Evaluations of Regenerable Flue Gas Desulfurization Procedures

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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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1.0 SUMMARY

Twelve flue gas desulfurization processes have been evaluated to (1) provide EPRI with an assessment of the future potential and limitations of second-generation FGD processes and (2) aid in planning future research and development efforts for these processes. Five evaluation criteria were used: (1) environmental effects, (2) raw material and utility requirements, (3) developmental status, (4) unique design features, and (5) special problems.

Raw material and utility costs were determined for each process; capital costs were not. Raw material and utility costs will likely represent less than half of a process's total annualized operating cost, assuming that capital investment costs are in the vicinity of $100/Kw.

In general, the "dry" second-generation FGD processes were found to have higher raw material and utility costs than the "wet" processes. The added costs result basically from an increased use of reductant. This is because the "dry" processes first oxidize SO_2 to H_2SO_4 or $CuSO_4$ and therefore must reduce $SO_4^=$ instead of SO_2 to sulfur. From a technical feasibility standpoint, design and operating problems for "dry" second-generation FGD processes have been primarily mechanical in nature, whereas the problems for "wet" processes have been more of a chemical nature.

Design and operating data currently available for the second-generation processes does not appear to be adequate for scale-up to a commercial-sized (100 Mw or greater) unit. Successful operation of these processes on a prototype (20 to 40 Mw) scale should precede commercial scale application. Although

they appear technically feasible at this stage of development, the second-generation FGD processes can be expected to encounter problems of acceptability with the utility industry. This is particularly true with regard to the regeneration and reduction sections of these processes where much of the equipment design and operation is similar to that found in the chemical industry.

Production of either elemental sulfur or sulfuric acid is technically feasible for some of the regenerable FGD processes. However, the economics of conditioning certain FGD process effluent streams to produce a suitable acid plant feed stream may limit the applicability of some processes for acid production. As the second-generation processes become more fully developed, utilities should use market projections for sulfur and sulfuric acid as one criterion for selecting one regenerable FGD process over another for specific site applications.

The use of premium fuels for energy and for reducing gas production is an important consideration at this point in time. A clarification from the Federal Energy Administration on the status and availability of premium fuels for use in sulfur dioxide control methods is needed to guide the planning of future developmental activities. Of course, natural gas and light hydrocarbons are the preferred fuels. Currently, the only commercial process to convert sulfur dioxide to elemental sulfur uses methane as a reductant. Other reductants or sulfur-producing processes must be developed due to the uncertain availability of methane. The use of coal or heavy fuel oil for production of an H_2/CO_2 reducing gas for FGD process use is expected to increase in the future. Currently, steam methane and steam naphtha reforming are the preferred methods of H_2/CO production due to the high reliability they have obtained in the refining industry. However, the use of reforming may be limited by the availability of raw materials in the future. Several of the second-generation FGD processes use coal or coke as their reducing agent.

2.0 RESULTS AND CONCLUSIONS

Twelve flue gas desulfurization processes have been evaluated and compared on a common basis to assess their future potential as SO_2 control options for the electric utility industry and to provide a basis for planning and implementing future research and development activities in this technology area. The results and conclusions derived from this study are presented below.

1) Capital investment costs of the second-generation processes are uncertain at this point in time because of the relatively early stage of development of these processes in application to treating flue gas from coal-fired boilers. Although capital costs cannot be explicitly defined with confidence, it is clear that this factor and other indirect costs will represent the major cost item in the total annual operating costs of FGD processes. A more precise estimate of these capital costs must be based upon detailed process engineering designs for utility power plant application. This will become a key factor in the selection of one process over another for a specific utility application.

   Raw material and utility costs were, however, evaluated for each of the processes and were found to range from

1.2 to 4.0 mills/KwHr. Based upon capital investment costs in the proximity of $100/Kw and an annualized fixed charge of 25 percent of capital investment, raw material and utility costs represent only 20 to 45 percent of the total annualized operating cost.

2) Design and operating data currently available for most second-generation FGD processes do not appear to be adequate for scale-up to a commercial size (100 Mw) unit. Although the second-generation processes appear to be technically feasible at this stage of development, any process installation must be considered as a developmental prototype. These processes may encounter initial problems with acceptance by the utility industry because much of the chemical technology used is unfamiliar to the utility industry.

3) From a technical feasibility standpoint, design and operating problems for "dry", second-generation FGD processes have been more mechanical in nature, whereas the problems for "wet" processes have been more of a chemical nature. Mechanical and chemical problem areas remain to be solved, however, in both "wet" and "dry" processes. Dry processes have an advantage over wet processes in that the

energy requirements associated with stack gas reheat (155 Btu/KwHr) are eliminated.

4) Five methods of producing an H_2/CO low Btu reducing gas were evaluated to assess their applicability for use with FGD systems. Product gas costs were also determined for each H_2/CO production method.

   All processes produce a gas that can be cleaned to be suitable for FGD application. These processes, however, have not been demonstrated in this application. Further development activities to investigate process chemistry interferences resulting from trace contaminants in the H_2/CO reducing gas is needed to reduce the technical liabilities of using a coal or oil derived reducing gas.

   Costs for the product gas from these processes (which include capital charges) ranged from \$3.05 to \$7.80/MM Btu. The cost of reducing gas produced from the air blown gasification process, \$4.00 MM Btu, was used in the FGD process evaluations to determine reducing gas costs. The use of low Btu gas for reducing SO_2 to sulfur resulted in economic liabilities of about 0.5 mills/KwHr when compared to the use of methane as a reductant. The economic liabilities of using low Btu gas as a reductant are expected to decrease, however, as natural gas prices increase due to its short supply.

5) Each of the FGD processes was evaluated to determine its suitability for sulfur and sulfuric acid production. Seven of the processes were found to be suitable for production of either sulfur or acid, three processes are more suited for sulfur production, one is capable of producing acid only, and one is a throwaway process and is not suitable for the production of either.

Acid production costs, neglecting costs for feed pretreatment, are currently only about 12 percent of the cost of sulfur production when low Btu gas is used as the reductant. Acid production does not require a reductant, which accounts for the large cost differential. Product marketability, however, is more of a concern with sulfuric acid production as storage and handling problems are encountered which are not present with sulfur. The selection of producing either sulfur or sulfuric acid as an FGD process by-product is dependent upon both site specific and FGD process specific factors and should be individually evaluated for each installation.

6) The FGD processes evaluated during this study are in varying stages of development. Three processes, Lime/Limestone, Magnesia Slurry, and Wellman-Lord, have been successfully operated on a 100 Mw or greater installation. The Reheat Cat-Ox process has also been constructed on a 100 Mw demonstration scale but operation was not satisfactorily demonstrated due to equipment problems. Two processes, BF/FW and Shell/UOP, have been operated on a prototype size scale (20-40 Mw) and appear to be ready for scale-up to a 100 Mw size installation. The other processes are still in the pilot plant stage with units of around 1 to 2 Mw capacity. Operation of these units on a prototype scale appears necessary to obtain additional process data before attempting construction of commercial (100 Mw or greater) size facilities on coal fired power plants.

7) Energy consumption of the FGD processes is an evaluation criterion of interest in view of the large number of energy conservation programs occurring throughout the country. The Shell/UOP Process

is the most energy intensive process (1420 Btu/KwHr), while the Cat-Ox and Lime/Limestone Processes require the least amount of incremental energy (less than 400 Btu/KwHr). Of the regenerable processes producing sulfur, the Atomics International and Citrate/Phosphate Processes consume the least amount of incremental energy (about 700 Btu/KwHr). The remaining processes all consume between 850-1150 Btu/KwHr. If sulfuric acid is produced instead of sulfur, the incremental energy requirements of these processes would decrease by about 250 Btu/KwHr.

8) The amount of electrical power consumption by the FGD processes directly affects the power production of the utility boiler. For the base case conditions, the Ionics and ABS Processes are large electric power consumers using 35 and 27 Mw, respectively. These electric power consumption rates result in boiler derating of 7 and 5.4 percent. The remaining processes consume from 6-13 Mw of electric power and result in boiler deratings of 1.2-2.6 percent.

9) All of the FGD processes are capable of achieving 90 percent or greater SO_2 removal efficiencies, although the cost of achieving higher removals may differ

somewhat from one process to another. Only the Shell/UOP Process has been able to demonstrate high removals of NO_x (60-70 percent). BF/FW has reported NO_x removals of 40-60 percent, but recent testing at their plant in Lunen, Germany has not substantiated this claim. The Ionics Process also reports NO_x removal from 20-40 percent. An environmental problem which is currently unresolved is control of the ammonia plume from the Catalytic/IFP and ABS Processes. The occurrence of this plume affects the feasibility of using ammonia scrubbing systems as SO_x control options.

10) Sludge disposal land requirements for the Lime/Limestone Process (about 120 acres) may exclude that process from some power plant applications. Land requirements for the other processes do not greatly distinguish one process from another.

11) Several methods of producing usable sulfur products from lime/limestone waste sludge were examined to evaluate their applicability for regenerating calcium based sludges from lime/limestone scrubbing processes. The energy requirements for the calcium sulfite/sulfate decomposition are high, on the order of 300 MM Btu/hr, due to the stability of the calcium species. Although regeneration of calcium carbonate or calcium oxide from

calcium sulfite and sulfate appears to be technically feasible, it will be attractive only if other SO_2 recovery processes have outstanding drawbacks in other processing areas.

Areas for further research and development were suggested for each regenerable process evaluated during this study, although several of these processes are already in an advanced state of development. Recommendations are presented for each of these processes for further development efforts which would provide data in areas of both a technical and economic nature.

3.0 INTRODUCTION

The combustion of fossil fuels in conventional utility boilers will undoubtedly play an important role in meeting the Nation's future energy needs. The application of flue gas desulfurization (FGD) processes to control atmospheric emissions from these generating stations represents one alternative for utilizing the vast reserves of high-sulfur coal in an environmentally acceptable fashion. A great deal of effort has already been expended toward the development of FGD processes. Some FGD processes, such as lime/limestone and magnesia scrubbing processes, are considered to be technically viable SO_2 control options. The development of new, or "second-generation", FGD processes which provide the electric utility industry with potentially more attractive SO_2 control options is currently being pursued.

Under contract to the Electric Power Research Institute (EPRI), Radian has recently evaluated the status of eleven regenerable FGD processes along with the lime/limestone throwaway process to assess the future potential of these processes and to make recommendations regarding the scale of additional developmental activities. The twelve FGD processes evaluated are listed below:

✓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

? W-L 9) Wellman-Lord Sulfite Scrubbing Process

✓ 10) Cat-Ox Process

11) Magnesia Slurry Scrubbing Process

12) Lime/Limestone Wet Scrubbing Process.

This volume will contain brief summaries of the process evaluations, a process-by-process comparison, and the conclusions and recommendations of this study. Volume II contains the detailed evaluations of each of the twelve FGD processes.

3.1 Program Objectives

The objectives of the program were basically twofold. First, this study was performed to evaluate the future potential of the FGD systems with regard to their technical viability as SO_2 control options for the utility industry. Economic evaluation was limited only to defining the technical and operating factors which could be expected to define the relative commercial costs of these processes. Secondly, it was to provide EPRI and the utility industry with a basis for planning and implementing future research and development in this technology area.

To accomplish these objectives, a common basis was established for evaluation of all of the FGD processes. The eight developing second-generation processes were then compared with the more developed first-generation processes (Wellman-Lord, Cat-Ox, Magnesia Scrubbing and Lime/Limestone Scrubbing) to highlight process areas in need of further development. Finally, recommendations for the development of processes already demonstrated on a large scale were prepared. The study basis, process comparisons, and conclusions and recommendations are included in later sections of Volume I of this report.

3.2 Study Basis

A common basis was used for evaluating the design considerations of each process. Table 1-1 lists the design basis used for this study. Raw material and utility costs were determined for each FGD process and the cost basis for the process comparisons is listed in Table 1-2.

