10-15% H_2O	.Addition of air	
5) Wellman-Lord Sulfite Scrubbing Process	.Temperature = 85-90°F 90% SO_2 10% H_2O	.Addition of air	
6) Magnesia Slurry Scrubbing Process	.Temperature = 1600°F .Typical composition (ZO-008) = 73% N_2 6% CO_2 5% O_2 7% H_2O 9% SO_2	.Cyclone and hot ESP to remove particulates .Waste heat boiler to recover heat .Addition of air	.Production of sulfuric acid from the Mag-Ox Process is proven technology. Over 5000 tons of 98 percent sulfuric acid was produced using $MgSO_3$ from two demonstration units.
7) Westvaco Activated Carbon Process	.Temperature = 300°F 10% SO_2 20% H_2O remainder is N_2, CO_2 particulates from the carbon bed are entrained in the gas stream	.ESP to remove particulates .Water separator to lower H_2O concentration below SO_2 concentration in the gas. .Addition of air	.Further development work appears warranted to demonstrate this process alternative.

14.3.2 Processes Suitable for Sulfuric Acid Production Only

The Cat-Ox process is the sole process which is suitable only for sulfuric acid production. The Cat-Ox process can only produce sulfuric acid due to the fact that the basic design of the process is very similar to the design of a sulfuric acid production unit. The product acid concentration produced by the Cat-Ox process is 78 percent H_2SO_4.

14.3.3 Processes Suitable for Sulfur Production Only

Three processes are suitable only for elemental sulfur production. These processes are:

1) Atomics International Aqueous Carbonate Process
2) Catalytic/IFP Ammonia Scrubbing Process
3) Citrate/Phosphate Buffered Absorption Process

The AI process produces a gas from the carbonation unit which is 35 percent H_2S, 10 percent CO_2, and 45 percent H_2O. This H_2S stream is sent to a Claus unit to produce elemental sulfur. It would be unwise to attempt to produce sulfuric acid from this process since the SO_2 is already reduced to H_2S.

The Catalytic/IFP Ammonia Scrubbing Process presently produces elemental sulfur in a "Liquid Claus" sulfur production unit. The H_2S required for the conversion is produced from a gasification product reducing gas and from SO_2 produced from the decomposition/reduction of the ammonium sulfite and sulfate compounds. It would not be feasible to produce sulfuric acid from the SO_2 stream because the feed gas would contain about 12 percent NH_3, 8 percent SO_2, 62 percent H_2O, and some H_2, CO, and sulfur vapor. The ammonia would be difficult to separate from the SO_2

stream. The H_2, CO, and sulfur vapor would have to be oxidized to H_2O, CO_2, and SO_2. Then the gas would have to be dried in order that 98 percent sulfuric acid could be produced. The combination of these three steps that are required for the preparation of an acid plant feed gas make the Catalytic/IFP process not well suited for acid production.

The Citrate/Phosphate Absorption process is not suited for sulfuric acid production as sulfur is produced in the regeneration step of the process.

14.3.4 Process That Is Not Suitable for Either Sulfur or Sulfuric Acid Production

The Lime/Limestone Wet Scrubbing Process is not suitable for either sulfur or sulfuric acid production. The process is currently a throwaway FGD process which produces a calcium sulfite/sulfate sludge. The calcium sulfite/sulfate sludge is disposed of in settling ponds or as landfill after dewatering. Regenerating the scrubber sludge generally requires high temperatures and large amounts of fuel to dehydrate and thermally decompose the calcium sulfite/sulfate. Section 15.0 discusses the different processes that can be used to regenerate lime/limestone scrubber sludge. High fuel costs make calcium sulfite/sulfate regeneration an unattractive alternative, although the technology to regenerate the sludge and produce sulfur, SO_2 or sulfuric acid is available. Therefore, the lime/limestone FGD process is not suitable for the production of sulfur or sulfuric acid due to the high operating cost of the sludge regeneration process.

14.4 Summary

Both sulfur and sulfuric acid are viable products from FGD processes. Economics will ultimately determine which product will be produced on a site-specific basis. The following points summarize the suitability of sulfur and sulfuric acid as by-products from the processes under evaluation.

1) Table 14-3 illustrates the suitability of the eleven regenerable FGD processes to produce sulfur or sulfuric acid. Seven of the processes are well suited for producing either sulfur or sulfuric acid. Although the Atomics International Aqueous Carbonate Process and the Catalytic/IFP Ammonia Scrubbing Process are able to produce both sulfur and sulfuric acid, significant feed gas pretreatment steps are required for acid production. The Cat-Ox Process produces only sulfuric acid, and the Citrate/Phosphate Process produces only sulfur. The Lime/Limestone Wet Scrubbing Process can be integrated with a sludge regeneration process to produce both sulfur and sulfuric acid, but the high cost of the regeneration reduces its suitability to produce either.

2) Neglecting the cost of feed pretreatment, the raw material and utility cost of sulfuric acid production is currently about one-half the cost of sulfur production when a natural gas reductant is used. It is about 12 percent of the cost of sulfur production when a coal

TABLE 14-3

SUITABILITY OF THE FGD PROCESSES TO PRODUCE EITHER SULFUR OR SULFURIC ACID

FGD Processes	Throwaway Process	Produces Sulfur Only	Produces Sulfuric Acid Only	Produces Sulfur and Sulfuric Acid
Westvaco Activated Carbon				x
Shell/UOP Copper Oxide				x
Bergbau Forschung/Foster Wheeler Dry Adsorption				x
Atomics International Aqueous Carbonate		x		
Catalytic/IFP Ammonia Scrubbing		x		
Citrate/Phosphate Buffered Absorption		x		
TVA Ammonia-Ammonium Bisulfate				x
Ionics Electrolytic Regeneration Process				x
Wellman-Lord Sulfite Scrubbing				x
Cat-Ox			x	
Magnesia Slurry Scrubbing				x
Lime/Limestone Wet Scrubbing	x			

gasification reducing gas is used. Sulfur production costs depend directly upon the cost of the reducing gas used while sulfuric acid costs depend primarily on capital charges. Table 14-4 summarizes these costs.

3) The principal disadvantage of the present Allied Chemical Sulfur Production Process is its requirement for natural gas as a reductant. To overcome this, Allied Chemical is preparing to offer a process which uses CO/H_2 Syngas. The RESOX Sulfur Process currently uses anthracite coal as a reductant; however, petroleum coke and devolatized bituminous coal are being considered as potential substitutes for anthracite coal.

4) Product marketability is more of a concern with sulfuric acid production than sulfur production. This is due to the handling and storage problems encountered with sulfuric acid which are not present with sulfur.

TABLE 14-4

ECONOMIC COMPARISON OF SULFUR AND SULFURIC ACID PRODUCTION

	Sulfur Production with Natural Gas Reductant (90% SO_2 feed)	Sulfur Production with Coal Gasification Reducing Gas (90% SO_2 feed)	Sulfuric Acid Production (9 vol. % SO_2 feed)
Capital Investment Cost ($/kw)	12.4	12.4 (estimated)	11.9
Annualized Capital Cost (mills/kwhr)	0.59	0.59 (estimated)	0.57
Raw Material and Utility Cost (mills/kwhr)	0.15	0.73	0.09
By-Product Selling Price ($/ton)	40.0	40.0	15.0
Annualized By-Product Revenue (mills/kwhr)	0.39	0.39	0.48
Net Cost to FGD Process (mills/kwhr)	0.35	0.93	0.18

15.0 THE DECOMPOSITION OF CALCIUM SULFITE/SULFATE INTO USABLE PRODUCTS

Processes that decompose calcium sulfate into commercially usable products have been investigated since World War I. Recently, with the higher cost of sulfur and sulfuric acid and the increased production of lime/limestone scrubber sludges, processes to decompose $CaSO_3$ and $CaSO_4$ into usable products have received renewed attention. The history and status of $CaSO_3/CaSO_4$ decomposition processes will be discussed in this section and a technical and economic evaluation of two of these processes will also be presented. This section is a result of a cursory review of the subject and is by no means exhaustive.

The stability of calcium compounds produced by lime/limestone FGD systems is an important criteria that should be considered in this evaluation. Calcium sulfate is a very stable compound and calcium sulfite is a moderately stable compound. As a result, the energy requirements to decompose the sulfite and sulfate will be greater than those for many other SO_2 sorbents. Furthermore, the temperature at which this energy must be added is higher than for many other sorbents. A comprehensive study of all metal oxide sorbents was made by Parsons et al. (PA-016).

As a consequence of this chemical stability, regeneration of calcium carbonate or calcium oxide from calcium sulfite and calcium sulfate will be attractive only if other SO_2 recovery processes have outstanding drawbacks in other process areas. Such drawbacks could be slow kinetics in the SO_2 scrubbing or regeneration section, the presence of a toxic intermediate in the process, or a high price and low absorbent availability coupled with an unacceptable loss or purge rate. It appears from the present status of FGD recovery processes that these potential drawbacks have not been a problem.

Materials containing large amounts of $CaSO_4$ such as natural anhydrite, natural gypsum, wet phosphoric acid plant filter cake, and lime/limestone scrubber sludges have been examined as possible supply sources for sulfur. Several processes have been developed to recover the sulfur values from these materials. These processes, listed below, are described in this section.

- Double Salt Precipitation
- Cement-Sulfuric Acid
- CO/H_2 Reduction
- Bacteriological Digestion
- U.S. Bureau of Mines
- Ontario Hydro
- Pullman Kellogg

Information concerning the first five processes was gathered from the available open literature. The last two processes, Ontario Hydro and Pullman Kellogg, are described using information supplied by the process developers. Material and energy requirements calculated by the process developers are also presented for these two processes.

15.1 Double Salt Precipitation

Recovery of sulfur as ammonium sulfate may be accomplished by double salt precipitation (MA-501). Processes which have been used to produce ammonium sulfate commercially have been developed by Merseberg, ICI, and OSW companies. In this method ammonia and carbon dioxide are first reacted by produce ammonium carbonate.

$$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3 \qquad (15\text{-}1)$$

Natural or by-product gypsum is reacted in an aqueous solution with ammonium carbonate to yield ammonium sulfate and calcium carbonate.

$$CaSO_4 \cdot 2H_2O + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4 + 2H_2O \qquad (15\text{-}2)$$

The process has the advantage that both the reaction yielding ammonium carbonate and ammonium sulfate are exothermic. Thus, the fuel requirements for decomposing the calcium sulfate are minimized. The process produces pure ammonium sulfate liquor or crystals and calcium carbonate. Heat is required to concentrate the liquor or for drying to produce ammonium sulfate crystals. This process is limited to applications where there is a need for ammonium sulfate fertilizer.

15.2 Cement-Sulfuric Acid

Recovery of sulfuric acid and cement by calcination with clinker-forming additives is the most widely used process employing a $CaSO_4$ feed (MA-501). The first cement-sulfuric acid plant was built at Leverkusen, Germany in 1916. In current times this recovery method has been used commercially in several European countries. Processes which have been used have been operated by OSW, Marachon, ICI, Chemieanlagen, Polimex, and United Sulfur Acid. A flow diagram of the process is shown in Figure 15-1.

In a typical dry cement production process the raw materials would include fly ash, sand, coke, and calcium carbonate. The raw materials are crushed, properly proportioned, ground, blended, and then fed to a kiln. The feed is calcined and burned in the kiln and converted into a material called clinker, the main constituent of cement.

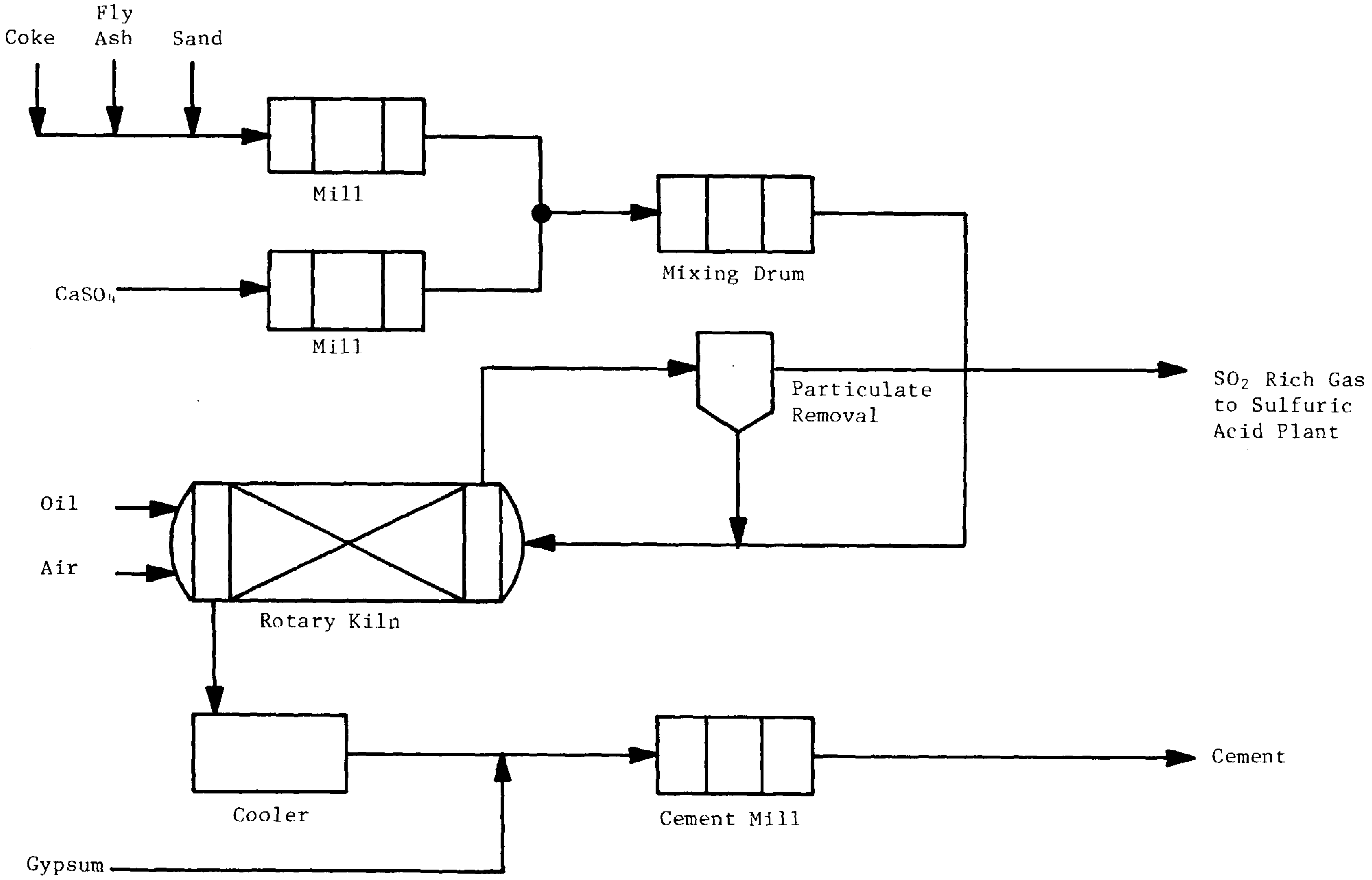


FIGURE 15-1

PROCESS FLOW DIAGRAM FOR THE CEMENT SULFURIC ACID PROCESS

In the cement-sulfuric acid process, calcium sulfate is the source of lime instead of calcium carbonate which is used in typical cement manufacture. Once the calcium sulfate is dissociated, the clinkering reaction is free to proceed as in the manufacture of portland cement. The calcium sulfate is reduced by coke according to the following reaction.

$$CaSO_4 + 2C \rightarrow 2CO_2 + CaS \qquad (15\text{-}3)$$

The calcium sulfide that is produced reacts with calcium sulfate to form lime and SO_2. High efficiency electrostatic precipitators and tail gas scrubbers are employed to remove all dust prior to introduction of the SO_2 gas stream to the acid plant.

$$3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2 \qquad (15\text{-}4a)$$

The $CaSO_3$ present in limestone scrubber sludges would be dissociated according to the following reaction.

$$CaSO_3 \rightarrow CaO + SO_2 \qquad (15\text{-}4b)$$

The lime reacts with the sand and fly ash to form clinker compounds.

$$2Ca + SiO_2 \rightarrow (CaO)_2 \cdot SiO_2 \qquad (15\text{-}5a)$$

$$3CaO + SiO_2 \rightarrow (CaO)_3 \cdot SiO_2 \qquad (15\text{-}5b)$$

$$3CaO + Al_2O_3 \rightarrow (CaO)_4 \cdot Al_2O_3 \qquad (15\text{-}5c)$$

$$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow (CaO)_3 \cdot Al_2O_3 \cdot Fe_2O_3 \qquad (15\text{-}5d)$$

Sulfur content of clinker, expressed as SO_3, can be limited to 1.5 per cent as in normal practice. Analysis of clinker samples indicate characteristics typical of portland cement produced from a calcium carbonate source of lime.

Coal, oil, or gas can be used as fuel and higher sulfur fuels can be used advantageously. Fuel consumption is somewhat higher than experienced in conventional cement kilns. The conventional cement process requires 700,000-900,000 Btu/bbl of cement whereas the cement-acid process requires about 1.2 million Btu-bbl. The reaction temperature in the kiln is around 2100°F. The kiln resembles a normal cement kiln except that higher temperatures and the corrosive atmosphere requires the use of specially resistant materials. A typical feed to the process contains 82.6 percent anhydrite, 7.4 percent fly ash, 5.9 percent coke, and 4.1 percent sand. The cement-sulfuric acid process requires about 40 percent of the fuel needed to produce elemental sulfur from calcium sulfate. This is because three atoms of oxygen must be removed from the sulfur to reduce $CaO \cdot SO_3$ to sulfur whereas only one atom of oxygen must be removed to produce SO_2. Production of sulfuric acid from either S or non-diluted SO_2 streams has the potential to proceed autothermally.

15.3 CO/H_2 Reduction

The recovery of SO_2 and lime from gypsum can be achieved by reduction with CO and H_2. A typical process is the Wheelock-Kent Feeds Process (WH-067) which has been tested on the pilot plant scale. In this process the feed containing $CaSO_4$ is heated in the presence of a reducing gas mixture produced by the partial combustion of a hydrocarbon fuel with air. A two-stage fluidized bed reactor is the proposed contacting device to carry out both the combustion reaction and the reductive decomposition reaction. The SO_2-rich gas stream leaving the reactor can be sent to a sulfur or sulfuric acid plant. The lime product is suitable for industrial use. A conceptual flow sheet for the process is given in Figure 15-2.

Hydrocarbon fuel is burned in the first stage of the reactor at 2200°F to produce a CO/H_2 reducing gas. The calcium sulfate enters the second stage of the reactor which operates at 1565°F and flows countercurrently to the combustion gases. As the calcium sulfate passes through the reducing zone it undergoes the following reactions.

$$CaSO_4 + CO \rightarrow CaO + CO_2 + SO_2 \qquad (15\text{-}6)$$

$$CaSO_4 + H_2 \rightarrow CaO + H_2O + SO_2 \qquad (15\text{-}7)$$

Moisture in the feed should be kept to a minimum since this will result in greater fuel requirements and reduced capacity.

Virtually all carbonaceous or hydrocarbon fuels may be used in the process. Fuels with a high sulfur content are advantageous since they increase SO_2 production. Fuels with a high ash content, however, could contaminate the lime product. Aside from these considerations, natural gas, fuel oil, and powdered coal should work equally well. The process, integrated with a sulfuric acid plant, would require about half of the fuel needed for processes yielding elemental sulfur.

Straight reduction decomposition of calcium sulfate has some limitations and must be carried out under carefully controlled conditions of temperature and gas composition. Sintering, incomplete decomposition, a slow rate of decomposition, and formation of CaS can all result when operating the system outside the optimum range of conditions. In order to overcome the limitations of straight reductive decomposition, a

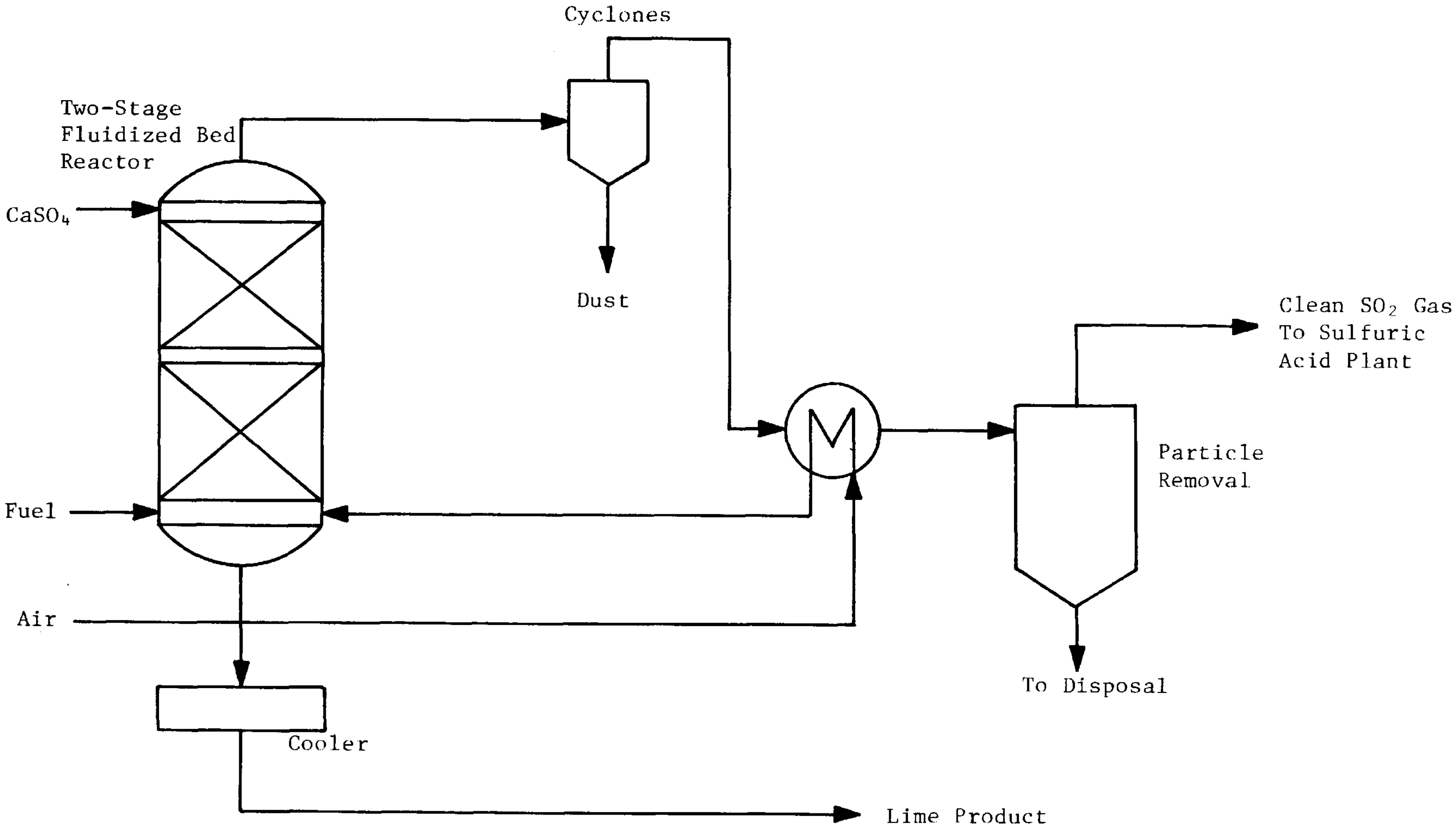


FIGURE 15-2

PROCESS FLOW DIAGRAM FOR THE
WHEELOCK-KENT FEED PROCESS

new process was conceived and tested on the bench scale by Swift and Wheelock (SW-028). In this process calcium sulfate is decomposed in a fluidized bed with two reaction zones where reducing conditions are maintained in one zone and oxidizing conditions in the other. The different zones are obtained by controlling the ratio of air to fuel in different parts of the bed. In the reducing zone the $CaSO_4$ is reduced to CaO and CaS by the following reactions.

$$CaSO_4 + CO \rightarrow CaO + CO_2 + SO_2 \qquad (15\text{-}6)$$

$$CaSO_4 + H_2 \rightarrow CaO + H_2O + SO_2 \qquad (15\text{-}7)$$

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2 \qquad (15\text{-}8)$$

$$CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O \qquad (15\text{-}9)$$

In the oxidizing zone the CaS is oxidized to CaO or $CaSO_4$.

$$CaS + 3/2O_2 \rightarrow CaO + SO_2 \qquad (15\text{-}10)$$

$$CaS + 2O_2 \rightarrow CaSO_4 \qquad (15\text{-}11)$$

Whereas calcium sulfide formation should not be tolerated in the old process, the new process has the advantage of a built-in mechanism for eliminating calcium sulfide. Since each particle is likely to pass through both reaction zones a number of times, any calcium sulfide produced in passing through the reducing zone is eliminated in subsequent passes through the oxidizing zone. In the same way, any calcium sulfate produced in the oxidizing zone is eliminated in the subsequent passes through the reducing zone. Without the need to prevent CaS formation, lower temperatures and higher concentrations of reducing gases can be employed than in the process of straight reductive decomposition.