Several basic assumptions were set at the beginning of this study to serve as guidelines throughout the evaluation. These were:

1) Premium fuels (methane or fuel oil) were not to be used by these processes. This constraint led to the use of coal

TABLE 3-1

DESIGN BASIS FOR FGD SYSTEM COMPARISON

Power Plant Characteristics

Size	• 500 Mw
Excess Air	• 20% to Boiler
	• 13% Inleakage in Preheater
Efficiency	• 38%
Load Factor	• 60% (5260 hr/yr)

Horizontal Frontal Fired Boiler

0.013 lb H_2O/lb Dry Air in Combustion Air (80°F 60% H)

Coal Properties

Sulfur Content	• 3.5% (dry)
Chlorine Content	• 0.1%
HHV	• 12,000 Btu/lb

92% of sulfur in coal evolves as SO_2

75% of ash in coal evolves as ash

Moderately caking coal

Coal Ultimate Analysis

Compound	lb/100 lb fuel
H_2O	2.6
C	70.5
H_2	4.5
S	3.4
N_2	1.0
O_2	6.0
Ash	12.0

TABLE 3-2

COST BASIS FOR FGD SYSTEM COMPARISON

Energy Cost Basis

HP Steam	\$1.00/MM Btu
LP Steam	\$0.50/MM Btu
Electricity	\$0.02 kwhr
Coal	\$1.00/MM Btu
No. 6 Oil	\$2.30/MM Btu
Distillate Oil	\$2.50/MM Btu
Natural Gas	\$1.00/MM Btu
Coal Gasification-Low Btu Gas	\$4.00/MM Btu

Raw Material Cost Basis

Sodium Hydroxide	\$120/ton
Soda Ash	\$52/ton
Lime	\$22/ton
Limestone	\$4/ton
Citric Acid	\$900/ton
Phosphoric Acid	\$300/ton
Magnesium Oxide	\$150/ton
Process Water	\$.08/mgal
Ammonia	\$270/ton
Bergbau Char	\$390/ton
Activated Carbon	\$1000/ton
Petroleum Coke	\$45/ton
H_2/CO Reducing Gas	\$4/MM Btu
Sand	\$40/ton
Hydrogen Peroxide (35%)	\$270/ton

gasification low Btu gas by many processes as a source of fuel and a reductant which resulted in technical liabilities for these processes as low Btu gas has not yet been demonstrated for this application. Furthermore, the cost of the low Btu gas, which is about four times the cost of methane, resulted in economic liabilities for these processes.

2) Reducing gas production methods (reforming, partial-oxidation, and coal gasification) were considered commercially available processes.

3) Process evaluations were to be based on the production of sulfur as a by-product.

4) Effluent flue gas was to exit the processes at a temperature equal to or greater than 175°F. High pressure steam was to be used as an energy source for stack gas reheat when needed.

5) Flue gas had undergone particulate removal prior to introduction to the FGD system.

6) No economic credits were to be given for by-product marketability. Costs for by-product storage and/or disposal were also not to be considered except for lime/limestone sludge.

4.0 EVALUATION APPROACH

The twelve FGD systems mentioned above were evaluated by accomplishing the following tasks:

1) establishing the information base and the evaluation criteria,
2) performing material and energy balances for each process,
3) assessing the technical feasibility of each process and identifying key design and scale-up considerations,
4) assessing the economic feasibility of each process, and
5) comparing each process on a common basis.

In addition to the FGD process evaluations mentioned above, three other investigations were also performed during this study. These were evaluations of

1) reducing gas production methods,
2) limestone sludge ($CaSO_3/CaSO_4$) regeneration methods, and
3) suitability of the FGD processes for sulfuric acid production.

Discussions of the three investigations listed above can be found in Volume II of this report.

Several information sources were utilized during this program. The open literature was screened to assemble available information. Mr. A. V. Slack of Slack Advisory Services Corporation was retained as a consultant and proved to be a valuable source of information. Each of the FGD system suppliers was contacted regarding information about their systems. In several cases, nondisclosure (secrecy) agreements had to be arranged with process developers due to the proprietary nature of their processes. An annotated bibliography, describing the nature of the proprietary information used during this study in addition to listing the open sources, is included in Section 16 of Volume II. A list of process vendors to contact for information on a particular process is also included in Section 16 of Volume II.

Nondisclosure agreements were arranged with the following companies:

1) Universal Oil Products for proprietary information relating to the Shell/UOP Copper Oxide Adsorption Process,

2) Atomics International for their Aqueous Carbonate Process,

3) Catalytic for the Catalytic/IFP Ammonia Scrubbing Process,

4) McKee for the Citrate Process,

5) Chemico for the Stauffer/Chemico Phosphate Process,

6) Foster Wheeler for the Bergbau-Forschung/Foster Wheeler Dry Adsorption Process, and

7) Davy Powergas for the Wellman-Lord Sulfite Scrubbing Process.

Radian performed material and energy balance calculations for each FGD system to provide a sound basis for the engineering assessment of each process. The design basis for these calculations is listed in Table 1-1. The material and energy balances were the key point of this study as they permitted independent evaluations which were used to:

1) define the amount and compositions of process influent and effluent streams,

2) provide a basis for rough sizing of equipment,

3) determine energy requirements for each process, and

4) highlight process design considerations.

Detailed calculations are omitted from this report because they are, in part, based upon proprietary data.

Key design factors and the technical feasibility of each process were then evaluated using the raw material and energy balance calculations as a basis. This included the identification of process areas thought to present potential operating problems. Process vendors were contacted to discuss the process problems identified in this study.

Radian personnel visited the facilities of Westvaco, Foster-Wheeler, Atomics International, Bureau of Mines, Stauffer, Ionics, TVA, and Davy Powergas to gather additional information and discuss process details with these process developers. Representatives from UOP and McKee visited Radian offices to discuss details of their processes. In addition, phone conversations were held with process developers throughout the evaluation to keep abreast of the latest developmental activities which would impact the process evaluations.

Material and energy balance calculations were also used to determine the annualized raw material and utility costs for each process. Table 1-2 lists the cost basis for these calculations. These costs are detailed in the process evaluations found in Volume II and compared for each process in Section 6 of Volume I.

Capital investment costs were not evaluated for the processes considered during this study, although they will play an important role in guiding future developmental efforts on these processes. A thorough assessment of capital costs for these processes should be based upon a detailed design study which was beyond the scope of this program. Capital investment costs have been reported by other investigators (MC-136, PE-180) and have shown that FGD capital costs range from around $50/kw to well over $200/kw. The actual cost of the FGD systems is highly dependent upon site specific factors.

To illustrate the importance of capital costs on total annualized costs, Radian has assumed a single capital investment cost of $100/kw or $50 million for all FGD processes. It should be emphasized that a capital investment cost is being assumed only for the purpose of evaluating the relative effect of raw material and utility costs on the total annualized costs of a process. Annual fixed costs, which are to include such items as maintenance, depreciation, cost of money, etc., have been assumed to be 25 percent of the capital investment cost. These assumptions result in an annual charge of 4.7 mills/kwhr for each of the FGD processes.

5.0 PROCESS SUMMARY

Each of the twelve FGD processes was evaluated using the approach outlined in the previous section. In this section, the highlights of each process will be discussed with regard to 1) environmental considerations, 2) design considerations, 3) status of development, 4) utility applicability, 5) raw material and energy requirements, and 6) process economics. Detailed process descriptions are given in Volume II of the report. Following this process-by-process discussion, these twelve FGD processes will be compared based upon five evaluation criteria: 1) environmental effects, 2) utility and raw material requirements, 3) developmental status, 4) unique design features, and 5) special problems.

5.1 Westvaco Activated Carbon Process

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 the 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.

The adsorption section employs a multistaged, fluidized bed unit to contact the SO_2-laden flue gas with carbon.

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \xrightarrow[\text{carbon}]{} H_2SO_4 \tag{5-1}$$

Five shallow beds are used in the design for 90 percent SO_2 removal. The acid-laden carbon is regenerated by reducing the acid with hydrogen in several steps.

$$H_2SO_4 + 3H_2S \longrightarrow 4S + 4H_2O \qquad (5\text{-}2)$$

$$H_2 + S \longrightarrow H_2S \qquad (5\text{-}3)$$

These steps are accomplished in the sulfur generator/acid converter and H_2S generator/sulfur stripper units. Additional parts of the system include the hydrogen production facility, inert gas generation system, and storage vessels for both clean and loaded carbon.

Environmental Considerations

The Westvaco Process is capable of high (99 percent) SO_2 removal efficiencies with only moderate increases in adsorber size and pressure drop. According to Westvaco, the system can be designed to achieve 99 percent SO_2 removal with only about a 20 percent increase in carbon depth and pressure drop over a system designed for 90 percent SO_2 removal efficiency. Westvaco has not demonstrated any NO_x removal for their process although a similar process, Bergbau-Forschung, has reported NO_x removals in the 40-50 percent range. Carbon fines produced by adsorbent attrition in the highly agitated fluid beds could present a particulate problem in the cleaned stack gas, but these fines could be adequately controlled by a moderate pressure drop cyclone.

Design Considerations

The design and scale-up of the multistaged, fluidized bed contactors used in the Westvaco Process is a major concern with this process. Although fluidized bed units are generally difficult to scale up, there has been a significant amount of potentially helpful experience in designing and operating units similar to the main adsorber. The fluid bed adsorber operates at a lower gas velocity (4 fps) and a higher pressure drop (20 to 40 inches of H_2O) than most wet scrubbers. Thus, the contacting unit will be larger in diameter and the power requirement for the blowers will be greater for the Westvaco Process than for wet scrubbing FGD systems. The need for a hard, reactive activated carbon adsorbent is another important design consideration, both from the standpoint of minimizing adsorbent make-up requirements (raw material costs) and particulate emissions.

Status of Development

Westvaco has done a substantial amount of research work under EPA contract. 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 downtime due to sulfur plugging. Bench-scale studies have enabled Westvaco to develop a kinetic model of the reaction system which provides a sound basis for design of the adsorber and the sulfur generator. Before a large-scale application of the Westvaco Process is attempted, it would appear desirable to demonstrate the process on an intermediate scale at a coal-fired utility in order to confirm design and scale-up techniques, increase confidence in system operability, and firm up process economics.

Utility Applicability

There should be no serious limitations on applying the Westvaco Process in new plant situations, although space requirements for this process, as for most other FGD processes, are rather large – about 25,000 sq ft per 250 Mw module. Retrofit applications could be seriously hampered by the large amount of space required close to the boiler for the adsorber. Boiler load swings could be accommodated by using duplicate adsorber modules, each one capable of 50 percent turndown, and by providing intermediate storage. This would result in a turndown capability of 25 percent of full load. The SO_2 can be stored as H_2SO_4 adsorbed on carbon at the relatively dense loading of 0.22 lb H_2SO_4 per lb carbon.

Raw Material and Energy Requirements

Material and energy balance calculations show that the Westvaco Process is a relatively energy intensive process with high hydrogen consumption. For the base case 500 Mw plant, the energy requirement for the flue gas blower is equivalent to 13.2 Mw, or 2.6 percent of the power plant rating. The heat requirements for the process are 75 MM Btu/hr and can be supplied by either fuel oil or low Btu gas from a gasifier. Hydrogen consumption is an important consideration in process economics. The Westvaco Process is in an intermediate position with regard to theoretical hydrogen consumption (3 moles H_2 theoretically required per mole SO_2 sorbed). The Westvaco Process actually uses 3.3 to 3.9 moles H_2 per mole SO_2, but the efficiency of H_2 usage is good because hydrogen is also needed to react with chemisorbed oxygen in order to completely reactivate the carbon adsorbent. High quality hydrogen is not essential. Dilute gas from an air blown basifier is acceptable as long as the tars are removed and the CO is reduced to a low level.

Process Economics

Based upon the utility and raw material requirements determined by Radian material and energy balances, annual costs were estimated to be approximately 8 million dollars for the 500 Mw "base case" plant, or 3.1 mills/kwhr. The adsorption section contributes approximately 21 percent of this operating expense and the regeneration section contributes 79 percent.

5.2 Shell/UOP Copper Oxide Adsorption Process

The Shell/UOP Process is a dry metal oxide system which uses a copper oxide (CuO) on alumina sorbent to remove SO_2. The sorbent is subsequently regenerated with the sorbed SO_2 ultimately being recovered in the form of elemental sulfur. The unique design feature of the process is a dual set of specially designed, parallel passage, fixed-bed reactors.