15.4 Bacteriological Digestion of Gypsum

A process has been developed by J. L. Laseter and Associates, Houston, Texas that makes sulfur from gypsum by bacteriological action (GY-003). Gypsum is crushed and ground so that it will easily go into solution before being sent to a reaction tank along with an organic (hydrocarbon) substrate. This substrate can be a petroleum fraction; but molasses, brewery waste, and in many cases, raw sewage also work well. The bacteria must be fed by nutrients such as ammonia or ammonium salt. Phosphates may also have to be added.

The bacteria are anaerobic, so it is important to keep air out of the system. A hydrogen purging system is recommended since the presence of hydrogen markedly promotes fermentation. Removal of carbon dioxide (CO_2 tends to inhibit the work of the bacteria) helps control pH, which must be held between 7.6 and 8.0. The tanks also act as cells with a cell voltage of 150-200 millivolts. The temperature is kept between 77 to 95^{o}F and the tank must be stirred to prevent settling.

Part of the mix is withdrawn from the reactor and centrifuged and the solids are recycled back to the reactor. The liquid and the carbon dioxide and hydrogen sulfide gas stream generated in the tank are sent to a stripping tower where the gases are taken overhead and the bottoms discarded. The carbon dioxide is removed, such as in an amine system, and the resulting hydrogen sulfide gas is then converted into sulfur by conventional means.

A 115.6 long ton/day sulfur plant, the size of the base case plant, would require the equivalent of eight 500,000 gallon tanks. Seven tanks would be in service at any time, while the eighth was being cleaned. In addition to sulfur production, vitamins, such as B-12, steriods and other valuable by-products, could be recovered.

15.5 U.S. Bureau of Mines

The U.S. Bureau of Mines (GY-003) has worked on two processes to produce elemental sulfur from low-cost gypsum supplies, such as phosphoric-acid by-product. One process (labeled Process A) produces sulfur and calcium carbonate. Another process (labeled Process B) produces sulfur, sodium carbonate, and calcium chloride. These processes are illustrated in Figure 15-3.

In Process A, gypsum is reduced in a rotary kiln or fluidized bed reactor to calcium sulfide.

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \tag{15-3}$$

The sulfide is ground and mixed with water. Then, saturated flue gas containing carbon dioxide is passed countercurrently through the slurry, reacting with the calcium sulfide to form calcium carbonate and hydrogen sulfide. The hydrogen sulfide off-gas is processed by conventional means to form sulfur.

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S \tag{15-12}$$

The process recovers about 90 percent of the sulfur in the gypsum feed. The technique is not new, being used in Europe in the latter part of the last century before falling victim to low free-sulfur prices.

Process B has the advantage of producing sodium carbonate, a valuable by-product. Gypsum is again converted to calcium sulfide by heat in a reducing atmosphere.

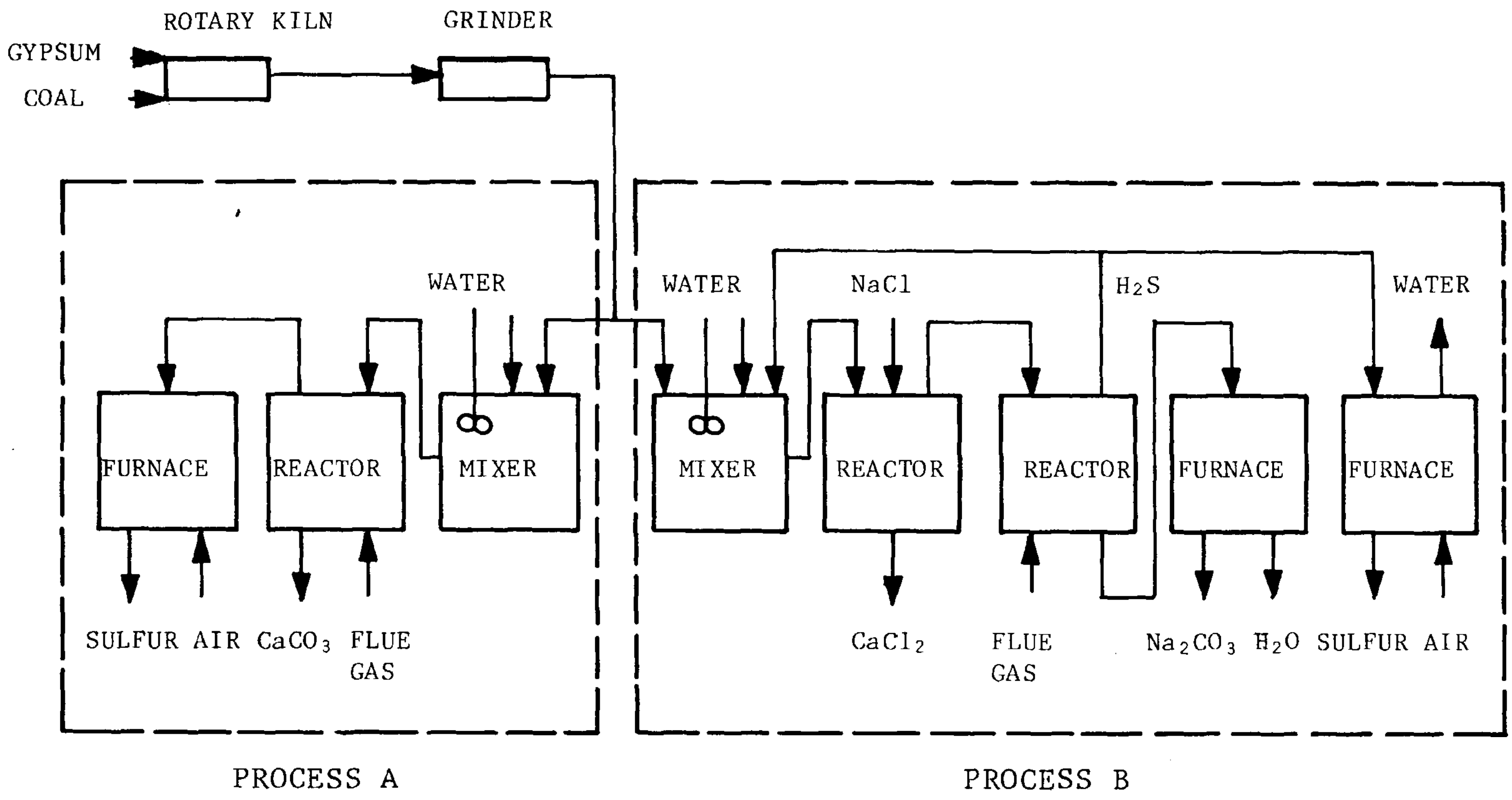


FIGURE 15-3. PROCESS FLOW DIAGRAM FOR BUREAU OF MINES PROCESSES TO PRODUCE SULFUR FROM GYPSUM

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \qquad (15\text{-}3)$$

After grinding the calcium sulfide it is dissolved in water with some hydrogen sulfide (recycled from a later step) to produce a calcium hydrosulfide solution.

$$CaS + H_2S \rightarrow Ca(SH)_2 \qquad (15\text{-}13)$$

This solution is reacted with sodium chloride to yield sodium hydrosulfide and calcium chloride.

$$Ca(SH)_2 + 2NaCl \rightarrow 2NaHS + CaCl_2 \qquad (15\text{-}14)$$

The calcium chloride can be sold or further processed to convert the calcium and chlorine to useful or disposable forms.

When the sodium hydrosulfide is carbonated with flue gas, sodium bicarbonate precipitates and hydrogen sulfide is given off. Part of the hydrogen sulfide is burned to give sulfur. The remainder is recycled for reaction with calcium sulfide.

$$NaHS + CO_2 + H_2O \rightarrow NaHCO_3 + H_2S \qquad (15\text{-}15)$$

The bicarbonate is then thermally converted to sodium carbonate (soda ash).

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \qquad (15\text{-}16)$$

Three tons of soda ash are made for each ton of sulfur. The current price for Na_2CO_3 is in the neighborhood of $52/ton, thus significant revenue could be obtained from both products.

15.6 Ontario Hydro

The Ontario Hydro process to regenerate limestone scrubber sludge has been tested on the bench scale stage since early in 1973. Results from the laboratory work indicate that the process is technically feasible. Ontario Hydro, however, does not plan to develop the process further at this time (MO-198). A flow diagram of the process is shown in Figure 15-4.

In this process, dewatered $CaSO_3/CaSO_4$ sludge from a limestone scrubber is thermally decomposed to calcium sulfide in a dryer/calciner. The temperature is maintained near $1800^{\circ}F$ by combustion of fuel oil and either coal or coke can be used as the carbon reducing agent.

$$CaSO_4 + 2C \rightarrow CaS + CO_2 \qquad (15\text{-}21)$$

The calcium sulfide product is then slurried with water and carbonated at $125^{\circ}F$ with the off-gas from the dryer/calciner.

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S \qquad (15\text{-}22)$$

The calcium carbonate product from the carbonator is recycled for use in the SO_2 scrubber. The gas stream from the carbonator contains hydrogen sulfide which can be treated in a Claus unit to produce elemental sulfur. Products from the process are elemental sulfur and a $CaSO_3/CaSO_4$ sludge purge stream which must be bled off to maintain a low level of inert material in the system.

A material and energy balance provided by Ontario Hydro was extrapolated to the Radian base case conditions. The material and energy requirements and the annual operating cost for the limestone recovery process are shown in Table 15-1. The

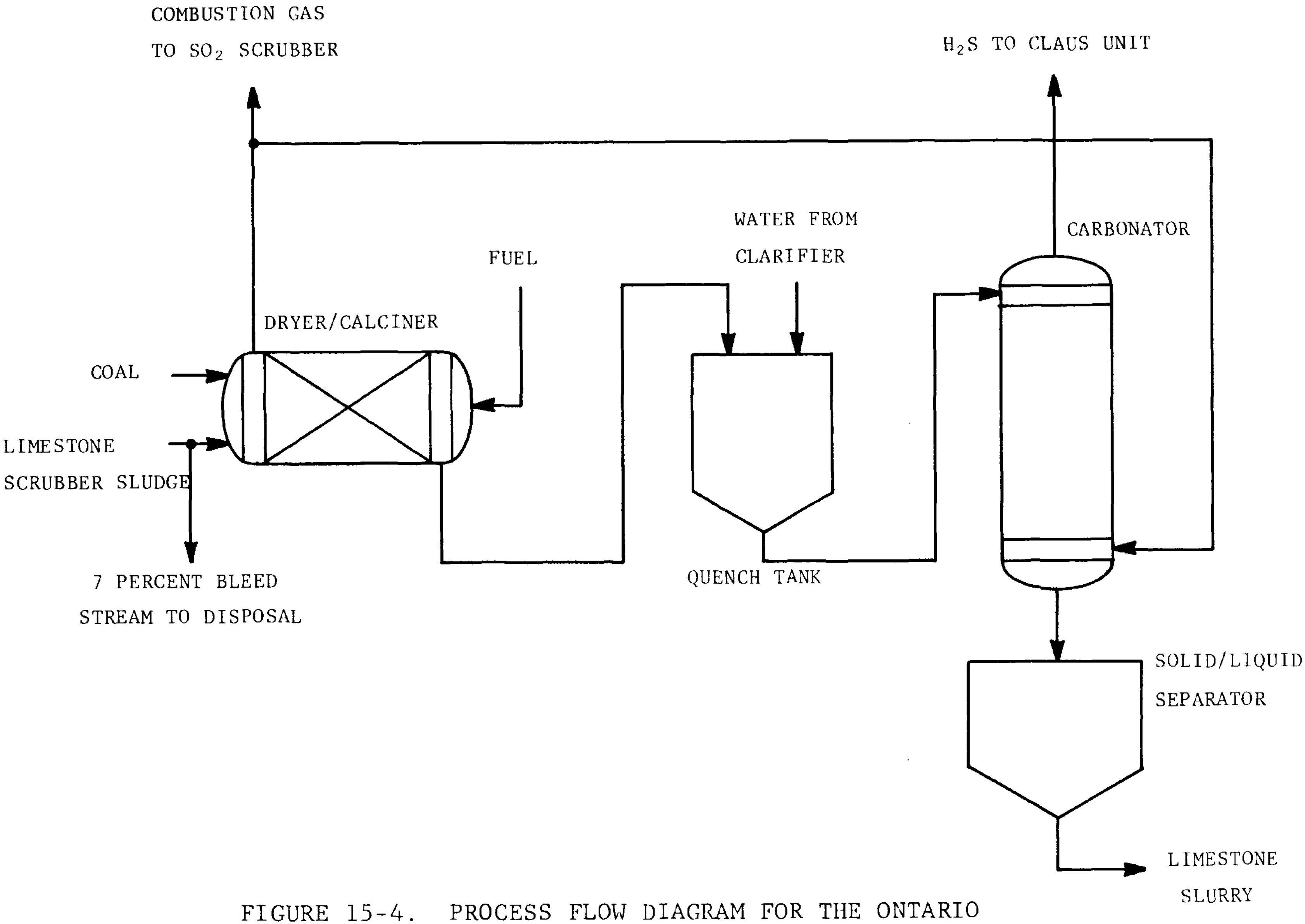


FIGURE 15-4. PROCESS FLOW DIAGRAM FOR THE ONTARIO HYDRO LIMESTONE REGENERATION PROCESS

TABLE 15-1

RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE ONTARIO HYDRO $CaSO_3/CaSO_4$ REGENERATION PROCESS

Basis: 500 Mw, 3.5 Weight Percent Sulfur, 90 Percent SO_2 Removal, 5,260 hr/yr

CASE 1: No. 6 Fuel Oil Used in Dryer/Calciner	Quantity	Annual Cost	Percent of Total Annual Cost
Coal (for reduction)	155 MM Btu/hr	815,000	17
No. 6 Fuel Oil	310 MM Btu/hr	3,859,000	82
Make-Up Limestone	12,700 tons/yr	51,000	1
		$4,725,000	

Equivalent to 1.8 mills/kwhr

CASE 2: Coal Used in Dryer/Calciner	Quantity	Annual Cost	Percent of Total Annual Cost
Coal	474 MM Btu/hr	2,493,000	98
Make-Up Limestone	12,700 tons/yr	51,000	2
		$2,544,000	

Equivalent to 1.0 mills/kwhr

table does not include the cost for processing the SO_2 produced by the limestone regeneration process.

The process is extremely energy intensive. About 474 MM Btu/hr are required in the process for the dryer/calciner and carbonator. This is equivalent to 10.5 percent of the energy requirement for the 500 Mw coal-fired boiler or 53 Mw.

The process, because of its high energy usage, has a high operating cost. When using No. 6 fuel oil to fire the dryer/calciner the operating cost is 1.8 mills/kwhr. This is over twice the operating cost of a conventional limestone scrubbing process with on-site disposal. If coal can be used in the dryer/calciner for both the reducing and heat requirements the operating cost would be approximately 1.0 mills/kwhr, almost half as much as when fuel oil is used. Coal would be greatly preferred in this process because of its price of $1.00/MM Btu versus $2.30/MM Btu for No. 6 fuel oil.

The process produces a limestone sludge waste stream that must be bled off to maintain a low level of inert material in the system. About 7 percent of the sludge that is sent to the regeneration process must be bled off and sent to disposal. This amounts to 40,000 tons/yr of scrubber sludge made up of 45 weight percent solids.

The regenerated calcium carbonate was found to be a suitable sorbent for the removal of SO_2 from flue gases. However, the regenerated calcium carbonate was found to be about 13 percent less efficient, as a sorbent, than limestone. The reactivity of the regenerated carbonate decreases about 8 percent in the first regeneration, 4.5 percent in the second, and very little further in subsequent cycles.

Independent of the number of recyclings, the reductive roasting results in 93-96 percent conversion of sulfate and sulfite to sulfide. The carbonation of calcium sulfide results in more than 98 percent conversion to calcium carbonate. The overall efficiency of the two regeneration steps ranges between 91 and 95 percent.

15.7 Kellogg's $CaSO_3/CaSO_4$ Regeneration Process

The Pullman Kellogg Kel-S Process was developed to regenerate limestone and recover SO_2 or sulfur for a limestone SO_2 removal process. A U.S. patent was obtained on the chemistry of the process in 1971 (SU-083), but process development was not pursued because the economics of the process were not favorable. However, due to increasing sulfur prices, Kellogg has decided to resume testing of the process. They are currently proposing to do pilot scale work for EPA. A flow diagram for the process is shown in Figure 15-5.

Spent limestone scrubber sludge is dewatered and first sent to the reduction reactor. The sludge should be dewatered as much as possible by physical means (i.e., centrifuge, vacuum filtration) to reduce the evaporation heat requirement in the reduction reactor. The reductant can be produced from a relatively cheap fuel source such as coal. Combustion of the fuel to produce the reducing gas takes place in the reduction reactor to minimize equipment and for maximum heat utilization.

When coal is used as a reductant source a temperature of 1600-2000°F is normally used in the reactor. The reduction which takes place is as follows:

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \qquad (15\text{-}23)$$

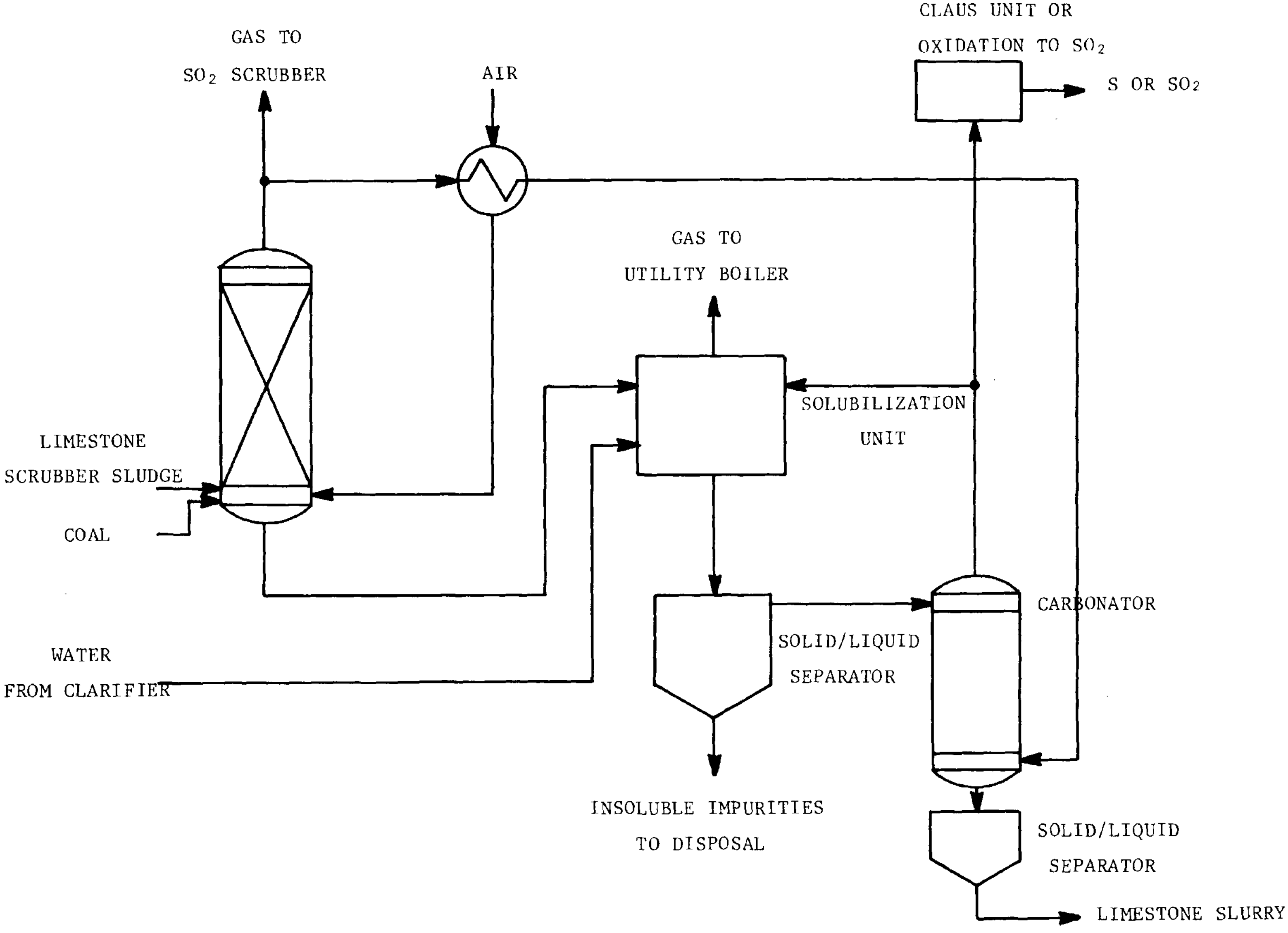


FIGURE 15-5. PROCESS FLOW DIAGRAM FOR THE PULLMAN-KELLOGG KEL-S PROCESS

Coal is used in 50 percent excess over the reduction requirement to help supply the necessary heat to the reaction. The coal is mixed with the calcium waste solids in the reactor. Fuel oil is burned in the reactor to help maintain the high temperatures necessary for the reduction reaction and also supplies some of the heat of reaction.

The CaS product from the reactor is sent to the solubilization unit. Here an H_2S stream is reacted with the CaS in the aqueous phase to produce calcium hydrosulfide.

$$CaS + H_2S \xrightarrow{(H_2O)} Ca(SH)_2 \text{ solution} \qquad (15\text{-}13)$$

The $Ca(SH)_2$ is soluble in water enabling it to be separated from the fly ash and insoluble impurities by filtration, centrifuge, or settling.

After removal of the insoluble impurities, the $Ca(SH)_2$ is sent to a carbonation unit. A portion of the reactor off-gas is reacted with the dissolved $Ca(SH)_2$ solution to produce $CaCO_3$.

$$Ca(SH)_2 + H_2O + CO_2 \rightarrow CaCO_3 + 2H_2S \qquad (15\text{-}17)$$

The temperature in the carbonation unit is near the boiling point of the solution which is about 220°F. The temperature in the solubilization and carbonation unit is maintained so that the aqueous reaction is carried out in the liquid phase.