The basic system design involves four major processing steps: (1) adsorption/regeneration, (2) SO_2 recovery and concentration, (3) sulfur production, and (4) reducing gas production. The acceptance/regeneration steps operate at about 750°F.

$$CuO + \frac{1}{2}O_2 + SO_2 \longrightarrow CuSO_4 \qquad (5\text{-}4)$$

$$CuSO_4 + 2H_2 \longrightarrow CU + SO_2 + 2\ H_2O$$

Any CuO which is unused during SO_2 adsorption is reduced back to copper.

$$CuO + H_2 \longrightarrow Cu + H_2O \qquad (5\text{-}6)$$

There exist several means of concentrating and preparing the SO_2-rich regeneration gases for further processing. Water absorption/stripping, solvent absorption, compression and condensation of water vapor, and complete liquefaction are all possibilities. Radian's evaluation is based upon a water gathering system. This is a rather poor choice in the situations where steam costs are high. UOP has developed alternatives which have fewer problems and use less energy. SO_2 conversion can also be accomplished in several ways. One method involves catalytic SO_2 reduction followed by a two-stage Claus plant.

$$3H_2 + SO_2 \longrightarrow H_2S + 2H_2O \tag{5-7}$$

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O \tag{5-8}$$

Environmental Considerations

UOP has guaranteed 90 percent SO_2 removal on certain system applications. Obtaining higher removal efficiencies may be a problem for this process. The Shell/UOP Process has demonstrated the system's ability to control SO_2 and NO_x simultaneously in a commercial-scale installation at the SYS refinery in Japan. They were able to remove 60 to 70 percent of the flue gas NO_x by adding NH_3 which reduces NO to N_2. Ammonia carryover in the flue gas was reported to be 2 ppm maximum. Water is produced by the regeneration reactions and is also added to the system at various points as steam resulting in a fairly large quantity of excess water leaving the stripper bottoms. The water contains approximately 50 ppm SO_2 and varies from 120 to 185 gpm for a 500 Mw plant, depending upon the hydrogen supply.

Design Considerations

A major design 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. The long-term reliability of the process will depend upon the ability of the large flue gas switching 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. Another design area needing further consideration is the water gathering system used to concentrate the SO_2 stream. This system is rather inefficient and very costly in terms of energy. The concept of sending the dilute SO_2 stream directly to the reduction and Claus steps is being considered.

Status of Development

Shell has gone through several phases of testing, but a completely integrated unit applied to a coal-fired utility has yet to be built. A commercial-scale unit went on stream in mid-1973 at the SYS refinery. This unit consists of two adsorbers operating on flue gas from an oil-fired boiler equivalent to about 40 Mw of capacity. Only the acceptors and water gathering system were installed and tested because refinery hydrogen and excess Claus plant capacity were available. The longest period of continuous operation has been two months. 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. Overall, the availability of design information is good, but more confidence could be placed in the system's reliability for utility application if a fully integrated system were in operation, possibly answering the troubling question of system operability under varying loads.

Utility Applicability

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 is somewhat of a limitation to application of the Shell/UOP Process to new coal-fired stations. Test work at Tampa should indicate whether this criterion is really necessary. Two factors may limit retrofit applications of the Shell/UOP Process. Space requirements are fairly large and flue gas from existing cold electrostatic precipitators must be reheated from 300°F to 750°F (this energy can be provided by heat exchange).

Raw Material and Energy Requirements

Material and energy balances for the Shell/UOP Process indicate that this process has large energy and hydrogen requirements. Energy requirements are large due to the large quantities of water being circulated, the steam required to heat the stripper reboiler, and especially the large amount of energy consumed as hydrogen reducing gas. The stoichiometric hydrogen consumption for the Shell/UOP Process is 4 moles H_2 per mole SO_2. Actual consumption figures show 6.2 moles H_2 required per mole SO_2 removed, the highest of the processes evaluated.

Process Economics

The Shell/UOP Process's high consumption of reducing gas and fuel is a strong liability and provides motivation to smooth out adsorption cycles and to eliminate the energy intensive water gathering system. Based upon the utility and raw material requirements for the base case 500 Mw station, the annualized raw material and utility costs would be approximately 4.0 mills/kwhr. It should be noted that this cost includes ammonia addition to provide 70 percent NO_x removal at an incremental cost of 0.6 mills/kwhr.

5.3 Bergbau-Forschung/Foster Wheeler Dry Adsorption Process

The Bergbau-Forschung/Foster Wheeler (BF/FW) Process is a dry process which uses a moving bed of char to adsorb SO_2 from flue gas and produce elemental sulfur. Unique features of the process are the louvered, moving bed adsorber, the use of hot inert sand as a means of providing heat for thermal regeneration of the adsorbent char, and the use of an unproven proprietary process utilizing coal to reduce concentrated SO_2 to sulfur.

The BF/FW Process involves three major processing steps for application to coal-fired utility boilers: (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. The adsorption and regeneration steps were developed by Bergbau-Forschung in Germany, while the reduction step is proprietary technology of Foster Wheeler.

Sulfur dioxide, sulfur trioxide, oxygen, and water vapor are adsorbed on the char in a two-stage adsorber, where the flue gas passes horizontally in cross flow through a vertical char bed.

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \xrightarrow[char]{} H_2SO_4 \qquad (5\text{-}9)$$

The char pellets are regenerated by raising their temperature to about 1200°F in an inert atmosphere.

$$H_2SO_4 + \tfrac{1}{2}C \xrightarrow{1200°F} H_2O + \tfrac{1}{2}CO_2 + SO_2 \qquad (5\text{-}10)$$

Physically, the regeneration occurs in a vessel in which char at the flue gas temperature is mixed with hot sand at about 1500°F. Reduction of SO_2 to elemental sulfur is accomplished using crushed anthracite coal via the RESOX Process.

$$SO_2 + C \xrightarrow[H_2O]{1100\text{-}1500°F} S + CO_2 \qquad (5\text{-}11)$$

The RESOX product gas then passes to an inclined shell-and-tube condenser for sulfur recovery.

Environmental Considerations

The BF/FW Process reportedly has the capability to remove SO_2, NO_x, and particulates. Pilot plant tests have shown that the system can achieve up to 99 percent SO_2 removals. Nitrogen oxide removals in the 40 to 60 percent range also have been reported, but have not been confirmed in subsequent testing. System design is based upon particulate removal upstream of the adsorber to maintain inlet dust loadings in the 0.1-0.2 grains/scf range. Removal of 95 to 96 percent of the inlet dust loading has been accomplished. There are two major waste streams associated with the BF/FW Process. The first of these is a stream of fly ash that is separated from the char out of the adsorber. A second stream of fly ash, unreacted coal, and tars is removed from the bottom of the reduction vessel.

Design Considerations

A major design consideration for the BF/FW Process is reduction of SO_2 to elemental sulfur using pulverized anthracite coal. This technology is unique and unproven presenting several potential operating problems that must be examined. Reliable solids handling equipment that can operate at 1200°F must be included in the design. Char combustion, which has been a concern with carbon adsorption processes, must be prevented by controlling the temperature and oxygen concentration in the adsorber. An assessment of the need for particulate removal capability prior to the adsorber is also needed. High-efficiency electrostatic precipitators are currently specified by BF/FW ahead of the adsorber in order to minimize the amount of fly ash that enters the gas cleaning section. The potential of the adsorber to act as the primary particulate collector should be evaluated.

Status of Development

The adsorption and regeneration systems of the BF/FW Process have been piloted by BF in Germany on two units treating flue gas from a coal-fired station at rates varying between 1100 and 1800 scfm. The adsorber/thermal regeneration unit operated on a continuous basis for over 6000 hours, removing up to 95 percent of the SO_2, 40 to 60 percent of the NO_x, and 95 percent of the inlet particulates. Pilot data for the RESOX Process (FW process for reducing SO_2 with coal) were generated with a 2 ft^3 volume bed. The feed consisted of 20 to 30 percent SO_2 in a sumulated flue gas, and the unit demonstrated 90 percent SO_2 reduction to yield commercial grade elemental sulfur. A prototype (35 Mw) unit of the adsorption/regeneration sections has been installed at the Kellerman Power Plant in Lunen, West

Germany. A fully integrated application of the BF/FW Process will be demonstrated on a 47.5 Mw coal-fired boiler at Gulf Power Company's Scholz Steam Plant. The unit consists of a 20 Mw adsorption section and 47.5 Mw regeneration and RESOX sections. This unit was started up in August 1975 and ran for ten days before being shut down for modifications and data analysis.

Utility Applicability

The BF/FW Process is generally suitable to new applications on fossil fuel-fired utility boilers. Unless expensive conveying systems are employed, it will be necessary to locate both the adsorption and regeneration subsystems in the general proximity of the stack. This requirement could restrict retrofit applications. The design temperature for the adsorption reactions is in the range of 250-300°F, which is about the normal flue gas temperature after the air preheater. One possible limiting factor to application of the BF/FW Process in the United States is the availability of adsorbent char.

Raw Material and Energy Requirements

Material and energy balances indicate that the BF/FW Process is intermediate with regard to energy consumption, about 900 Btu/kwhr. The major raw material requirement is 3000 lb/hr of activated char which is chemically consumed in the regeneration step. Current installations employ an oil-fired sand heater (210 MM Btu/hr), but coal-fired heaters are specified for future installations. The other primary raw material and energy requirements are anthracite coal for RESOX (160 MM Btu/hr) and electric power (8 Mw).

Process Economics

Based upon Radian material and energy balance calculations, the annual raw material and utility costs for a new 500 Mw BF/FW installation were estimated to be $5,929,000 or 2.3 mills/kwhr. Of this cost, the SO_2 adsorption section contributes 11 percent, the char regeneration contributes 74 percent, and the RESOX reduction section contributes 15 percent.

5.4 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 SO_2 from power plant flue gas. The dry scrubber product is treated to regenerate the scrubbing solution and to produce elemental sulfur. Two key 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) complete reduction of the sodium salts in a molten pool.

In the spray dryer, gaseous SO_2 is sorbed into the scrubbing liquor where it reacts to form solid sodium sulfite granules.

$$SO_2 + Na_2CO_3 \longrightarrow Na_2SO_3 + CO_2 \qquad (5\text{-}12)$$

Sulfite reduction occurs in a molten salt reactor at a temperature of 1700-1900°F. Carbon is injected in the form of petroleum coke to serve as the reductant.

$$Na_2SO_3 + 3/2C \longrightarrow Na_2S + 3/2CO_2 \qquad (5\text{-}13)$$

Technology for the sodium carbonate regeneration and sulfur production steps of this process has largely been borrowed from established practice in the pulp and paper and chemical industries.

$$Na_2S + CO_2 + H_2O \longrightarrow Na_2CO_3 + H_2S \qquad (5\text{-}14)$$

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O \qquad (5\text{-}15)$$

The regeneration step which utilizes the products of the reduction step is carried out in a series of carbonation towers using AI's proprietary carbonation scheme. Standard Claus plant technology is used for sulfur production.

Environmental Considerations

Although the AI Process has been developed primarily for SO_2 pollution control, tests have shown that the system is also capable of significant reductions of SO_3, particulates, and halogen gases. The waste materials leaving the system consist of a fly ash filter cake and a chloride purge stream discharged with the spent cooling water. The AI Process 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. Pilot plant tests with the spray dryer indicate that the NO_x removal capability of the AI Process is limited to less than 5 percent under normal operating conditions.

Design Considerations

The spray dryer and the molten salt reactor are two important design areas. The key to reliable operation of the spray dryer is efficient atomization of the scrubbing solution.

Control of spray dryer operations is important as too much water can cause condensation downstream and too little water will lower the efficiency of the atomizers and hence reduce the ability to remove SO_2. Operation of molten salt beds in reducing atmospheres has historically been a difficult process operation. AI has identified problem areas with the reactor and have taken appropriate control measures. It is felt that unexpected operating problems, which occur as processes become more developed, are likely to occur in this process area.

The design of the molten salt reducer is a rather complex problem. Attempts to characterize the kinetics of the reduction reactions have not been successful as the reaction goes to completion before a sample can be analyzed. At the present time, AI is adopting a rather conservative stance in scale-up of this vessel. Presently, petroleum coke is used as the carbon source in the reducer. The use of coal as a carbon source would be desirable; but other design problems as yet undefined could arise due to increased amounts of fly ash, chloride, and trace contaminants. Technology for quench and filtration of the reducer melt is considered standard practice in the pulp and paper industry. It is important that the quench/dissolver be properly designed to avoid explosive conditions.

Status of Development

All of the processing steps in the AI Process have been tested on a 1000 scfm scale or are considered proven technology by AI. 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. 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. The molten salt regeneration unit is a backmix reactor. Its development has proceeded from bench-scale to pilot-scale at AI test laboratories. Extensive development work has been performed for each of the major processing areas, but development work on the integrated process has not been conducted and would provide key design information for a process such as this.

Utility Applicability

The AI Process is well suited for application to new power plants. Its relatively large space requirement, 32,000 ft^2, may cause some difficulties when it is retrofitted to an existing plant. Turndown ratios of 4 to 1 have been demonstrated with a single scrubber. Even greater turndown is achievable for a large installation with four scrubbing modules, as dampers could be arranged to take one or more modules out of service. The major factor limiting utility applicability of this process is associated with the operation of the molten salt reducer.