In the carbonation unit a 60 percent H_2S stream is produced. Approximately half of the outlet H_2S stream is sent to the solubilization unit to produce $Ca(SH)_2$ and the other half is sent to a Claus unit to produce sulfur or to a furnace to produce a 6-8 percent SO_2 stream at about 1500°F. The SO_2 could be used as a feed stream to a sulfuric acid plant.

The raw material and energy requirements for the process were calculated by Pullman Kellogg for the Radian 500 Mw base case plant. The results of the calculations are shown in Table 15-2. The coal requirement for the reduction reactor is the major expense for the process, representing 87 percent of the annual cost. The coal is used as both a reducing agent and heat source in the reactor. The annualized raw material and utility requirements come to 0.8 mills/kwhr. This cost is a substantial addition for a limestone scrubbing process since the raw material and utility cost for the entire throwaway process is only 0.8 mills/kwhr. It should be noted that the cost for processing the H_2S produced in the regenerative limestone process is not included in this evaluation.

The process produces a solid waste stream of insoluble impurities which are separated from the soluble calcium hydrosulfide stream prior to the carbonation unit. The solid waste production for the 500 Mw Radian base case plant amounts to about 27,000 tons/yr. The primary constituents of the waste stream are calcium compounds and ash.

15.8 Energy Consumption

In order to determine the theoretical energy consumption for lime/limestone regeneration processes, a detailed material and energy balance was performed for several regeneration schemes. The energy requirements were calculated on the basis of regenerating a useful SO_2 sorbent and producing an SO_2-rich off-gas. Two cases were chosen:

TABLE 15-2

RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE KEL-S PROCESS

Basis: 500 Mw Plant, 3.5 Weight Percent Sulfur Coal, 90 Percent SO_2 Removal, 5,260 hr/yr

	Quantity	Annual Cost	Percent of Total Annual Cost
Coal	326 MM Btu/hr	1,715,000	87
Fuel Oil	30.8 MM Btu/hr	162,000	8
Process Water	25.0 Mgal/hr	11,000	1
Cooling Water	397 Mgal/hr	63,000	3
Make-up Limestone	3,170 tons/yr	13,000	1
		$1,964,000	

Equivalent to 0.8 mills/kwhr

1) Production of CaS followed by carbonation (U.S. Bureau of Mines, Ontario Hydro, Pullman Kellogg-Kel-S Process).

2) CO/H_2 Reduction - Production of SO_2 and lime (Wheelock-Kent Feed Process).

The calculations were performed for the base case conditions defined in this study. The lime and limestone waste sludge was taken to be 65 weight percent solids and typical feed compositions were used. The inlet stoichiometry to the scrubber was taken to be 1.0 moles CaO/mole SO_2 for the lime case and 1.2 moles $CaCO_3$/mole SO_2 for the limestone case. A rough estimation was made for some of the enthalpy and heat capacity data, but the error introduced into the calculations by these estimations were not significant for this study. Tables 15-3 and 15-4 show the results of these calculations.

The material and energy balances show that the limestone regeneration scheme is slightly lower than the lime. This is because more heat is required to reduce the calcium species to CaO in the lime scheme than to reduce the calcium species to CaS in the limestone scheme. The limestone utilization in the scrubber can be lowered to approach the lime utilization by employing more expensive feed preparation. This would further lower the energy requirements for the limestone case by decreasing the amount of unreacted $CaCO_3$ in the sludge. Assuming an overall dryer and calciner efficiency of 30 percent, the regeneration energy requirement would be 297 MM Btu/hr for the limestone system and 319 MM Btu/hr for the lime system. Assuming that coal was used as the fuel and reducing agent, the annual energy cost for the regeneration systems would be about 0.6 mills/kwhr.

TABLE 15-3

THEORETICAL HEAT REQUIREMENT FOR DRYING AND CALCINING LIMESTONE SCRUBBER SLUDGE

Basis: 500 Mw, 3.5 Percent Sulfur, 90 Percent SO_2 Removal,
1.2 $CaCO_3/SO_2$ (inlet) mole ratio in scrubber, 5,260 hr/yr,
Limestone Sludge is 65 Weight Percent Solids

Component	Quantity (lb/hr)	Heat Requirement	$\bar{C}_p$ (Btu/lb°F)	Btu/lb	MM Btu/hr
$CaSO_3 \cdot \frac{1}{2}H_2O$	39.938	Heating from 41° to 437°F	0.231	91.3	3.65
		Loss of hydrated water		86.8	3.47
$CaSO_4 \cdot 2H_2O$	4,705	Heating from 41° to 437°F	0.186	73.6	0.35
		Loss of hydrated water		301.1	1.42
$CaCO_3$	14,096	Heating from 41° to 437°F	0.229	90.6	1.28
Water	31,629	Heating from 41° to 212°F	1.0	171.0	5.41
		Heat of evaporation		970.3	30.69
			TOTAL HEAT FOR DRYING		46.27
$CaSO_3$	37,152	Heating from 437° to 1800°F	0.273	372.1	13.82
$CaSO_4$	3,720	Heating from 437° to 1800°F	0.277	377.6	1.40
$CaCO_3$	14,096	Heating from 437° to 1800°F	0.287	391.2	5.51
Coal	7,138	Heating from 41° to 1800°F	0.230	404.6	2.89
($CaSO_3$ basis)	37,152	$CaSO_3 \rightarrow 3/4CaSO_4 + 1/4CaS$		-134.7	-5.00
($CaSO_4$ basis)	35,295	$CaSO_4 + 2C \rightarrow CaS + 2CO_2$		401.5	14.17
($CaCO_3$ basis)	14,096	$CaCO_3 \rightarrow CaO + CO_2$		702.0	9.90
			TOTAL HEAT FOR CALCINER		42.69
		TOTAL HEAT REQUIREMENT FOR DRYER, CALCINER			88.96

TABLE 15-4

THEORETICAL HEAT REQUIREMENT FOR DRYING AND CALCINING LIME SCRUBBER SLUDGE

Basis: 500 Mw, 3.5 Percent Sulfur, 90 Percent SO_2 Removal,
1.0 CaO/SO_2 (inlet) mole ratio in scrubber, 5,260 hr/yr,
Lime Sludge is 65 Weight Percent Solids

Component	Quantity (lb/hr)	Heat Requirement	$\bar{C}_p$ (Btu/lb°F)	Btu/lb	MM Btu/hr
$CaSO_3 \cdot \frac{1}{2}H_2O$	39,938	Heating from 41° to 437°F	0.231	91.3	3.65
		Loss of hydrated water		86.8	3.47
$CaSO_4 \cdot 2H_2O$	4,705	Heating from 41° to 437°F	0.186	73.6	0.35
		Loss of hydrated water		301.1	1.42
$CaCO_3$	6,011	Heating from 41° to 437°F	0.229	90.6	0.54
Water	27,275	Heating from 41° to 212°F	1.0	171.0	4.66
		Heat of evaporation		970.3	26.46
			TOTAL HEAT FOR DRYING		40.55
$CaSO_3$	37,152	Heating from 437° to 2200°F	0.288	507.6	18.86
$CaSO_4$	3,720	Heating from 437° to 2200°F	0.296	521.6	1.94
$CaCO_3$	3,368	Heating from 437° to 2200°F	0.287	391.2	2.35
Coal	189	Heating from 41° to 2200°F	0.230	496.6	0.09
($CaSO_3$ basis)	37,152	$CaSO_3 \rightarrow CaO + SO_2$		665.7	24.73
($CaSO_4$ basis)	3,720	$CaSO_4 + \frac{1}{2}C \rightarrow CaO + SO_2 + \frac{1}{2}CO_2$		759.2	2.82
($CaCO_3$ basis)	6,011	$CaCO_3 \rightarrow CaO + CO_2$		702.0	4.22
			TOTAL HEAT FOR CALCINER		55.01
		TOTAL HEAT REQUIREMENT FOR DRYER, CALCINER			95.56

It is important to separate the dryer heat requirement from the calcination or reduction heat requirement. The energy required to heat and evaporate the free water in the feed to the dryer represents about one-third of the total energy requirement. Therefore, the most efficient dewatering device available should be used in conjunction with these processes. If it were possible to increase the solids content of the lime and limestone waste sludge to 90 weight percent solids, an energy savings of about 9-10 MM Btu/hr would result.

15.9 Summary

Seven basic methods of recovering sulfur values from a $CaSO_3/CaSO_4$ feed were found to be available or in the development stage. Table 15-5 is a summary of the characteristics of the different processes.

All but one of the processes, the bacteriological digestion process, require large amounts of fuel or highly priced chemicals. The double salt precipitation method requires ammonia or ammonium salt while the other four regeneration methods require coal or fuel oil for heating and reducing.

The regeneration method which shows the most promise for application to FGD systems is production of CaS followed by carbonation. The method was used commercially during the latter part of the last century so that its technical feasibility has been established. The three processes utilizing this method suffer from the amount of fuel and reducing agent required to reduce the $CaSO_3/CaSO_4$ feed. High temperatures are also required for both the lime system (2200°F) and limestone system (1800°F). Expensive materials of construction are associated with these high operating temperatures. With the trend to higher fuel

TABLE 15-5

SUMMARY OF THE CHARACTERISTICS OF PROCESSES FOR THE REGENERATION OF $CaSO_3/CaSO_4$

Process	Feed Requirements	Products	Status of Development	Comments
(1) Double Salt Precipitation	Ammonia, Carbon Dioxide	Ammonia Sulfate, Calcium Carbonate	Commercial	Can only be used where there is a need for ammonium sulfate fertilizer
(2) Cement-Sulfuric Acid Process	Fly Ash, Coke, Sand	Cement, Sulfuric Acid	Commercial	
(3) CO/H_2 Reduction (Wheelock-Kent Feed Process)	CO/H_2 Reducing Gas	Lime, Sulfur Dioxide	Pilot Plant	High fuel requirement
(4) Bacteriological Digestion	Hydrocarbon Substrate (can be a petroleum fraction, brewery waste, or raw sewage in many cases)	Sulfur, Vitamins, Steriods, Other Valuable By-Products		
(5) U.S. Bureau of Mines Process (a) Production of limestone and sulfur	Coal	Calcium Carbonate, Sulfur	Used commercially in Europe in the latter part of the last century	High fuel requirement
(b) Production of soda ash and sulfur	Coal, Sodium Chloride	Sodium Carbonate, Sulfur, Calcium Chloride		High fuel requirement, can only be used where there is a market for soda ash and calcium chloride
(6) Ontario Hydro	Fuel Oil, Coal	Calcium Carbonate, Sulfur or Sulfuric Acid	Bench Scale	High fuel requirement
(7) Pullman Kellogg Kel-S Process	Coal, Fuel Oil	Calcium Carbonate, Sulfur or Sulfuric Acid	Pilot plant work proposed	High fuel requirement, insoluble impurities can be easily removed

costs it is unlikely that a regenerable lime or limestone FGD process could be competitive with other regenerable FGD recovery processes.

16.0 INFORMATION SOURCES

16.1 Bibliography

The information for this report was obtained from two types of sources. Basic information on process descriptions, development status, and design and operating problems was gathered by a thorough search of the open literature. More detailed information on stream compositions, temperatures, extents of reaction needed for heat and material balances, and on more subtle design problems was obtained under secrecy agreements with the vendors. Those items in the bibliography which are not part of the open literature are annotated with a description of their source and general content.

Westvaco Activated Carbon Process

AV-011 Avery, D. A. and D. H. Tracey, "The Application of Fluidized Beds of Activated Carbon to Solvent Recovery from Air or Gas Streams," Inst. Chem. Engrs, Symposium Series No. 30, 28 (1968).

BA-003 Bartok, W., et al., Systems Study of Nitrogen Oxide Control Methods for Stationary Sources, Final Rept. Vol. 1, PH-22-68-55, Esso Research and Engineering Co., Linden, NJ (1969).