Raw Material and Energy Requirements

Material and energy balance calculations show that the AI Process is relatively efficient in its use of energy. For the base case 500 Mw plant, approximately 13,000 lb/hr of petroleum coke is used as both a reductant and a source of process heat for the molten salt reducer. About half of the coke is used for each purpose. About 210 gph (32 MM Btu/hr) of fuel oil is consumed as an energy requirement for the Claus plant incinerator.

Process Economics

Annualized raw material and utility costs for a new 500 Mw AI installation have been estimated based upon material balance calculations to be 1.2 mills/kwhr. Of this cost, the SO_2 removal section contributes 30 percent, the Na_2CO_3 regeneration contributes 56 percent, and the sulfur production facility contributes 14 percent.

5.5 Catalytic/IFP Ammonia Scrubbing Process

The Catalytic/IFP Process is an aqueous process which uses an ammonium sulfite and bisulfite solution to absorb SO_2 from flue gas and subsequently process it to form elemental sulfur. The process employs a unique four-stage absorber 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 cleaned gas is reheated to 175°F.

A solution of ammonium sulfite is used in the absorber to effectively sorb SO_2 from the flue gas to form ammonium bisulfite.

$$SO_2 + (NH_4)_2SO_3 + H_2O \longrightarrow 2NH_4HSO_3 \qquad (5\text{-}16)$$

Concentrated brine from the absorber passes to the reduction section where the ammonium sulfite and bisulfite are thermally decomposed in a forced circulation evaporator operating at about 300°F.

$$(NH_4)_2SO_3 \longrightarrow 2NH_3 + H_2O + SO_2 \qquad (5\text{-}17)$$

$$NH_4HSO_3 \longrightarrow NH_3 + H_2O + SO_2 \qquad (5\text{-}18)$$

The concentrated sulfate slurry from the bottom of the evaporator is decomposed in a sulfate reducer at 600-700°F. Concentrated SO_2 from these reduction steps passes through an SO_2 reactor which reduces any SO_3 to SO_2 enroute to the H_2S generating facility. Generation of H_2S is controlled to yield a 2:1 product composition of $H_2S:SO_2$ which is fed to a liquid Claus unit for sulfur production.

$$(NH_4)_2SO_4 \longrightarrow NH_4HSO_4 + NH_3 \qquad (5\text{-}19)$$

$$2NH_4HSO_4 + S \longrightarrow 2NH_3 + 2H_2O + 3SO_2 \qquad (5\text{-}20)$$

Ammonia is condensed from the Claus plant tail gas, concentrated, and recycled for use in the absorber.

Environmental Considerations

This process has the capability of attaining high (99 percent) SO_2 removal efficiencies. More absorption stages must, however, be added to increase removal efficiencies from 90 to 99 percent which will result in increased operating costs of roughly 8-10 percent for the system. The effect of the process on NO_x emissions has not been reported but is assumed to be negligible. Only two small waste streams are produced: a 25 gpm purge from the venturi flue gas cooler which contains fly ash and calcium salts, and a 2 gpm purge containing fly ash and ammonium salts from a brine filter located between the absorber and forced circulation evaporator. An environmental consideration unique to ammonia scrubbing is the formation of an ammonium sulfate plume. Catalytic has developed a patented "fumeless" technology for operation of the absorber including control strategy and process instrumentation.

Design Considerations

The basic design problem associated with an ammonia scrubbing system is elimination of the ammonia plume. To prevent fuming, $HC\ell$ should be removed from the flue gas before it contacts the ammonia and the partial pressure of NH_3, SO_2, and H_2O in the gas must be maintained at such levels that ammonium salts do not form in the gas phase. The absorber is designed for removal of SO_2 in the lower stages, and ammonia and other volatiles in the upper stages. The staged absorber with semi-independent operation of stages is designed to permit stage-to-stage material balance adjustments to eliminate formation of ammonia salts in the gas phase. As a safety measure, a sulfuric acid injection system could be installed on the top stage to control any excess ammonia emissions which might occur.

A potential process problem area is the operation of the sulfate reducer since this unit operates at 600-700°F and is exposed to a corrosive environment. A submerged combustor with a lined entry tube is specified for sulfate reduction with alternate linings proposed in the event the original fails.

Status of Development

Catalytic has used a four-inch diameter absorber in their laboratory to obtain data on "fumeless" operations. Also, a 2 Mw pilot plant on a coal-fired industrial boiler was operated for four months in the spring of 1976. Commercial ammonia scrubbing units are available but they have not operated without a plume. Scale-up of Catalytic's "fumeless" operating technology remains to be demonstrated.

Institut Francais du Petrole (IFP), the developer of the brine regeneration and sulfur recovery process sections, currently has three ammoniacal brine recovery processes in various stages of development. A fully integrated 30 Mw unit located at the Champagne EDF power plant has operated for one month. Operational results from this installation should provide data on the compatibility of a totally integrated system and on the probability of successful scale-up.

Utility Applicability

Retrofit applicability of the Catalytic/IFP Process may be limited due to the large space requirements for the absorption section, about 65,000 square feet. This process has the ability to turndown to 20 percent of boiler capacity by operating only one absorber at 40 percent capacity for a 500 Mw system.

Raw Material and Energy Requirements

Material and energy balance calculations show that the Catalytic Process is about average with regard to fuel consumption, 860 Btu/kwhr. Major energy consumption items are stack gas reheat, sulfate reducer heat, and reducing gas for H_2S production. For the base case 500 Mw plant, energy consumption for these areas is 77 MM Btu/hr of steam for reheat, 50 MM Btu/hr of low Btu gas for sulfate reducer heat, and 103 MM Btu/hr low Btu gas for H_2S production. Relatively small amounts of raw materials (160 lb/hr NH_3 and 560 lb/hr lime) are required.

Process Economics

Material and energy balance calculations were used to estimate an annualized raw material and utility cost of 2.0 mills/kwhr. Of this cost, the absorption section contributed 26 percent, the reduction section 65 percent, and the sulfur production and ammonia separation and recycle 9 percent.

5.6 Citrate/Phosphate Buffered Absorption Process

The Citrate/Phosphate Process is a buffered aqueous absorption process which uses either a sodium citrate or a sodium phosphate solution to absorb SO_2 from flue gas. Several process developers offer versions of this process which differ mainly in absorber configuration, absorber liquor pumping rates, type of buffer, operating pH, methods of H_2S production, and methods of sulfur separation. The basic processing sequences are, however, similar for all.

Flue gas is first cooled to its adiabatic saturation temperature before entering the SO_2 absorption tower. SO_2-laden liquor from the absorber proceeds to a regeneration reactor where it is reacted with H_2S to form elemental sulfur.

$$SO_2 + H_2O \rightleftharpoons HSO_3- + H^+ \qquad (5\text{-}21)$$

$$Hcit^= \text{ or } HOP_4{}^= + H^+ \rightleftharpoons H_2Cit^- \text{ or } H_2PO_4{}^- \qquad (5\text{-}22)$$

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O \qquad (5\text{-}23)$$

Sulfur is separated from the liquor, melted, decanted, and sent to storage. Sulfates are purged from the sulfur-free absorbing liquor before recycle to the absorber. Flue gas exiting the absorber is reheated to 175°F before release to the atmosphere.

Environmental Considerations

This process has demonstrated a high SO_2 removal capability (99 percent), but no capability for removing NO_x. A waste stream of 1500 lb/hr of anhydrous Na_2SO_4 is produced by the Citrate/Phosphate Process assuming 3 percent oxidation of absorbed SO_2 to sulfates. Oxidation reported by the developers varies from 1.3 to 4 percent. This relatively low oxidation is due in part to the presence of the buffer and thiosulfate in the absorbing solution.

Design Considerations

Major process problems have been associated with the H_2S production system. The Citrate/Phosphate Process is unique in that H_2S is generated outside the actual system and then utilized as a reactant to produce sulfur. The method chosen for H_2S production, which has not yet been demonstrated, is reaction of product sulfur with reducing gas from coal gasification. Processes are available which produce H_2S using methane as a reducing gas source, but these are less acceptable due to limited methane availability.

Other than H_2S generation, the absorber and regeneration reactors comprise the main areas of design considerations. A basic process handicap is the low pickup of SO_2 by the absorbing liquor which results in large regeneration equipment and high costs. Absorber design is based on both gas and liquid phase resistance. A kinetic model has been prepared and used for this design. Sulfur regeneration reactors are apparently mass transfer controlled in the early stages and reaction rate controlled in the final stages, a situation allowing ingenious reactor design configurations. The chemistry of the regeneration step is not well defined. Process developers do not agree on the rate controlling reactions.

Status of Development

The Phosphate Process has been piloted (100 scfm) on a low sulfur oil-fired utility boiler. The Citrate Process has been piloted on a coal-fired industrial boiler (1 Mw) and on a slip stream of tail gas from a lead smelter sintering furnace (0.5 Mw). These were not totally integrated operations since gas cylinders of pure H_2S were utilized rather than H_2S production units. Methane-produced H_2S is being examined at the lead smelter plant but has met with many operational problems. The overall result of these tests was a demonstration of the technical feasibility of the process and the development of design data for scale-up.

Kinetic models exist for use in scaling up the absorber and regeneration reactors although they have not been demonstrated. Sulfur separation technology does exist. The main area of concern lies with the H_2S generation which has not yet been operated successfully.

Utility Applicability

There should be few restrictions on the application of this process to a new facility. Absorber space requirements of 32,000 sq ft could, however, limit the applicability for retrofit situations. Availability of both citric and phosphoric acid should not be a problem, but the future cost of citric acid could escalate. Using four absorber trains for a 500 Mw installation would result in a turndown capability to about 15 percent of full load. This turndown capability results from operating only one of the absorber trains at half load.

Raw Material and Energy Requirements

Material and energy balance calculations show that the Citrate/Phosphate Process is one of the more efficient processes in terms of incremental fuel consumption. The major uses of incremental fuel are stack gas reheat, heat for producing an anhydrous Na_2SO_4 by-product, and reducing gas for H_2S production. Incremental fuel consumption for the base case 500 Mw plant is 77 MM Btu/hr of steam for reheat, 39 MM Btu/hr of steam for sulfur melting and anhydrous Na_2SO_4 production, and 103 MM Btu/hr of low Btu gas for H_2S production. Raw material make-up rates are rather large due to the need to purge the Na_2SO_4 by-product from the system.

Process Economics

Material and energy balance calculations were used to estimate an annualized raw material and utility cost of 1.4 mills/kwhr. Of this cost, the absorption section contributes 22 percent, the regeneration system 2 percent, the sulfate purge system 1 percent, and the H_2S generation system 75 percent.

5.7 Ammonia-Ammonium Bisulfate (ABS) Process

The Ammonia-Ammonium Bisulfate (ABS) Process is a regenerable process which removes SO_2 from flue gas by absorption in an aqueous ammonium sulfite and bisulfite solution. A staged absorber is specified by TVA to produce an outlet liquor with the high ammonium salt concentration necessary for regeneration while maintaining low salt concentrations on the final stage to reduce ammonia losses and the potential for fuming. The clean gas is reheated to 175°F with steam before it is exhausted.

A solution of ammonium sulfite flows countercurrently to the flue gas in the absorber to effectively sorb SO_2 and form ammonium bisulfite by Equation 5-24.

$$SO_2 + (NH_4)_2SO_3 + H_2O \longrightarrow 2NH_4HSO_3 \qquad (5\text{-}24)$$

The product liquor from the absorber is fed to the acidulator where ammonium bisulfate (ABS) reacts with the liquor to chemically release SO_2.

$$NH_4HSO_3 + NH_4HSO_4 \longrightarrow (NH_4)_2SO_4 + H_2O + SO_2 \uparrow \qquad (5\text{-}25)$$

$$(NH_4)_2SO_3 + 2NH_4HSO_4 \longrightarrow 2(NH_4)_2SO_4 + H_2O + SO_2 \uparrow \qquad (5\text{-}26)$$

The liquor is subsequently stripped with either air or steam to remove the remaining SO_2 and fed to a crystallization and separation section that produces ammonium sulfate crystals. A thermal decomposer then decomposes the crystals at 700°F to produce ammonium bisulfate for acidulation and NH_3 for recycle to the absorber.

$$(NH_4)_2SO_4 \xrightarrow{700°F} NH_3 \uparrow + NH_4HSO_4 \qquad (5\text{-}27)$$

The 65 percent SO_2 gas stream produced by the acidulator and stripper is a suitable feed for a sulfuric acid plant or a sulfur production unit.