BA-254 Ball, F. J., et al., "Westvaco Activated Carbon Process for SO_x Recovery as Elemental Sulfur," Presented at the Symposium on Flue Gas Desulfurization, Atlanta, GA, November 1974, Westvaco Corp., N. Charleston, S. Carolina (1974).

HA-402 Hampel, Clifford A. and Gessner G. Hawley, eds., *The Encyclopedia of Chemistry*, 34d ed. Van Nostrand Reinhold, NY (1973).

KU-001 Kunii, D. and O. Levenspiel, *Fluidization Engineering*, Wiley, NY (1969).

RO-204 Rowson, H. M., "Fluid Bed Adsorption of Carbon Disulphide," *Brit. Chem. Eng. 8* (3), 180 (1963).

ST-293 Stuebner, D. O., Private communication, Radian Corp., with S. L. Torrence of Westvaco Corp. concerning reducing gas requirements, carbon consumption, NO_x removal, adsorber pressure drop, and production of SO_2 rather than sulfur (7 August 1975).

WE-184 Westvaco Corporation, *Development of Westvaco Activated Carbon SO_x Sorption and Sulfur Recovery Process*, Final Report Draft, Contract No. 68-02-003, N. Charleston, SC, (December 1974). Contains detailed heat and material balance information including stream compositions for a 1000 Mw plant burning 3.5% sulfur coal, in addition to complete test results from 3½ years of development work.

Shell/UOP Copper Oxide Adsorption Process

DA-030 Dautzenberg, F. M., J. E. Nader, and A. J. J. von Ginneken, "Shell's Flue Gas Desulfurization Process," *Chemical Engineering Progress 67* (8), 86-91 (1971).

DA-147 Dautzenberg, F. M., J. E. Naber and A. J. J. von Ginneken, "The Shell Flue Gas Desulphurization Process," paper 31d, Presented at the 68th National AIChE Mtg., Houston, TX (1971).

NA-226 Naber, J. E., J. A. Wesselingh, and W. Gorenendaal, "The Shell Claus Off-Gas Treating Process," *CEP 69* (12), 29 (1973).

PO-109 Pohlenz, J. B., "The Shell Flue Gas Desulfurization Process," Presented at the Flue Gas Desulfurization Symposium, Atlanta, GA, November 1974, Universal Oil Products Co., Des Plaines, IL (1974).

SC-341 Schneider, Gilbert G., et al., "Selecting and Specifying Electrostatic Precipitators", *Chem. Eng. 82* (May 26), 94 (1975).

SL-062 Slack, A. V., *Process Evaluation, Shell Copper Oxide Process for Flue Gas Desulfurization*, SAS Corp., Sheffield, Alabama (March 1975).

SL-065 Slack, A. V., Private communication, Shell/UOP Process (July 1975). Information received included a heat and material balance for a 100 Mw plant burning 2.5% sulfur coal but stream composition and kinetic data was unavailable. Other data included were a detailed flowsheet with temperature and pressures.

UN-030 Universal Oil Products Company, *Shell Flue Gas Desulfurization Process*, Des Plaines, IL (April 1974).

Bergbau-Forschung/Foster Wheeler Dry Adsorption Process

BI-031 Bischoff, W. F., "FW-BF Dry Adsorption System for Flue Gas Clean Up," Presented at the Flue Gas Desulfurization Symposium, New Orleans, 14-17 May 1973.

BI-072 Bischoff, W. F. and Peter Steiner, "Coal Converts SO_2 to S," Reprint, Chem. Eng. 82 (1) (6 January 1975).

BI-073 Bischoff, W. F. and Y. Habib, "The FW-BF Dry Adsorption System," CEP *71* (5), 59 (1975).

CI-018 Private Communication, Foster Wheeler Energy Corporation (August 1975). Proposal information for a 500 Mw plant burning 4% sulfur coal.

DR-050 "Dry Scrubbing of Utility Emissions," *Env. Sci. Tech.* *9* (8), 712 (1975).

FO-075 Private Communication, Foster Wheeler Energy Corporation, (July 1975). Proposal information for two 650 Mw plants burning 2.3% sulfur coal.

FO-076 Private Communication, Foster Wheeler Energy Corporation (August 1975). Proposal information for a 500 Mw plant burning 4% sulfur coal.

HA-352 Habib, Yosuf and W. F. Bischoff, "Dry System for Flue-Gas Clean Up," Oil Gas J., 53 (24 February 1975).

LI-137 Lisle, E. W. and J. D. Sensenbaugh, "The Determination of Sulfur Trioxide and Acid Dew Point in Flue Gas," *Combustion*, 1 (January 1975).

MU-085 Murthy, K. S., et al., *Assessment of SO_2 Control Processes by Discussion With Vendors During 1974*, Draft Final Report, Battelle Columbus Labs., Columbus, Ohio (January 1975).

ST-292 Steiner, P., "Process for Removal and Reduction of Sulfur Dioxides from Polluted Gas Streams," Presented at the 16th National Meeting of the American Chemical Society.

US-335 "U. S. Oil-Gas Value Jumps Nearly $7 Billion," *Oil Gas J. 12*, 57 (January 1976)

Atomics International Aqueous Carbonate Process

BO-103 Botts, W. V. and R. D. Oldenkamp, "The Molten Carbonate Process for SO_2 Removal From Stack Gases: Process Description Economics and Pilot Plant Design," *J. APCA 23* (3), 190 (1973).

RO-158 Rockwell International, Atomics International Div., *Advanced Flue Gas Desulfurization Process, Vol. 1*, Statement of Qualifications, Response to EPA Solicitation DU-75-Z0001, Undated. References includes heat and material balances for a 500 Mw power plant burning 3.5% sulfur coal, however stream compositions are not given.

SL-064 Slack, A. V., Private communication, Atomics International Process (July 1975). Material received is a process evaluation done by A. V. Slack discussing advantages and disadvantages of the process.

Catalytic/IFP Ammonia Scrubbing Process

AI-020 Air Products and Chemicals, Inc., Private communication (20 August 1975). An information package prepared by Catalytic, Inc. specifically for Radian's base case including complete heat and material balances with stream compositions, temperatures, pressures, and economic analysis. Also includes discussion of design considerations, and operating experience.

EN-125 Environmental Protection Agency, Flue Gas Desulfurization Symposium, 1973, Proceedings, EPA 650/2-73-038, Research Triangle Park, NC (1973).

EN-269 Environmental Protection Agency, Office of Toxic Substances, Activities of Federal Agencies Concerning Selected High Volume Chemicals, EPA 560/4-75-001, Washington, D. C. (Feburary 1975).

HA-353 Harris, L. S. and G. R. Haun, "The Ejector Venturi Scrubber," Reprint, CEP 60 (5), 100 (1964).

HA-419 Hartley, Edwin M., Jr. and Michael J. Matteson, "Sulfur Dioxide Reactions with Ammonia in Humid Air," Ind. Eng. Chem., Fundam., Vol. 14, No. 1 (1975).

NA-248 Nagel, Dan, Private communication, Ametek (8 September 1975). Information on chloride removal from flue gas using venturi scrubbers.

RE-151 "Removal of Sulfur Oxides from Stack Gas," U. S. Patent 3,843,789.

SL-063 Slack, A. V., Private communication, Catalytic/IFP Process, (July 1975). Information received from A. V. Slack under secrecy agreement on a 100 Mw proposal and heat and material balances for a 500 Mw plant.

TE-188 Tennessee Valley Authority, Process Engineering Branch and Power Research Staff, Pilot-Plant Study of an Ammonia Absorption-Ammonium Bisulfate Regeneration Process, Topical Report, Phases I and II, PB 237-170, EPA 650/2-74-049a, Muscle Shoals, AL (June 1974).

Citrate/Phosphate Buffered Absorption Process

BE-343 Beard, H.R., Private communication, Salt Lake City Metallurgy Research Center (1972). Progress reports for the U.S. Bureau of Mines Citrate Pilot Plant.

BE-344 Beard, H. R., Private communication, Salt Lake City Metallurgy Research Center (1972). Progress reports for the U.S. Bureau of Mines Citrate Pilot Plant.

BE-345 Beard, H. R., Private communication, Salt Lake City Metallurgy Research Center (1973). Progress reports for the U.S. Bureau of Mines Citrate Pilot Plant.

BE-346 Beard, H. R., Private communication, Salt Lake City Metallurgy Research Center (1973). Progress reports for the U.S. Bureau of Mines Citrate Pilot Plant.

BE-347 Beard, H. R., Private communication, Salt Lake City Metallurgy Research Center (1973). Progress reports for the U.S. Bureau of Mines Citrate Pilot Plant.

BE-348 Beard, H.R., Private communication, Salt Lake City Metallurgy Research Center (1974). Progress reports for the U.S. Bureau of Mines Citrate Pilot Plant.

BE-349 Beard, H.R. Private communication, Salt Lake City Metallurgy Research Center (1974). Progress reports for the U.S. Bureau of Mines Citrate Pilot Plant.

BR-256 Bradley, Rosemary F. and Judith L. Blackford, "Citric Acid," 636.5021 A., Chemical Economics Handback, Stanford Research Institute, Menlo Park, CA (December 1974).

CH-195 Chemico, (Chemical Construction Corporation), Elemental Sulfur Recovered from Stack Gases Via the Phosphate Process -- A Regenerative Process to Control SO_2 Emissions.

CH-198 Chalmers, Frank S., "Citrate Process Ideal for Claus Tailgas Clean Up," Hydrocarbon Proc. 1974 (April), 75.

CH-223 Chalmers, Frank S., Louis Korosy, and A. Saleem, "The Citrate Process to Convert SO_2 to Elemental Sulfur," Presented at the Industrial Fuel Conferences, Purdue Univ., W. Lafayette, IN (October 1973).

CH-252 Chemico, Private communication (20 May 1975). Information on a 50,000 scfm, 3.5% sulfur coal, demonstration plant for the phosphate process including heat and material balances and partial stream composition data.

GA-172 Gakeler, C. J., Private communication, Armstrong Engineering Associates, Inc., West Chester, PA (October 1975). Information on salt crystallization equipment.

GR-196 Graham, R. R., Private communication, United States Filter Corp., Fluid Systems Div. (October 1975). Data on use of flotation equipment to separate sulphur from citrate solution.

KA-159 Katell, Sidney and William C. Morel, "An Evaluation of a Citrate Absorption Process for the Removal of SO_2 from Flue Gas," Proc. API, Division of Refining 1972, 215.

KE-063 (M. W.) Kellogg Co., Research & Engineering Development, Evaluation of SO_2 - Control Processes, Final Report, Contract No. CPA 70-68, Task 5, PB 204-711, Piscataway, NJ (1971).

KE-149 Keller, James L., "Removal of Sulfur Dioxide from Gases Containing the Same," U.S. Patent 2,729,543 (3 January 1956).

KO-150 Korosy, L., et al., "Chemistry of SO_2 Absorption and Conversion to Sulfur by the Citrate Process," Presented at the Symposium on Sulfur Removal and Recovery from Industrial Sources, 167th ACS National Mtg., Los Angleles, CA (April 1974).

KO-168 Korosy, Louis, Private communication, Pfizer, Chemicals Div. (10 September 1975). Letter discussing chemistry of the citrate process and comments on the differences between the citrate and phosphate processes.

MC-125 McKinney, W. A., et al., "Pilot Plant Testing of the Citrate Process For SO_2 Emission Control," Presented at the Flue Gas Desulfurization Symposium, Atlanta, GA, November 1974, Bu Mines, Salt Lake City, Utah (1974).

MC-170 (Arthur G.) McKee and Co., Private communitation (4 April 1975). General information provided to enable comparison of citrate with other FGD processes; total heat and material balances with operating temperatures but no stream composition data for 500 Mw, 3.5% sulfur; economic analysis.

MC-171 McKinney, W. A., W. I., Nissen, and J. B. Rosenbaum, "Design and Testing of a Pilot Plant for SO_2 Removal from Smelter Gas", Presented at the Annual AIME Mtg., Dallas, TX (February 1974).

MC-172 McKinney, W. A., et al., "Status of the Citrate Process for SO_2 Emission Control", Presented at the 1975 Lignite Symposium, Grand Forks, ND (May 1975).

PE-171 Peabody Engineered Systems, Private communication, (May 1975). General information on Peabody's Citrate Process.

RO-032 Rosenbaum, J. B., et al., "The Citrate Process for Removing SO_2 and Recovering Sulfur from Waste Gases", Presented at the AIME Environmental Quality Conference, Washington, D.C., June 7-9 (1971).

RO-115 Rosenbaum, J. B., et al., *Sulfur Dioxide Emission Control by Hydrogen Sulfide Reaction in Aqueous Solution: The Citrate System*, PB 221 914, Salt Lake City Metallurgy Research Cntr., Salt Lake City, Utah (1973).

SA-192 Saleem, A. and J. D. Sheeham, "Application of the Phosphate Process to a Large Utility Boiler", Paper 75-08.7, Presented at the 68th Annual APCA Mtg., Boston, MA (June 1975).

US-323 U.S. Bureau of Mines, Private Communication, not dated. Computer calculations of the utility and raw materials requirements of citrate process for 50 Mw, 3.5% sulfur coal plus an economic analysis.

VA-112 Vasan, S., "The Citrex Process for SO_2 Removal", CEP 71 (5), 61 (1975).

TVA Ammonia-Ammonium Bisulfate Process

EN-125 Environmental Protection Agency, Flue Gas Desulfurization Symposium, 1973, Proceedings, EPA 650/2-73-038, Research Triangle Park, NC (1973).

HA-419 Hartley, Edwin, M., Jr. and Michael J. Matteson, "Sulfur Dioxide Reactions with Ammonia in Humid Air," Ind. Eng. Chem., Fundam., Vol. 14, No. 1 (1975).

MA-497 Mathews, John C., et al., SO_2 Control Processes for Non-Ferrous Smelters, Draft Copy, Research Triangle Park, NC, Research Triangle Inst. (July 1975)

TE-011 Tennessee Valley Authority, Sulfur Oxide Removal from Power Plant Stack Gas, Ammonia Scrubbing, Conceptual Design and Cost Study No. 3, Contract No. TV-29233A, Knoxville, TN (1970).

TE-188 Tennessee Valley Authority, Process Engineering Branch and Power Research Staff, Pilot-Plant Study of an Ammonia Absorption-Ammonium Bisulfate Regeneration Process, Topical Report, Phases I and II, PB 237-170, EPA 650/2-74-049a, Muscle Shoals, AL (June 1974).

TE-233 Private Communication, Tennessee Valley Authority, 19 November 1975. Preliminary Flow Diagram and Heat and Material Balance for TVA Ammonia - ABS Process. The data presented is for a 500 Mw plant burning 3.5% sulfur coal. No stream compositions were given.

Ionics Electrolytic Regeneration Process

EN-125 Environmental Protection Agency, *Flue Gas Desulfurization Symposium, 1973, Proceedings*, EPA 650/2-73-038, Research Triangle Park, NC (1973).

HU-014 Humphries, J. J., Jr., S. B. Zdonik, and E. J. Parsi, "Sulfur Dioxide Removal and Recovery Process", *CEP* *67* (5), 64-8 (1971).

IO-015 Ionics, Inc., Private Communication, October 1975. News release concerning application of SULFOMAT cells to an FGD Process in Japan.

IO-016 Ionics, Inc., Private Communication, October 1975. News release concerning use of electrochemical cells to produce citric acid from sodium citrate.

IO-017 Ionics, Inc., *Stone & Webster/Ionics SO_2 Removal and Recovery Process*, Phase I, Final Report, EPA 650/2-75-045, Contract No. 68-02-0297, Wisconsin Electric Power Co., Milwaukee, WI (May 1975).

JO-003 Johnstone, H. F., et al., "Recovery of SO_2 from Waste Gases - Equilibrium Vapor Pressures Over Sulfite and Bisulfite Solutions", Ind. Eng. Chem. *30* (1), 101-109 (1938).

KU-058 Kuhn, A. T., ed., *Industrial Electrochemical Processes*, NY, Elsevier (1971).

ME-086 Meliere, K. A., et al., "Description and Operation of the Stone and Webster/Ionics SO_2 Removal and Recovery Pilot Plant at the Wisconsin Electric Power Co., Valley Station, in Milwaukee", Presented at the Flue Gas Desulfurization Symposium, Atlanta, GA, November 1974, Stone and Webster Engineering Corp., Boston, MA (1974).

Wellman-Lord Sulfite Scrubbing Process

BA-251 Bailey, E. E., "Continuing Progress for Wellman-Lord SO_2 Processes", Presented at the Flue Gas Desulfurization Symposium, Atlanta, GA, November 1974, Davy Powergas Inc., Lakeland, Florida (1974).

BA-372 Bailey, E. E. and R. M. Heinz, "SO_2 Recovery Plants--Materials of Construction", *CEP 71* (3), 64 (1975).

CR-005 Craig, T. L., "Recovery of Sulfur Dioxide from Stack Gases: The Wellman-Lord SO_2 Recovery Process", Presented at the Industrial Coal Conference, Lexington, KY, April 8, 1970, Preprint, Kentucky University, Lexington, KY (1970).

DA-037 Davis, John C., "SO_2 Absorbed from Tail Gas with Sodium Sulfite", *Chem. Eng. 78* (27), 43 (1971).

DA-170 Davy Powergas, Private communication, January 1975. General information on use of the Wellman-Lord Process in power plant applications.

DA-171 Davy Powergas, Private communication, November 1975. Detailed information on the Wellman-Lord Process technology including heat and material balances for a 100 Mw plant burning 3.5% sulfur coal. Also includes utility and raw material costs for 500 Mw, 3.5% sulfur coal.

DA-172 Davy Powergas, Private communication. September 1975. List of Wellman-Lord units operating, under construction or planned world wide.

MA-322 Mann, E. L., "The Dean H. Mitchell Station (Northern Indiana Public Service Company) Wellman-Lord (Davy Powergas Inc.) Allied Chemical Corporation SO_2 Emission Control Facility", Presented at the Flue Gas Desulfurization Symposium, Atlanta, GA, November 1974, Michigan City, Indiana, Northern Indiana Public Service Co. (1974).

MC-136 McGlamery, G. G., et al., Detailed Cost Estimates for Advanced Effluent Desulfurization Processes, Interagency Agreement EPA IAG-134 (d), Pt. A, Research Triangle Park, NC, Control Systems Lab., NERC (1974).

PO-091 Potter, B. H. and T. L. Craig, "Commercial Experience with an SO_2 Recovery Process", CEP 68 (8), 53 (1972).

PO-139 Potter, Brian H. and Christopher B. Earl, "Wellman-Lord SO_2 Recovery Process", AIChE Symp. Ser. 70 (137), 160-4 (1974).

SC-116 Schneider, Raymond T. and Christopher B. Earl, "Application of the Wellman-Lord SO_2 Recovery Process to Stack Gas Desulfurization", Presented at the Flue Gas Desulfurization Symposium, New Orleans, 14-17 May 1973.

SC-134 Schmidt, Max, "Fundamental Chemistry of Sulfur Dioxide Removal and Subsequent Recovery Via Aqueous Scrubbing", *Int. J. Sulfur Chem. Pt. B 7* (1), 11 (1972).

SE-011 Semrau, K. T., *Feasibility Study of New SO_2 Control Processes for Application to Smelters and Power Plants, Pt. 4. Wellman-Lord SO_2 Recovery Process for Application to Power Plant Flue Gases*, Final Report, Contract No. CPA-22-69-78, Stanford Research Inst., Palo Alto, CA (not dated).

TS-013 Tsushima, Yoshio, "First Japanese-Made Sulfur Dioxide Recovery Plant of the Wellman-Lord Process", *Chem. Econ. Eng. Rev. 3* (12), 21-4, 32 (1971).

WE-015 "The Wellman-Lord SO_2 Recovery Process", *Sulfur (London) 1967*, 24-27 (1967).

Cat-Ox Process

BE-326 Bee, R. and A. Wallo, *Cat-Ox Product Acid Strength Study*, Rough Draft, Mitre Corp., McLean, VA (1975).

BR-272 Browder, T. J., Private communication, October 1975. Comments on the production of sulfuric acid by oxidation of sulfur dioxide.

BU-132 Bucy, J. I. and P. A. Corrigan, "TVA-EPA Study of the Marketability of Abatement Sulfur Products", Presented at the Flue Gas Desulfurization Symposium, Atlanta, GA, November 1974, TVA, Muscle Shoals, AL (1974).

CA-268 Caederbank, P. H., "Contact - Process Converter Design", CEP 49 (11), 585 (1953).

EV-022 Evarett, Paul, Catalysis, Vol. VII, New York, Reinhold, 322-45 (1960).

MA-481 Mathias, D., D. Korneman, and E. Cannon, Private communications, Illinois Power, Comments in the Cat-Ox Process at Wood River (1975).

MC-136 McGlamery, G. G., et al, Detailed Cost Estimates for Advanced Effluent Desulfurization Processes, Interagency Agreement EPA IAG-134 (D), Pt. A., NERC, Control Systems Lab., Research Triangle Park (1974).

MC-187 McGlamery, G. G. and J. I. Bucy, Private communication, TVA, Comments on the Technical and Economic Feasibility of the Cat-Ox Process and on the Marketability of the Cat-Ox Product Acid (1975).

MO-179 Monsanto Enviro-Chem Systems, Inc., Cat-Ox System Design Manual; Wood River Generating Station, Unit No. 4, Illinois Power Company, Monsanto Enviro-Chem Systems Inc., St. Louis, MO (1975).

PH-029 Phillips, N. P., Thermodynamic Screening of Dry Metal Oxides for High Temperature SO_2 Removal, Technical Note 200-045-10-01, Radian Corp., Austin, TX (September 1974).

SO-005 Southern Research Inst., A Manual of Electrostatic Precipitator Technology, Part II, Application Areas, Prepared under NAPC Contract CPA 22-69-73, Birmingham, AL (1970).

TE-219 Texas Air Control Board, Regulation II, Sulfur Emissions, pp. B1-8.

TE-223 Teague, R. and R. Prolocker, Private communications, Monsanto Corp. (1975).

VO-049 Vosper, Richard R., Private communication, The Coen Company, November 1975.

WA-215 Walker, Alan B., "Hot-Side Precipitators", J. APCA 25 (2), 143 (1975).

WA-219 Waitzman, D., J. Nevins, and G. Slappey, Marketing, H_2SO_4 from SO_2 Abatement Sources--The TVA Hypothesis, EPA 650/2-73-051, Office of Agricultural and Chemical Development, TVA, Muscle Shoals, AL (1973).

Magnesia Slurry Scrubbing Process

AN-056 Ando, Jumpei, Recent Developments in Desulfurization of Fuel Oil and Waste Gas in Japan - 1973, EPA-R2-73-229, Processes Research, Inc., Cincinnati, OH (1973).

DO-015 Downs, W. and A. J. Kubasco, Magnesia Base Wet Scrubbing of Pulverized Coal Generated Flue Gas--Pilot Demonstration, PB 198 074, Babcock and Wilcos Co., Alliance, OH (1970).

EN-316 Environmental Protection Agency, Flue Gas Desulfurization and Sulfuric Acid Production Via Magnesia Scrubbing, EPA-625/2-75-007, Research Triangle Park, NC (1975).

KO-111 Koehler, George R., "New England SO_2 Recovery Project System Performance", Presented at the AIChE 66th Annual Mtg., Philadelphia, PA, 11-15 November 1973, Paper 21d.

KO-174 Koehler, George, The Magnesia Scrubbing Process as Applied to an Oil-Fired Power Plant, Final Report, EPA-600/2-75-057, Contract No. CPA 70-114, Chemical Construction Corp., NY (October 1975).