Environmental Considerations

An SO_2 removal efficiency of up to 99 percent can be obtained with this process. However, more absorber stages with associated liquor loops would probably be added to the 90 percent removal design resulting in about a 10 percent increase in ammonia throughput and roughly an 8 to 10 percent increase in operating costs. The capability of the process for NO_x removal has not been quantified but is assumed to be negligible. The primary waste or by-product streams are approximately 6,300 lb/hr of ammonium sulfate crystals and a 100 gpm (56,000 lb/hr) particulate slurry from the prewash section. A purge of the mother liquor out of the ammonium sulfate separation equipment may also be required. The formation of an ammonium salt plume in the absorber has been a persistent environmental problem for all ammonia processes. TVA is examining fine particulate control technology to solve the fuming problem since adjustments in the operation of the absorber have not adequately controlled the plume.

Design Considerations

A basic design criterion for an ammonia FGD process is elimination of the plume. To control fuming, chlorides, particulates, and SO_2 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 low enough levels that a gas phase reaction to form ammonium salts does not occur. A low pressure drop venturi is used to humidify the gas and remove chlorides, particulates, and SO_3 while the staged operation of the absorber allows adjustment of the material balance on each stage to control the partial pressures of NH_3, SO_2, and H_2O.

The primary design considerations for the regeneration section are the uniform and complete acidulation of the absorber product liquor and the use of a thermal decomposer to produce ammonium bisulfate from ammonium sulfate. As previously mentioned, the SO_2 product gas can be converted to sulfur or sulfuric acid.

Status of Development

TVA has operated a 1.2 Mw pilot plant on a slipstream from a coal-fired boiler since 1968. The facility is not totally integrated, however, since a thermal decomposer is not included and sulfuric acid is used to acidulate the liquor from the absorber. Ammonia scrubbing units are commercially available, but they have not been able to operate without a plume. The technical feasibility of the individual unit operations of this process have been demonstrated in industrial applications. Nevertheless, completely integrated operation of the TVA pilot plant, design and operating data for a thermal decomposer, and a solution to the fuming problem remain to be demonstrated before this process is considered for full-scale application.

Utility Applicability

Although the space requirements for a 500 Mw system have not been specified by TVA, they are expected to be on the same order as other regenerable processes and may limit the retrofitability of the process. A raw material supply problem may exist if the Allied Chemical Process, which requires methane, is used to produce sulfur. The system should have the ability to turndown to 15 percent of full load.

Raw Material and Energy Requirements

Material and energy balance calculations indicate that the TVA Process has an incremental fuel consumption of 1030 Btu/kwhr which is about average for the processes examined. Major energy requirements are electric power for the thermal decomposer (15.5 Mw), electric power for fans and pumps (11.7 Mw), high pressure steam for stack gas reheat (77 MM Btu/hr), and low Btu gas for sulfur production (92 MM Btu/hr). The raw material requirements are roughly 1,800 lb/hr of ammonia.

Process Economics

Based on material and energy balance calculations, Radian estimated the annual raw material and utility costs to be 2.5 mills/kwhr. The relative contribution of each process section to this cost is 39 percent for absorption, 31 percent for regeneration, and 30 percent for SO_2 conversion.

5.8 Ionics Electrolytic Regeneration Process

Ionics does not offer a complete process, only their electrolytic cell technology for sodium sulfate regeneration. In order to perform the evaluation Radian assumed an absorption section similar to Wellman-Lord's using caustic as the scrubbing media. The unique feature of the process is the use of electrolytic cells in the regeneration section to convert sodium sulfate solution to caustic and sulfuric acid. Also, sulfate ions formed by oxidation are purged from the scrubbing loop as dilute sulfuric acid.

The process chemistry can be described by a few basic reactions. Caustic solution entering the absorber picks up SO_2 according to Equations 5-28 and 5-29.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O \quad (5\text{-}28)$$

$$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2NaHSO_3 \quad (5\text{-}29)$$

Oxygen in the flue gas oxidizes some of the sodium sulfite to sodium sulfate.

$$Na_2SO_3 + \tfrac{1}{2}O_2 \longrightarrow Na_2SO_4 \quad (5\text{-}30)$$

The rich absorber solution is acidulated to release the SO_2 and then it is steam stripped.

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + H_2O \quad (5\text{-}31)$$

$$2NaHSO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2SO_2 + H_2O \quad (5\text{-}32)$$

The stripped solution undergoes electrolytic regeneration to produce recycle caustic and sulfuric acid and purge sulfate ions as dilute sulfuric acid.

Environmental Considerations

The use of strong caustic solution as a scrubbing media will permit the Ionics Process to achieve removals up to 99 percent, depending on the inlet SO_2 concentration, but at the expense of increased oxidation. Available data from other sources indicate that 20 percent removal of NO_x is feasible with caustic scrubbing. During pilot plant work, Ionics has obtained removals as high as 40 percent, but reliability of the instruments was questionable. Rather than eliminate unregenerable sulfates formed by oxidation as sodium sulfate, the Ionics Process purges them as dilute sulfuric acid (300 gpm). This acid could possibly be used to regenerate the power plant ion exchange units. Chlorine gas may also be produced from the electrolytic cells.

Design Considerations

The major consideration in design is minimizing the number of electrolytic cells required and the power they use. Efficient utilization of solutions and control of oxidation minimizes the number of cells required and proper design of cell components will lower the cell voltage necessary. Work is still being done to reduce cell voltage from its present 4.5 volts (at 80 amps per sq ft) by raising cell temperatures and reducing electrode spacing and membrane thicknesses. The exact extent of oxidation in a full-scale Ionics installation is unpredictable but should be similar to Wellman-Lord's figure of approximately 5 percent. Cell feed treatment with hydrogen peroxide to reduce dissolved metal ion content of the solution needs to be examined and possibly modified in order to reduce costs.

Development Status

The Ionics process has been piloted at Wisconsin Electric Power Company's Valley Station on coal-fired flue gas treating 2200 cfm (0.75 Mw), containing 2000 ppm SO_2. The pilot plant was operated jointly by Ionics and Stone and Webster. Stone and Webster provided the scrubbing, acidulating, and stripping equipment and know-how, while Ionics provided the chemical reaction sequence and their proprietary electrolytic cell technology for regeneration. Although the pilot plant included the absorption, acidulation, and stripping steps, data collection on sections other than regeneration was limited. Almost all the development work has been finished on the SULFOMAT cells although minor modifications are still continuing to reduce the cell voltage.

Utility Applicability

The Ionics Process should not be limited in new plant applications; however, as with most other processes, space limitations may hinder retrofit applications. The large number of cells required (approximately 12,000 for a 500 Mw case) gives the regeneration great flexibility and provision of solution storage could decouple absorption and regeneration to the extent that off peak power could be used in order to reduce regeneration costs. The absorption units should be able to turndown as low as 35 percent of design capacity. The Ionics cells could also be used as a means of converting sodium sulfate purge streams from other processes to caustic and sulfuric acid.

Raw Material and Energy Requirements

The material and energy balance calculations show that the Ionics Process is a large consumer of electric power. For the 500 Mw base case, the process consumes 24.5 Mw for regeneration, 7.8 Mw for flue gas booster blowers and 1.8 Mw for other miscellaneous equipment. Off peak regeneration could reduce the cost of the power consumption but large reductions in the quantity of power used are unlikely. Major heat requirements are 77 MM Btu/hr for stack gas reheat and 46 MM Btu/hr for stripping, both of which are supplied by steam. Sulfur production by the

Allied Chemical Process requires 92 MM Btu/hr of low Btu gas as a reductant. Methane availability is questionable in most areas.

Process Economics

Based upon the utility and raw material requirements determined by Radian material and energy balances, annual costs were estimated to be approximately 6.2 million dollars for the base case plant or 2.4 mills/kwhr. The absorption section contributes 23 percent, the stripping section 2 percent, the regeneration section 44 percent, and the SO_2 conversion section 31 percent.

5.9 Wellman-Lord Sulfite Scrubbing Process

The Wellman-Lord Sulfite Scrubbing Process is based on the ability of sodium sulfite solution to absorb SO_2 forming sodium bisulfite which can be regenerated by addition of heat. It is a first-generation process and is being commercially employed. A concentrated stream of SO_2 is produced which can be converted to sulfur or sulfuric acid. Sodium sulfate produced by oxidation must be purged. The basic processing areas are gas pretreatment and absorption, purge treatment, regeneration, and SO_2 conversion.

The process chemistry is very simple. The sulfite scrubbing solution absorbs SO_2 according to Equation 5-29.

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3 \qquad (5\text{-}29)$$

As in most sodium systems, oxidation follows Equation 5-30.

$$Na_2SO_3 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4 \qquad (5\text{-}30)$$

Regeneration involves a simple reversal of the absorption reaction 5-29 by heating. Sulfur production by the Allied Chemical Process was assumed.

Environmental Considerations

The process can achieve 95 percent removal of SO_2 and may be able to go to 99 percent in some circumstances (high SO_2 concentration) at the expense of increased gas pressure drop and oxidation. The economically obtainable SO_2 level in the outlet gas appears to be in the range of 50 to 100 ppm. No NO_x removal has been shown for the process. The waste streams consist of a 5 percent slurry (1350 lb/hr of solids) of fly ash from gas pretreatment and 2725 lb/hr of mixed anhydrous sodium sulfate and sulfite (70 percent sulfate) from purge treatment. The purge sodium sulfate is acceptable for paper industry consumption.

Design Considerations

The area of major concern for the Wellman-Lord Process is sulfite oxidation. Although antioxidants have been tried and various techniques for recovering the sodium values from the purge solids are still under investigation, the best way of handling oxidation so far seems to be minimizing sulfate production through controlled operating techniques. In operation, the liquid flow in the absorber and the contact efficiency is kept to the minimum necessary for the desired SO_2 removal. A fractional freeze crystallization process is used to produce the 70 percent sulfate solids from absorber solution containing 7.1 weight percent sulfate, 5.7 percent sulfite and 21 percent bisulfite. Fly ash has been shown to increase oxidation rates. Double effect evaporators are used to reduce steam consumption in the regeneration area.

Status of Development

Pilot plant testing of the Wellman-Lord Process using sodium sulfite began in 1970. The first two units experienced initial difficulty but were eventually successful. Since then, 17 plants have been built and are operating reliably on industrial and utility boilers, Claus plant tail gas, and acid plant tail gas. The two most significant units are Chubu Electric Power's Nagoya Station and NIPSCO's upcoming demonstration unit. The Chubu plant is on a peaking, 220 Mw, oil-fired utility boiler. Turndown to 35 percent in 30 minutes has been shown and the load following capability of the process (using solution storage) is proven. The NIPSCO unit is a 115 Mw coal-fired installation (3.5 percent sulfur coal) which will demonstrate the process's capabilities in coal-fired applications and its integration with Allied Chemical technology to produce sulfur using methane as a reductant. Purge concentration and conversion is still under investigation.

Utility Applicability

Unless space constraints limit retrofit applications of the Wellman-Lord Process, there should be no other limitation to its employment. Turndown to 35 percent of flow for each absorber has already been demonstrated on a large scale and three or four units would be needed for a 500 Mw system. Operating flexibility and reliability is maintained by inclusion of large solution storage tanks for fresh and SO_2-laden solution. These serve as surge capacity to smooth out load changes and permit maintenance of the regeneration train while the absorbers continue to operate. Sixteen hours of storage is recommended which means two 600,000 gallon tanks.

Raw Material and Energy Requirements

Unlike some of the other processes evaluated, the Wellman-Lord Process does not have an item which stands out as the predominant cost. The major requirements are 12.2 Mw of electric power, mainly for blowers and recirculating pumps, 77 MM Btu/hr of steam for reheat, 168 MM Btu/hr of steam for evaporation, 2120 lb/hr of sodium carbonate, and 92 MM Btu/hr of low Btu gas to be used as reducing agent. The steam requirement for evaporation is based on the use of double effect evaporators which reduce steam consumption by 45 percent.

Process Economics

The Wellman-Lord Process possesses no one area where a predominance of the costs indicates need for further work, however, some reduction in costs might be achievable through improvements in oxidation control and purge separation. Based upon the raw material and utility requirements for the base case 500 Mw utility, annual costs would be approximately 4.4 million dollars or 1.7 mills/kwhr. Of this figure, the absorption section represents 38 percent, regeneration 15 percent, purge treatment 4 percent, and SO_2 conversion 43 percent.

5.10 Catalytic Oxidation Processes

The Monsanto Enviro-Chem Integrated Cat-Ox Process oxidizes sulfur dioxide in the flue gas to sulfur trioxide which subsequently combines with water in an acid absorber to form a 77.7 percent H_2SO_4 product acid. The unique features of the process are a "hot side" electrostatic precipitator that will reduce flue gas particulate loading to 0.005 gr/scf, a vanadium pentoxide catalyst to oxidize SO_2 to SO_3, and the combining of SO_3 and flue gas water vapor to form a 78 percent H_2SO_4 solution.