MC-076 McGlamery, G. G., et al., Conceptual Design and Cost Study. Sulfur Oxide Removal from Power Plant Stack Gas. Magnesia Scrubbing - Regeneration: Production of Concentrated Sulfuric Acid, EPA-R2-73-244, TVA, Muscle Shoals, AL (1973).

MC-136 McGlamery, G. G., et al., Detailed Cost Estimates for Advanced Effluent Desulfurization Processes, Interagency Agreement EPA IAG-134 (D), Pt. A, Research Triangle Park, N.C., Control Systems Lab., NERC, 1974.

RA-123 Radian Corp., Factors Affecting Ability to Retrofit Flue Gas Desulfurization Systems, Contract No. 68-02-0046, EPA 450/3-74-015, Austin, TX (1973).

RA-137 Radian Staff, Pollution Control Technology for Fossil Fuel-Fired Stations, EPA Contract No. 68-02-2008, Section 2.0: Air Pollution, Austin, TX (1974)

Lime/Limestone Wet Scrubbing Process

CH-207 Cheremisinoff, Paul N. and Robert T. Fellman, "Optimizing SO_2 Scrubbing Processes", Power Engineering 1974 (October), 54.

EP-012 Epstein, M., EPA Alkali Scrubbing Test Facility: Summary of Testing Through October 1974, EPA 650/2-75-047, EPA, Washington, D.C. (June 1975).

EP-013 Epstein, M., EPA Alkali Scrubbing Test Facility: Advanced Program, First Progress Report, EPA-600/2-75-050, EPA, Washington, D.C. (1975).

MC-147 McGlamery, G. G., et al., Detailed Cost Estimates for Advanced Effluent Desulfurization Processes, Final Report. EPA-600/2-75-006, Muscle Shoals, Ala. TVA, Jan. 1975.

PE-178 PEDCo-Environmental Specialists, Inc., Summary Report, Flue Gas Desulfurization Systems, September-October 1975. Contract No. 68-02-1321, Task No. 28. Cincinnati, 1975.

RA-122 Radian Corp., Evaluation of Lime/Limestone Sludge Disposal Options, Contract No. 68-02-0046, EPA 450/3-74-016, Austin, TX (1973).

RA-123 Radian Corp., Factors Affecting Ability to Retrofit Flue Gas Desulfurization Systems, Contract No. 68-02-0046, EPA 450/3-74-015, Austin, TX (1973).

RA-137 Radian Staff, Pollution Control Technology for Fossil Fuel-Fired Stations, EPA Contract No. 68-02-2008, Section 2.0: Air Pollution, Austin, TX (1974).

RA-200 Radian Corp., Pollution Control Technology for Fossil Fuel-Fired Electric Generating Stations, Final Report, Contract No. 68-02-2008, Austin, TX (March 1975).

RA-217 Radian Corporation, Report on the Status of Lime/Limestone Wet Scrubbing Systems, EPA 450/3-74-014, Contract Number 68-02-0046, Austin, TX (January 1974).

SA-094 Saleem, A., "Flue Gas Scrubbing W/Limestone Slurry", J. APCA 22 (3), 172 (1972).

SL-054 Slack, A. V., "Scrubber Survey: A Lime/Limestone Trend", Elec. World 1 Oct. 1974, 39.

TE-001 Tennessee Valley Authority, Sulfur Oxide Removal from Power Plant Stack Gas: Conceptual Design and Cost Study; Use of Limestone in Wet Scrubbing Process, NAPCA Contract No. TV-29233A, Knoxville, TN (1969).

Steam Methane/Steam Naphtha Reforming

BE-155 Beavon, David K. and T. R. Roszkowski, "Modern Hydrogen Manufacture", Presented at the Symposium on Hydrogen Manufacture-Chemistry and Catalytic Technology, ACS, Div. Petroleum Chemistry, Inc., Los Angeles, March 28 - April 2, 1971, Proc. Amer. Chem. Soc., Div of Petroleum C51 (1971).

BL-078 Bland, William F. and Robert L. Davidson, eds., Petroleum Processing Handbook, N.Y., McGraw-Hill (1967).

HY-020 "Hydrogen, Steam Reforming", Hydrocarbon Proc. 52 (4) 129 (April 1973).

KI-109 Kittzen, Maurice, Private Communication, Selas Corp., Sept. 6 & 10, 1976.

NA-242 "Naphtha Yet to Reach Commodity Status", C&EN 23 December 1974, 8.

NA-246 "Natural Gas Industry - Statistics", Energy Resources Rept. 3 (24), 235 (1975).

PR-103 Prescott, James H., "Continuous Regenerator Smooths Naphtha Reforming", Chem. Eng. 79 (18), 80 (1972).

SY-017 "Synthesis Gas", Chemical and Process Technology Encyclopedia, Douglas M. Considine, McGraw Hill, New York (1974).

ZE-024 Zeis, Larry A., "Critical Materials in Steam Reformers", Petro/Chem. Engr. 1970 (September), 38.

Partial Oxidation

KU-063 Kuhre, C. J. & C. J. Shearer, "Partial Oxidation Grows Stronger in U.S.", Oil Gas J. 6 September 1971, 85.

MI-161 Milner, M. J. and D. M. Jones, "Hydrogen Production by Partial Oxidation", 8th World Petroleum Congress, Proc. 4, 91-100 (1971).

PL-036 Plummer, J. B., et al., "The Generation of Clean Gaseous Fuels from Petroleum Residues", Presented at the AIChE Mtg., Tulsa, OK (March 1974).

SH-200 Shell Development Co., The Shell Gasification Process, brochure, Houston, Texas (1974).

SI-050 Singer, Sidney C., Jr. and L. W. Ter Haar, "Reducing Gases by Partial Oxidation of Hydrocarbons", CEP 57 (7), 68-74 (1961).

SL-055 Slater, W. L., A. M. Robin, and W. G. Schlinger, "Partial Combustion of High Sulfur Residual Fuels for Direct Production of Methane-Rich Fuel Gas", Paper 1733, Texaco, Inc., Montebello Research Lab., Montebello, CA (undated).

ST-206 Strelzoff, Samuel, "Partial Oxidation for Syngas and Fuel", Hydrocarbon Proc. 53 (12), 79-87 (1974).

Coal Gasification

WA-199 Waitzman, D. A., et al., Evaluation of Fixed-Bed Low-Btu Coal Gasification Systems for Retrofitting Power Plants, Palo Alto, CA, EPRI (February 1975).

WI-106 Wintrell, Reginald, "The K-T Process: Koppers Commercially Proven Coal and Multi-Fuel Gasifier for Synthetic Gas Production in the Chemical and Fertilizer Industries", Paper 29A, Presented at the 78th National AIChE Mtg., Salt Lake City, Utah, Aug. 1974, Koppers Co., Inc., Pittsburgh, PA (1974).

Sulfur/Sulfuric Acid

BI-072 Bischoff, W. F. and Peter Steiner, "Coal Converts SO_2 to S", Reprint, Chem. Eng. 82 (1) (6 January 1975).

BR-272 Browder, T. J., Private communication, October 1975. Comments on the production of sulfuric acid by oxidation of sulfur dioxide.

BR-283 Browder, T. J., "The Parsons Double Catalysis/Double Absorption Sulfuric Acid Process", *Sulfur*, No. 83, 31-33 (1969).

GM-015 Gmitro, John Irving and Theodore Vermeulen, "Vapor-Liquid Equilibria for Aqueous Sulfuric Acid", *AIChE J.* *10* (5), 740-6 (1964).

HU-051 Hunter, William D., Jr., "Application of SO_2 Reduction in Stack Gas Desulfurization Systems", Presented at the Flue Gas Desulfurization Symp., New Orleans, 14-17 May 1973.

HU-106 Hunter, William D., Jr., "Reducing SO_2 in Stack Gas to Elemental Sulfur", *Power 1973*, 63 (Sept.)

HU-108 Hunter, William D., Jr. and Aubrey W. Michener, "New Elemental Sulfur Recovery System Establishes Ability to Handle Roaster Gases", Eng. Mining J. 1973, 117 (June).

MC-147 McGlamery, G. G., et al., Detailed Cost Estimates for Advanced Effluent Desulfurization Processes, Final Report. EPA-600/2-75-006, Muscle Shoals, Ala., TVA, Jan. 1975.

WA-219 Waitzman, D., J. Nevins, and G. Slappey, Marketing H_2SO_4 from SO_2 Abatement Sources--The TVA Hypothesis, EPA 650/2-73-051, Office of Agricultural and Chemical Development, TVA, Muscle Shoals, AL (1973).

Calcium Sulfate/Sulfite Regeneration

AV-002 Avco Corp., A Survey of Metal Oxides as Sorbents for Oxides of Sulfur, PB 185-190, Lowell, MA (February 1969).

GY-003 "Gypsum Ready to Fill the Sulfur Gas?", Chem. Eng., 75, 94 (6 May 1968).

MA-501 Mandelik, B. G. and C. U. Pierson, "New Source for Sulfur", CEP 64 (11), 75 (1968).

MO-198 Mozes, M. S., Limestone Recovery Process Preliminary Material Balance, Ontario Hydro Research Division Report (June 1975). A preliminary design for a process to regenerate limestone scrubber sludge including process flow sheet, material balance, and energy requirements.

PA-016 Parsons, Terry, Gary D. Schroeder, and David DeBerry, Applicability of Metal Oxides to the Development of New Processes for Removing SO_2 from Flue Gases. 2 vols, PB 185 562, Austin, Texas, Tracor, Inc. 1969.

RE-174 Remirez, Raul, "Gypsum Finds New Role in Easing Sulfur Shortage", *Chem. Eng. 75* (23), 112 (1968).

SC-144 Schwitzgebel, Klaus and Philip S. Lowell, "Thermodynamic Basis for Existing Experimental Data in $Mg\text{-}SO_2\text{-}O_2$ and $Ca\text{-}SO_2\text{-}O_2$ Systems", Env. Sci. Tec. 7, (13), 1147 (1973)

SU-083 Suriani, E. and Thomas H. Milliken, "Method of Removing Sulfur Dioxide from Waste Gases", *U.S. Patent 3 574 530* (12 April 1971).

SW-028 Swift, William M. and Thomas D. Wheelock, "Decomposition of Calcium Sulfate in a Two-Zone Reactor", *I&EC Process Des. Develop. 14* (3), 323 (1975).

WH-067 Wheelock, T. S. and D. R. Boylan, "Sulfuric Acid from Calcium Sulfate", *CEP 64* (11), 87 (1968).

16.2 Process Vendors

In order to aid any of the readers of this report who may wish to obtain further information on one or more of the flue gas desulfurization processes discussed, a list of contacts is included. These contacts will be able to answer questions regarding specific applications and provide more detailed and up to date information than that obtainable by consulting the available literature which is listed in the annotated bibliography.

Many of these people have also rendered valuable assistance in the preparation of this document by answering questions and commenting on earlier drafts.

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Bergbau-Forschung/Foster Wheeler Dry Adsorption Process

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Ammonia-Ammonium Bisulfate Process

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Ionics Electrolytic Regeneration Process

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Wellman-Lord Sulfite Scrubbing Process

Christopher B. Earl - Sales Manager
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Magnesia Slurry Scrubbing Process

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George Kotnick
Philadelphia Electric Co.
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Ph. 215-841-4540

Cat-Ox Process

R. K. Teague
Monsanto Co.
800 N. Lindbergh Blvd.
St. Louis, MO 63166
Ph. 314-694-1000

Lime/Limestone Scrubbing Process

Although Radian does not vend a scrubbing process, it does have expertise in the area of lime/limestone scrubbing.

Philip S. Lowell - Vice President, Advanced Projects and Research
Delbert M. Ottmers, Jr. - Manager, Chemical Engineering Division
Radian Corporation
P.O. Box 9948
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Numerous vendors. For a summary of lime/limestone FGD process manufacturers, refer to PEDCo's bimonthly report on the Status of Flue Gas Desulfurization Systems in the United States (PE-178).