The Cat-Ox Process can be divided into three sections: (1) particulate removal; (2) catalytic conversion of SO_2 to SO_3; and (3) sulfuric acid production. The electrostatic precipitator and the catalytic converter are installed upstream of the economizer and air preheaters since the catalytic oxidation of SO_2 to SO_3 requires a temperature of approximately 850 to 900°F. The SO_3 combines with water in the flue gas to form sulfuric acid which is condensed and collected in the acid absorber.

$$SO_2 + \tfrac{1}{2}O_2 \xrightarrow[\text{catalyst}]{850\text{-}900°F} SO_3 \qquad (5\text{-}32)$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad (5\text{-}33)$$

Entrained sulfuric acid and acid mist in the flue gas are collected by high efficiency Brink demisters.

Environmental Considerations

The Cat-Ox Process will remove at least 90 percent of the inlet SO_2. The capability to remove NO_x has not been demonstrated, but 99.9+ percent of the particulates, SO_3, and halogens are reportedly removed. The waste streams include approximately 560 lb/hr fly ash, 15 lb/hr vanadium pentoxide catalyst solids, and roughly 620 lb/hr of sulfuric acid mist and vapor in the cleaned exit gas.

Design Considerations

The major design areas of concern for the Cat-Ox Process are the electrostatic precipitator (ESP), catalytic converter, acid absorber, and heat exchangers. The ESP design considerations are centered upon the ability of "hot-side" precipitators to achieve a reliable outlet particulate loading of 0.005 gr/scf during power unit operation. The catalytic converter considerations consist of the effects that temperature, composition, and flow rate variations of the flue gas have on SO_2 oxidation, catalyst poisoning by the flue gas constituents, and the dynamic temperature response of the catalyst bed. The primary factors that influence design of the acid absorber are the production of dilute acid during start-up, demister collection efficiency, and demister plugging with particulates. The primary problem with the heat exchangers in the absorption loop is the need for construction materials that are able to withstand hot, dilute sulfuric acid.

Status of Development

Research on the Cat-Ox Process began in 1961. Development has included a 15 Mw prototype on a coal-fired boiler and a 110 Mw commercial demonstration unit on a coal-fired boiler. The prototype facility operated for about one year and was pronounced successful and ready for sale to utilities in late 1968. This process was the first to be ready for demonstration.

Since the 110 Mw demonstration project was on an existing boiler, the Cat-Ox Process was placed in a retrofit application in which the flue gas out of the precipitator had to be reheated to 850 to 900°F before it was fed to the converter. The unit was operated for only 600 hours in 1973 at partial and full capacity. Currently, the unit needs refurbishment before it can be operational.

Utility Applicability

Application of this process to a new utility should encounter few technical limitations. The reheat requirement for a retrofit process will be a consideration for existing boilers, however. The primary criteria for assessing the applicability of the process include: (1) the marketability of the sulfuric acid produced and (2) raw material availability and low fuel requirements.

Raw Material and Energy Requirements

Material and energy balance calculations performed by Radian indicate that the Integrated Cat-Ox is one of the processes that requires the least amount of incremental fuel (about 300 Btu/kwhr). The primary energy requirement is electric power for the electrostatic precipitator and the fans. The only raw material make-up is 15 lb/hr of catalyst for the converter.

Process Economics

Based on material and energy balances, an annual raw material and utility cost of 0.5 mills/kwhr was estimated for the integrated Cat-Ox Process. The major cost item is electric power for operation of the precipitator and fans.

5.11 Magnesia Slurry Scrubbing Process

The Magnesia Slurry Scrubbing Process uses magnesium oxide to absorb SO_2 in a wet scrubber. The aqueous slurry of magnesium sulfite formed in the scrubber is dried and calcined to regenerate magnesium oxide and produce an SO_2-rich gas stream. The SO_2 stream can be used to produce sulfuric acid or elemental sulfur.

The absorption section consists of a wet scrubber with a circulating slurry of magnesium hydroxide and magnesium sulfite used to absorb the SO_2.

$$Mg(OH)_2 + SO_2 \longrightarrow MgSO_3 + H_2O \tag{5-34}$$

$$MgSO_3 + H_2O + SO_2 \longrightarrow Mg(HSO_3)_2 \tag{5-35}$$

The bisulfite in the spent scrubbing liquor is reacted with magnesium hydroxide to produce magnesium sulfite crystals.

$$Mg(HSO_3)_2 + Mg(OH)_2 + 4H_2O \longrightarrow 2MgSO_3 \cdot 3H_2O \tag{5-36}$$

The sulfite crystals, along with magnesium sulfate crystals formed by sulfite oxidation in the system, precipitate from the solution. The crystals are separated from the liquor by centrifuging, and then thermally dried in an oil-fired kiln. The $MgSO_3/MgSO_4$ solids are decomposed at 1600°F in an oil-fired calciner to regenerate the MgO.

$$MgSO_3 \longrightarrow MgO + SO_2 \tag{5-37}$$

The $MgSO_4$ is reduced in the calciner using carbon as a reducing agent.

$$MgSO_4 + \tfrac{1}{2}C \longrightarrow MgO + SO_2 + \tfrac{1}{2}CO_2 \qquad (5\text{-}38)$$

After dust removal, the sulfur dioxide rich gas from the calciner is piped to either a sulfur or sulfuric acid production unit. The regeneration MgO is slaked in a slurry tank with make-up MgO to form magnesium hydroxide which is recycled to the SO_2 absorber.

Environmental Considerations

The Magnesia Slurry 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 at demonstration units in the U.S., and the results of a pilot plant study showed negligible NO_x removal under all conditions tested. Two types of system losses can be identified in magnesia scrubbing: purge treatment of the magnesia slurry system when needed, and magnesia losses in the process. The purge treatment of the slurry stream depends on the level of impurities while magnesia losses occur through the stack and in different parts of the process equipment. Total magnesia losses were taken to be 3.5 percent per cycle.

Design Considerations

Venturi scrubbers have been used exclusively in this country on the demonstration scale for magnesia scrubbing, but other types of scrubbers could also be used successfully. The process sequence for magnesia slurry scrubbing has been fairly standard with the exception of an optional thickener used to concentrate the slurry prior to centrifuging.

The majority of the problems experienced at the oil-fired Boston Edison power plant installation were closely related to the solids-handling system. The system was designed to handle magnesium sulfite hexahydrate crystals, but the trihydrate crystals were produced in the scrubber instead. The trihydrate crystals require less heat in the dryer but are much finer and have caused dusting problems. Accurate predictions of the type of crystal which will be produced by each Mag-Ox scrubbing system will be needed for future installations. This will allow for the proper design of solids handling and processing equipment and will reduce operating problems.

Status of Development

The magnesia slurry scrubbing process has been proven to be feasible on a demonstration scale. Three 100 - 150 Mw retrofit units in the U.S. have demonstrated 90 percent SO_2 recovery on both oil-fired and coal-fired boilers. Three commercial Japanese units have also shown an SO_2 recovery of over 90 percent. Low system availability has been a problem with magnesia scrubbing in this country. The reliability of magnesia scrubbing installations must be improved.

Utility Applicability

The availability of magnesium oxide is not seen to present a problem. Magnesium oxide is currently mined and recovered from seawater. The plant location is an important consideration for this process when a sulfuric acid by-product is produced. The plant should be located near industrial consumers of sulfuric acid or on a navigable river that would permit shipping the acid to an acid consumer. The land requirement for the process scrubbing area is essentially the same as for lime/limestone scrubbing, about 22,500 square feet. The total land requirement is about 76,000 square feet.

Raw Material and Energy Requirements

Material and energy balance calculations indicate that the magnesia slurry scrubbing process has an incremental fuel value of 1038 Btu/kwhr when a sulfur by-product is produced. Major energy requirements are electric power for fans and pumps (9.2 Mw), No. 6 fuel oil for drying and calcining (130 MM Btu/hr), high pressure steam for stack gas reheat (77 MM Btu/hr), and low Btu gas for sulfur production (145 MM Btu/hr). If this process is used to produce a sulfuric acid by-product, the incremental energy is 604 Btu/kwhr with the difference being attributed to the low Btu gas necessary for sulfur production. Magnesia make-up is not large, being about 500 lbs/hr.

Process Economics

Material and energy balance calculations were used to estimate an annualized raw material and utility cost of 2.3 mills/kwhr for a Mag-Ox Process producing sulfur. Of this cost the SO_2 absorption section contributes 22 percent, $MgSO_3/MgSO_4$ separation and drying 15 percent, MgO regeneration and SO_2 recovery 13 percent, and sulfur production 50 percent. A Mag-Ox Process producing sulfuric acid has an estimated annualized raw material and utility cost of 1.2 mills/kwhr.

5.12 Lime/Limestone Wet Scrubbing Process

The Lime/Limestone Wet Scrubbing Process uses a slurry of calcium oxide or calcium carbonate to absorb SO_2 in a wet scrubber. This is commonly referred to as a "throwaway" process because the calcium sulfite and sulfate formed in the scrubber are disposed of as waste solids.

The principal reactions in the scrubber are as follows:

For lime systems,

$$SO_2 + CaO + \frac{1}{2}H_2O \longrightarrow CaSO_3 \cdot \frac{1}{2}H_2O \qquad (5\text{-}39)$$

For limestone systems,

$$SO_2 + CaCO_3 + \frac{1}{2}H_2O \longrightarrow CaSO_3 \cdot \frac{1}{2}H_2O + CO_2 \qquad (5\text{-}40)$$

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.

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 removal of NO_x by the scrubbing system is negligible. A single waste stream of calcium waste solids is produced from the process. The stream is usually bled off the process hold tank and dewatered before final disposal. Under the base case conditions, a limestone system waste stream of 59 tons/hr or a lime system waste stream of 48 tons/hr would be produced assuming the stream is concentrated to 50 weight percent solids. The stream consists of $CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$, and unreacted CaO or $CaCO_3$.

Design Considerations

Both open configuration and closed configuration (packed) type scrubbers have been used for lime/limestone SO_2 removal. The scrubbers differ in gas-side pressure drop, L/G ratio, gas velocity, and their resistance to plugging.

Both calcium sulfite and sulfate form scales. Prevention of scaling in lime/limestone scrubbing systems has been a major problem in the past but now appears to have been solved. Maintaining the proper system pH, allowing adequate residence time in the hold tank, and adjusting the L/G ratio are all techniques for maintaining a scale-free scrubbing system. Mist eliminator operation has also been a major trouble spot in lime/limestone scrubbing. Scaling and plugging of mist eliminators has occurred, but can be prevented by using proper washing techniques and by placing the mist eliminator devices in a horizontal duct to allow the water to run off.

Status of Development

The trend toward lime/limestone scrubbing for SO_2 removal is strong today due to the rapid progress being made in coping with the many process problems and the well-defined economics. At the present time, about 25,000 Mw have been committed to lime/limestone scrubbing. Disposal of the waste sludge from the process is the major area where technology is still developing. The large land requirement reasonably close to the point of waste sludge generation is a problem for some existing power plants.

Utility Applicability

The limiting factor in applying lime/limestone wet scrubbing to a new and retrofit power plants 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. Both lime and limestone are readily available, low-priced materials.

Raw Material and Energy Requirements

Material and energy balance calculations show that lime/limestone wet scrubbing has one of the lowest energy consumption figures of the FGD processes evaluated. This is due, of course, to the fact that it is a throwaway process so that no energy is needed to regenerate the SO_2 absorbent. The energy requirement comes to only 280 Btu/kwhr for a lime system and 290 Btu/kwhr for a limestone system. The only use of fuel is 77 MM Btu/hr of steam for stack gas reheat. Large amounts of lime or limestone are required since there is no regeneration and recycle of the SO_2 absorbent. About 131,500 tons/yr of limestone or 61,000 tons/yr of lime are required for the base case 500 Mw plant.

Process Economics

Material and energy balance calculations were used to estimate an annualized raw material and utility cost of 0.8 mills/kwhr for a limestone system and 1.1 mills/kwhr for a lime system. Of this cost for a limestone system, the limestone requirement contributes 24 percent, the electric power requirement 57 percent, the steam requirement for flue gas reheat 18 percent, and the process water requirement only 1 percent.

6.0 PROCESS COMPARISON

Each of the eleven regenerable FGD processes and the lime/limestone throwaway process has been discussed in some detail in the preceding sections. Table 6-1 presents a summary of the salient features of each process. This table lists information regarding (1) environmental effects, (2) unique design features, (3) utility and raw material requirements, (4) development status, and (5) special problems for each of the twelve FGD processes evaluated.

As may be seen from the information presented in Table 6-1, each of the twelve FGD processes has its strengths and weaknesses. From the standpoint of environmental effects, each process has demonstrated SO_2 removal efficiencies of acceptable ranges. All of these processes are capable of achieving 90 percent or greater SO_2 removal, although the cost of achieving higher removals may differ somewhat from one process to another. SO_2 removal ability is, consequently, not an important criterion for rating one process over another. Only three processes, Shell/UOP, BF/FW, and Ionics have reported NO_x removal capabilities ranging from 20 to 70 percent. Analytical difficulties in accurately measuring NO_x make reported NO_x removals somewhat suspect.

Waste streams will be produced by each of these processes. The Citrate/Phosphate and Wellman-Lord Processes result in large waste streams, since the SO_2 which becomes oxidized to Na_2SO_4 must be purged from the system. One vendor reports, however, that anhydrous Na_2SO_4 is a marketable by-product. Lime/limestone scrubbing has the largest waste stream since it is a

TABLE 6-1

PROCESS EVALUATION SUMMARY

Design Basis: 500 Mw, 3.5% Sulfur Coal

Evaluation Criteria	WESTVACO Activated Carbon Process	SHELL/UOP Copper Oxide Process	BERGBAU-FORSCHUNG FOSTER WHEELER Dry Adsorption Proc.	ATOMICS INT. Aqueous Carbonate Proc.	CATALYTIC/IFP Ammonia Scrubbing Process	CITRATE/PHOSPHATE Buffered Absorption Process
ENVIRONMENTAL EFFECTS:						
SO_2 Removal, %	90-99	90	97	90-95	90-99	90-99
Demonstrated NO_x Removal, %	-	70	40-60	-	-	-
Waste Streams	Contaminated carbon fines	40 ppm SO_2 in 185 gpm H_2O	Fly ash from adsorber	12,000 lb/hr fly ash filter cake	Fly ash + Ca Salts in 25 gpm H_2O	1,500 lb/hr Na_2SO_4 anhydrous
			Fly ash, coal, and tars from RESOX	Chloride purge	Fly ash + NH_4 salts in 2 gpm H_2O	
UNIQUE DESIGN FEATURES:	Multistaged fluidized bed	Copper oxide fixed bed adsorbent in parallel passage reactors	Parallel louvre moving bed	Spray dryer scrubber	Staged absorber	H_2S/SO_2 regeneration reactors
	Direct sulfur production within adsorbent		Reduction of SO_2 with coal	Molten salt reducer	Sulfate reducer	Sulfur flotation (kerosene for one developer - air for others)
UTILITY & RAW MATERIAL REQUIREMENTS:						
Electric Power (Mw)	13	6	8	10	9	8
Fuel Oil (mmBtu/hr)	75	50	210(c)	32	-	-
Low Btu Gas (MMBtu/hr)	-	-	-	-	70	-
Stack Gas Reheat-High Pressure Steam (MMBtu/hr)	-	-	-	-	78	79
Steam (MMBtu/hr)	6.4	228	-	-	-	39
Reducing Agent-H_2/CO (MMBtu/hr)	175	322	-	-	103	103
Reducing Agent-Coal/Coke (MMBtu/hr)	-	-	160	201	-	-
Raw Materials (lbs/hr)	Carbon - 280	NH_3 - 2,110	Char - 3,000	Na_2CO_3 - 850	NH_3 - 160 Lime - 560	Citric Acid - 27(d) Na_2CO_3 - 1,100(d) H_3PO_4 - 37(e) NaOH - 830(e)
Total Incremental(a) Fuel Consumption (Btu/kwhr)	950	1,420	900	670	860	670
Total Utility & Raw Material Costs (mills/kwhr)	3.1	4.0	2.3	1.2	2.0	1.4
DEVELOPMENT STATUS:						
Size (Mw)	0.2	40	20/47.5	1-2	30	1
Fuel Type	Oil-Fired Boiler	Oil-Fired Boiler	Coal-Fired Boiler	Coal-Fired Boiler	Coal-Fired Boiler	Coal-Fired Boiler
Longest Continuous Run	350 hours	2 months	10 days	-	1 month	180 hours
Degree of Process Integration(b)	2	2	3	1	2	2
SPECIAL PROBLEMS:	Carbon attrition	Operating complexity	Char losses	Spray dryer control	Fume formation	Use of H_2S as a reactant
	Fluid bed scale-up	Integration of swing mode adsorption with continuous conversion	Material handling	Material stress	Adsorber operating complexity	Hydrocarbon losses from kerosene flotation
	High pressure drop	High usage of H_2	Operation of RESOX Process	Possible quench melt explosion	SO_4 reducer operation	H_2S production from coal Syngas
						Integration with H_2S production

TABLE 6-1 (Continued)

PROCESS EVALUATION SUMMARY

Design Basis: 500 Mw, 3.5% Sulfur Coal

Evaluation Criteria	Ammonia-Ammonia Bisulfate (ABS) Process	IONICS Electrolytic Regeneration Process	WELLMAN-LORD Sulfite Scrubbing Process	CAT-OX Catalytic Oxidation Integrated Process	MAGNESIA Slurry Scrubbing Process	LIME/LIMESTONE Wet Scrubbing Process
ENVIRONMENTAL EFFECTS:						
SO_2 Removal, %	90-99	90-99	90-99	90-95	90-95	90
Demonstrated NO_x Removal, %	-	20-40	-	-	-	-
Waste Streams	6,300 lb/hr ammonium sulfate (commercial grade)	30 gpm dilute pure H_2SO_4 (10%)	Anhydrous sulfate purge stream 2700 lb/hr	Sulfuric acid mist	Intermittent slurry purge	Scrubber sludge lime - 96,000 lb/hr, limestone - 117,500 lb/hr
	100 gpm particulate slurry from prewash section	Small amount of chlorine gas from cells	Fly ash slurry from venturi prescrubber			
	Small quantity of ammonium salt slurry	Filter cake from cell feed treatment				
UNIQUE DESIGN FEATURES:	Staged absorber	Electrolytic cells for regeneration of scrubbing liquor	Double effect evaporation/crystallizers for regeneration	High efficiency electrostatic precipitator	Thermal drying and decomposition of $MgSO_3$/$MgSO_4$ crystals	Throwaway process with no regeneration or reduction steps
	Thermal decomposition of ammonium sulfate to NH_3 and ABS	Potential for use as sulfate purge treatment	Fractional crystallization purge treatment	Direct catalytic conversion of SO_2 to SO_3 and absorption to produce acid	Formation of either hexahydrate or trihydrate crystals in the absorber	Open or closed (packed) configurations for the scrubber
	Acidulation of absorber product liquor to release SO_2					
UTILITY & RAW MATERIAL REQUIREMENTS:						
Electric Power (Mw)	27	35	12	13	9	Lime - 11
Fuel Oil (MMBtu/hr)	-	-	-	-	130	-
Stack Gas Reheat High Pressure Steam (MMBtu/hr)	77	77	77	-	77	77
Steam (MMBtu/hr)	62	34	168	26	-	-
Reducing Agent H_2/CO (MMBtu/hr)	92	92	92	-	$145^{(sulfur)}$	-
Reducing Agent-Coal/Coke (MMBtu/hr)	-	-	-	-	Coke - 5	-
Raw Materials (lb/hr)	NH_3 - 1,800 lb/hr	Na_2CO_3 - 300 H_2O_2 (23.5%) - 125	Na_2CO_3 -2120	Catalyst - 15	MgO - 520	Lime - 23,200 Limestone - 50,000
Total Incremental[(a)] Fuel Consumption (Btu/kwhr)	1,030	1,160	840	290	1,038 - sulfur 604 - acid	Lime - 380 Limestone - 390
Total Utility & Raw Material Costs (mills/kwhr)	2.5	2.4	1.7	0.5 Integrated 1.4 Reheat	2.3 - sulfur 1.2 - acid	Lime - 1.1 Limestone - 0.8
DEVELOPMENT STATUS:						
Size (Mw)	1.2	0.75	220	110 Reheat	160	(f)
Fuel Type	Coal-Fired Boiler	Coal-Fired Boiler	Oil-Fired Boiler	Coal-Fired Boiler	Coal-Fired Boiler	Coal-Fired Boiler
Longest Continuous Run	2 months	11 days	Commercial Plants in Operation	Partial Capacity 600 hrs.; Full Capacity 300 hrs.	Commercial Plants in Operation	Commercial Plants in Operation
Degree of Process Integration[(b)]	2	2	3	3	3	3
SPECIAL PROBLEMS:	Fume formation	High electric power consumption	Sulfate purge reduction	Catalyst fouling with particulates	Formation of $MgSO_3$ Hexahydrate crystals in scrubber	Scaling and plugging
	Absorber operating complexity	Complete process not offered by single vendor	Evaporator/crystallizer maintenance	Materials of construction - hot dilute acid during startup	MgO fines problem in dryer and calciner	Solids disposal
	Thermal decomposition of ammonium sulfate			Demister plugging		
				Flue gas heat exchanger leakage (reheat)		

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[a] Increment fuel is defined as the sum of the following process requirements:

1) Electric Power @ 10,000 Btu/kw
2) Fuel Oil @ 1.0 Btu/Btu
3) High Pressure Steam @ 1.0 Btu/Btu
4) Low Pressure Steam @ 0.5 Btu/Btu
5) H_2/CO Reducing Agent @ 1.5 Btu/Btu
6) Coal/Coke Reducing Agent @ 1.0 Btu/Btu

[b] Integration ranking; 1) SO_2 collection demonstrated without integration of process steps
2) Demonstration of a partially integrated system
3) Complete integrated plant demonstration including production of reducing gas

[c] Coal-Fired Equipment Now Proposed

[d] Citrate Process

[e] Phosphate Process

[f] Several units of greater than 100 Mw are now operating

throwaway process. The calcium sulfite/sulfate sludge is a serious disposal problem requiring a large land area for dumping. The AI Process also has a large waste stream, but it is composed of primarily fly ash, which is easily disposed of. Material balance calculations indicate the Cat-Ox Process has the smallest waste stream. The Catalytic/IFP Process also has very small waste streams while the Ionics Process has a dilute sulfuric acid stream as its primary by-product.

Each FGD system under evaluation has unique design features which present potential problems of process acceptance by the electric utility industry. Although none of these design areas present insurmountable problems, they do represent potential operating problems which a particular utility may wish to avoid. A list of FGD processes and their potential operating problems resulting from their unique process design is presented below:

Process	Potential Operating Problem
Westvaco	High-pressure drop and adsorbent attrition resulting from multi-staged fluidized beds.
Shell/UOP	Integration of swing mode SO_2 acceptor beds with continuous conversion.
BF/FW	SO_2 reduction in the RESOX Process and char combustion in the adsorber.
Atomics International	Operation and control of the molten salt reactor.

Process	Potential Operating Problem
Catalytic/IFP	Control of fumes resulting from ammonia scrubbing operations.
Citrate/Phosphate	Off-site-production of H_2S from low Btu gas and product sulfur.
ABS	Fume formation and thermal decomposition of ammonium sulfate.
Ionics	High consumption of electric power by the regeneration section leading to derating of the power plant.
Wellman-Lord	Sodium sulfate purge control and disposal.
Cat-Ox	Requirement for very high efficiency electrostatic precipitator to protect the oxidation catalyst from fouling by particulates, and materials problems.
Magnesia	Energy requirements and MgO fines, problems in the dryer and calciner.
Lime/Limestone	Scrubber sludge disposal and scaling of equipment.

Material and energy balance calculations were used to independently determine raw material and utility requirements for each process, which were subsequently used to estimate raw material and utility costs. Results of these calculations, shown in Table 6-1, indicate the following:

1) The Shell/UOP Process is the most energy intensive process (1,420 Btu/kwhr), while the Cat-Ox and Lime/Limestone Processes require the least amount of incremental fuel (less than 400 Btu/kwhr). Of the regenerable processes producing sulfur the Atomics International, and Citrate/Phosphate Processes consume the least amount of incremental fuel (about 700 Btu/kwhr).

2) Utility and raw material costs are highest for the Shell Process and lowest for the Integrated Cat-Ox and Lime/Limestone Processes, followed closely by the AI, and Citrate/Phosphate Processes. The Shell Process stands out as the most costly system partly because of the inclusion of 0.6 mills/kwhr for ammonia for NO_x reduction.

3) Stack gas reheat (about 155 Btu/kwhr) is required by all the processes which utilize aqueous scrubbing media except the AI Process. Other processes reheat, although the AI Process would require reheat if the amount of water entering the spray dryer is not carefully controlled. Flue gas reheat prior to the FGD process is required in retrofit applications of the Shell and Cat-Ox Processes since these operate at high temperatures.

4) Fuel oil is now used by the Westvaco, Shell, AI, and Magnesia Processes for heat, but these systems could probably be adapted to use coal or low Btu gas.

5) Processes which do not oxidize the SO_2 theoretically require only 2 moles H_2/CO per mole SO_2 to produce sulfur. In actual practice, however, slightly more than 2 moles are used. The Westvaco Process oxidizes the SO_2 to sulfuric acid and its stoichiometric requirement to produce sulfur is 3 moles H_2 per mole SO_2. Actual requirements, however, are 3.3 to 3.9 moles H_2 per mole SO_2 depending upon the amount of chemisorbed oxygen. The Shell/UOP Process which oxidizes the SO_2 to a metal sulfate and then reduces both the sulfur and the metal, theoretically requires 4 moles H_2 per mole SO_2. Due to process inefficiencies, the actual usage is about 6.2 moles H_2 per mole SO_2.

6) The magnesia slurry scrubbing process which produces a dilute SO_2 stream containing oxygen requires 36 percent more reducing gas to produce sulfur than do other regenerable processes which produce an SO_2 stream. Excess reducing gas is required because the oxygen will consume an equal amount of reducing gas on a molar basis as SO_2.

7) Processes requiring low Btu gas as a reductant receive an economic liability when compared to processes employing coal or coke as reductants. The economic penalty can amount to about 0.5 mills/kwhr and is due to the fact that low Btu gas costing $4.00/MM Btu has the same reducing capacity on a Btu basis as coal or coke which are priced in the range of $1.00-$1.50/MM Btu.

8) The AI Process currently uses petroleum coke as a reductant and a heat source for the molten salt regenerator. The use of coal is under evaluation. The BF/FW Process currently uses anthracite coal as a reductant.

9) The Lime/Limestone Process has the largest raw material requirement, by far, due to its throwaway nature. The large raw material requirement does not seriously affect process economics due to the low cost of limestone. Sludge disposal costs, however, can be significant.

10) Raw material and utility costs for these processes are on the order of 20 to 45 percent of the total annualized process costs. This assumes that capital costs are in the proximity of $100/kw for all processes.

An important consideration for wet processes, which impacts raw material and energy requirements, is the liquor loading, or the amount of SO_2 absorbed in the circulating liquor. This is important as it determines the process pumping rate and the regeneration equipment size with small liquor loading values requiring higher circulation rates and larger regeneration equipment. Typical liquor loading ranges were calculated for each of the wet processes and are reported below.

Process	Typical Liquor Loading [(g SO_2/ℓ solution)]
Lime/Limestone	<1
Citrate/Phosphate	3-10
Magnesium Scrubbing	40
Wellman-Lord	70-80
Ionics*	110-120
Ammonia Scrubbing	>200

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*Radian's assumed absorber

The FGD processes are in varying stages of development. The Lime/Limestone, Magnesia Slurry, and Wellman-Lord Processes are already in commercial use on the demonstration scale (100 Mw) or greater. The Reheat Cat-Ox Process has also been built on a 100 Mw demonstration scale but operation was not satisfactorily proven due to equipment problems. The Shell and BF/FW Processes fall into a second group. The Shell FGD Process has operated on a 40 Mw scale in Japan but the unit was not intergrated. The

BF/FW Process is being demonstrated on a 20/47 Mw scale, but the unit will undergo modifications after the initial runs. The other processes are all still in the pilot plant stage with units of around 1 to 2 Mw capacity. The developers of these processes anticipate increasing the size and degree of integration of their processes, which may result in operating problems not yet experienced in pilot plant operations.

7.0 SPECIFIC AREAS OF INVESTIGATION FOR REGENERABLE PROCESSES

As an additional task Radian was requested to make recommendations to EPRI concerning areas where further development work is needed in the Wellman-Lord, Cat-Ox, and Magnesia Slurry Scrubbing Processes. Of the regenerable processes these three are the most highly developed and the closest to full-scale commercialization in the utility industry. However, problems of both an economic and technical nature continue to slow their acceptance.

The recommendations generally can be classified into two areas: (1) acquiring basic knowledge about the process and its chemistry, and (2) equipment development needs. In general, a thorough understanding of the chemical, kinetic, and thermodynamic relationships which govern a process is the most valuable tool available in designing and optimizing a process. This knowledge allows predictions concerning behavior of the process under varying conditions and increases the probability of successful operation. In some cases however, equipment limitations can ruin an otherwise workable process. Therefore equipment alternatives must be investigated as well.

Additional developmental efforts are also needed for the second generation processes before they can be considered fully demonstrated and viable. Areas suggested for further study are summarized for each of the second generation processes in a section following the first generation process recommendations. In many cases, efforts by process developers to study or demonstrate these items may already be underway. At this time, however, further investigation of each of the suggested study areas appears warranted.

7.1 Wellman-Lord Sulfite Scrubbing Process

There are three major areas in the Wellman-Lord Process where further development work could yield important results: (1) oxidation of sulfite to sulfate in the absorber, (2) sodium sulfate purge treatment, and (3) energy usage in the regeneration section. Understanding oxidation is a question of basic chemistry. The sodium sulfate purge treatment involves some thermodynamic considerations as well as problems in equipment selection.

Oxidation

Oxidation of sodium sulfite in the absorber to sodium sulfate by flue gas oxygen is not well understood theoretically. Work has been done by Davy Powergas in an attempt to correlate sulfate formation rates with various factors for their solution concentrations and absorber configuration. Controversy over the exact mechanism and the oxidized species is still going on. Recommendations for further work in this area are as follows:

- General studies of the mechanism or mechanisms of sulfite oxidation, and factors which effect the rate of oxidation in an attempt to control oxidation by varying the appropriate factors.

- Renewed investigation of antioxidants, possibly centering on inorganic agents which should be less expensive than organic compounds.

Sulfate Purge Treatment

In order to maintain the sulfate concentration at a reasonable level some purge treatment will be needed because it is extremely unlikely that complete control of oxidation will ever be achieved. The purge treatment involves using some separation technique to remove the required amount of sodium sulfate from the system while balancing the need to minimize the operating cost of the treatment and the need to purge as small an amount of active sodium compounds as possible with the sodium sulfate. Along these lines the following suggestions for investigation are made.

- Improve the sodium sulfate to sulfite ratio in purged solids. One means of accomplishing this would be staging the freeze crystallization process presently used.
- Determine the theoretical and operational feasibility of fractional crystallization at other temperatures.
- Develop information on use of technology from other fields to convert sodium sulfate to a reusable form or purge sulfate ion in some other manner than sodium sulfate.

Energy Usage in Regeneration

At present the Wellman-Lord Process uses double effect evaporator/crystallizers in the regeneration section to reduce steam requirements 45 percent from those necessary with single effect evaporators. However, this area still remains a major consumer of energy for the process. Improving the energy efficiency of sulfite regeneration and SO_2 stripping should be investigated as significant savings may still be possible. Along these lines further work should involve the following areas.

- Examination of the use of multiple effect evaporators beyond double effect in various flow configurations.
- Study of the crystallization properties of sodium compounds in multiple effects.
- General investigation of other methods of thermally regenerating the sodium bisulfite/sulfite solution, such as reboiler towers using heat pumps.

7.2 Cat-Ox Process

The Cat-Ox Process's development has been stalled due to problems experienced with the Wood River demonstration unit. Recommendations are based primarily on the difficulties at Wood River and are grouped in the two general areas of chemical investigations and equipment development. Research needs in the chemistry areas are as follows.

Experimental work to determine the effect of the flue gas environment on the vanadium pentoxide catalyst used for SO_2 oxidation.

- Assessment of the health and environmental effects of the trace elements in the sulfuric acid produced by the Cat-Ox Process.

Equipment problems were the major difficulty with the Wood River demonstration and the following areas for work are suggested.

- The Cat-Ox demonstration unit at Wood River needs to be refurbished and operated to evaluate the reheat Cat-Ox Proccess's feasibility.
- Evaluation of the materials of construction with respect to "thermal shock" in operating a "hot-side" electrostatic precipitator.
- Evaluation of different designs for the acid absorber which would enable the Cat-Ox Process to produce a more concentrated product acid.
- Evaluation of the cost of using a shell and tube heat exchanger in place of the Ljungstrom Flue Gas Heat Exchanger for the Reheat Cat-Ox Process.

7.3 Magnesia Slurry Scrubbing Process

The Magnesia Slurry Scrubbing Process still faces many problems both of a chemical and equipment nature. Thus far process operations have been aimed more at getting the process to run after it has been built rather than developing the basic chemical and kinetic data which might help in understanding the process. To correct this situation the following items are suggested as needing further investigation.

- Studies of the rates of dissolution of recycled MgO and MgOH as functions of the type of hydrate $MgSO_3$ crystals formed and the calciner temperature versus time profile.
- Investigation of the kinetics of precipitation of the two types of hydrates and the supersaturation required for nucleation.
- Inquiry into the effect of nozzle and agitator shear on nucleation.
- Vapor-liquid mass transfer studies in the scrubber to determine the limiting steps.
- Continuous runs on a pilot unit to check the levels to which impurities build up in order to determine purge rates.
- Bench scale testing and kinetic studies of direct production of sulfur in the calciner.

Equipment developments are most needed in the regeneration section because it is here that the largest energy consumption occurs. Magnesium oxide losses can also be significant in this area. Potential areas for further work are listed below.

- Evaluation of the use of power plant flue gas for drying the $MgSO_3/SO_4$ crystals.

- Testing of coal as the calciner fuel in place of fuel oil which would require major equipment modifications.

- Investigation of the use of a fluid bed calciner and a fluid bed dryer rather than rotary equipment to improve thermal efficiency and prevent dead burning.

- Studies to compare various types of scrubbers to the venturi equipment presently used.

7.4 Second Generation Processes

Areas suggested for further study for each of the second generation processes are as follows.

Westvaco

- Demonstrate the operability of large scale fluidized beds.

- Investigate methods of decreasing the large incremental fuel requirement associated with heavy usage of reducing gas, such as production of SO_2 instead of sulfur.

- Large scale demonstration is needed to conform the design of the regeneration area and ascertain if handling of the solid adsorbent will present problems.

Shell/UOP

- Demonstrate integrated operation with hydrogen production and SO_2 conversion to sulfur.
- Investigate other methods of concentrating and handling the SO_2 rich gas from regeneration.
- Improve the efficiency of reducing gas usage.
- Examine the chemistry of the catalytic reduction of NO_x with NH_3 to potentially improve the efficiency of NH_3 usage and verify that levels of NH_3 in the exit gas can be kept low.

BF/FW

- Examine the NO_x and particulate removal capability for the process.
- Obtain complete operating and design data including the chemistry and kinetics of the RESOX process.
- Demonstrate solids handling capability and reliability during integrated operations.

- Quantify the various methods of char consumption (e.g. physical attrition, chemical reaction during regeneration with SO_3, NO_x, and/or O_2).

Atomics International

- Verify on a pilot scale that the molten salt regeneration can be operated. Operability, corrosion, equipment (e.g. pumps and seals) must be adequately demonstrated.

- Demonstrate system operability on a completely integrated mode.

- Demonstrate large-sized spray dryer to examine gas distribution and gas temperature control at design conditions.

- Examine the system's potential for particulate control.

Catalytic/IFP

- Demonstrate fumeless technology on an integrated system while producing a liquor with a C_A* greater than 12.

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*C_A is the moles of ammonia as sulfite and bisulfite per 100 moles of water.

- Obtain operating and design data for the IFP hydrogen sulfide generator and sulfate reducer.

- Demonstrate the use of low Btu gas as a source of fuel and as a reductant.

Citrate/Phosphate

- Demonstrate integration of H_2/CO production and H_2S production with the process.

- Further define the process chemistry, particularly in the regeneration section.

- Study methods of minimizing the formation of sulfate and of purging the sulfates produced.

Ammonia-ABS

- Demonstrate fumeless operation through control of the absorber or application of fine particulates controls.

- Operate the Colbert Station pilot plant in a fully integrated mode.

- Obtain operating and design data for the thermal decomposer.

- Examine the intermittent formation of a yellow solid in the crystallization/separation steps.

Ionics

- Demonstrate an integrated process and obtain data for scale-up of all process segments.

- Examine in detail the potential for cost reduction by use of off-peak power for solution regeneration.

- Continue the electrolytic cell development efforts to reduce the system's power consumption.

- Investigate the use of the SULFOMAT cell for control of sodium sulfate purge streams from other sodium based scrubbing systems.