ADVANCED THIOCLEAR PROCESS TESTING

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FINAL REPORT

PREPARED FOR THE

OHIO COAL DEVELOPMENT OFFICE

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DRAVO LIME COMPANY
THE CINCINNATI GAS AND ELECTRIC COMPANY

DLC-5246

DISCLAIMER

Advanced ThioClear Process Testing

Final Report

OCDO Grant Agreement No: CDO/D-91-6

Project Manager

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I. EXECUTIVE SUMMARY

Abstract

Wet scrubbing is the leading proven commercial post-combustion FGD technology available to meet the sulfur dioxide reductions required by the Clean Air Act Amendments. To reduce costs associated with wet FGD, Dravo Lime Company has developed the ThioClear process. ThioClear is an ex-situ forced oxidation magnesium-enhanced lime FGD process. The ThioClear process differs from the conventional magnesium-enhanced lime process in that the recycle liquor has minimal suspended solids and the by-products are wallboard quality gypsum and magnesium hydroxide, an excellent reagent for water treatment. The process has demonstrated sulfur dioxide removal efficiencies of +95% in both a vertical spray scrubber tower and a horizontal absorber[1] operating at gas velocities of 16 fps, respectively. This report details the optimization studies and associated economics from testing conducted at Dravo Lime Company's pilot plant located at the Miami Fort Station of the Cincinnati Gas and Electric Company.

Introduction

In the United States, the Clean Air Act Amendments (CAAA) offer incentives for the use of high efficiency SO_2 removal technologies through a provision which allows the accumulation of excess emission allowances if scrubber performance exceeds CAAA requirements. These allowances can be used to meet reductions required at other affected generating units, offset emissions from new units, or be traded for cash. Thiosorbic®, or magnesium-enhanced lime FGD systems with their capability to efficiently scrub flue gases generated from the combustion of lower priced high sulfur coals have a strong position in the market. Currently, twenty-seven electric utility units with a combined generating capacity of 13,500 MW are utilizing magnesium-enhanced lime FGD systems.

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[1] The terms scrubber and absorber are utilized interchangeable in this report to denote the mass transfer vessel which provides the physical contact between the combustion flue gas and the alkaline liquor required to remove SO_2.

One drawback of wet FGD systems is the cost associated with disposal of the calcium based solids. Typically these solids require capital costs in land procurement for landfills. Operating costs are incurred for fixation to stabilize the solids and for transportation to deliver the solids to the landfill. Environmental restrictions and limitations regarding landfills have further increased these costs and in some instances, eliminated the option of a landfill. Therefore, determining what improvements and advancements that can be made to wet FGD processes to reduce the costs and generation of landfill materials is important.

To improve the economics of the Thiosorbic FGD process, DLC developed the ThioClear® process. The ThioClear process utilizes a magnesium based absorber liquor with minimal suspended solids to remove SO_2. Magnesium-enhanced lime regenerates an oxidized bleed stream of scrubbing liquor to produce magnesium hydroxide and gypsum as by-products. Bench scale testing was initiated in 1985 at DLC's Research Center in Pittsburgh, Pennsylvania. Subsequent pilot scale tests of various subsystems pertinent to the ThioClear process were conducted at Allegheny Power Services' Mitchell Station and Pennsylvania Power Company's Bruce Mansfield Station in 1989 and 1990, respectively. The encouraging results from these efforts led to a successful six week proof of concept test at the Miami Fort pilot plant in which the subsystems were integrated into a closed loop FGD system with a comparable rating of 1.5 MW. Although this short test period prevented optimization of the process or improvements in the recovery and purity of the by-products, it was determined that sufficient quantities of magnesium hydroxide could be recovered to meet the demands of the absorber and provide a product stream while simultaneously producing gypsum.

Prompted by the success of the proof of concept testing, a two phase program was developed for additional evaluations of the process. Phase I, which was conducted from May to October 1993, utilized a process flow scheme similar to that of the proof of concept testing. The goals of these studies were to optimize the process and improve the process control. Phase II, which was conducted from March to December 1994, incorporated a process modification which entailed a continuous filter operation. The goals of this phase were to maximize by-product purity and recovery, characterize SO_2 removals in both vertical and horizontal scrubbers, and determine process economics.

This Final Report details the optimization studies and corresponding economics resulting from these two phases of testing conducted at DLC's pilot plant at the Miami Fort Station of the Cincinnati Gas and Electric Company (CG&E). The testing was a joint effort between CG&E and DLC. Funding for the project was from the Ohio Coal Development Office (OCDO), CG&E, and DLC.

Technology Description

The ThioClear process takes advantage of the catalytic effect of magnesium to increase the alkalinity of the scrubbing liquor. Magnesium hydroxide is introduced to the recycle tank to control the pH between 6.0-6.5. The hydroxide reacts with captured sulfur dioxide in either the absorber or the recycle tank to form the alkaline salt, magnesium sulfite. This salt rapidly neutralizes additional absorbed SO_2 by forming magnesium bisulfite and thereby provides the scrubbing liquor greater capacity in absorbing SO_2 compared to systems where magnesium sulfite is not present.

Utilization of the scrubber effluent supplies a low pH liquor in the range of 5.5-6.0 to the oxidizer. Oxidation of the liquid phase magnesium sulfites and bisulfites produces magnesium sulfate. As a result of the formation of sulfuric acid from the oxidation of the bisulfites, magnesium hydroxide additions are required to maintain the pH of the oxidizer between 4.5-5.5.

The oxidized liquor is supplied to the regeneration tank which is the crystallizer of the process. Slaked magnesium-enhanced lime which is composed of +90% calcium oxide and 4-8% magnesium oxide is added to the regeneration tank to maintain the pH between 10.0-10.8. This mixture precipitates the sulfates as gypsum and regenerates the magnesium species to magnesium hydroxide. The resulting slurry is subjected to separation by hydroclones. The magnesium hydroxide-rich stream is utilized for pH control of the scrubber and oxidizer. The surplus material is available for by-product use. The gypsum-rich stream is dewatered for by-product use or can be stacked as a method of disposal.

This project evaluated two variations of the ThioClear process for their respective impact on by-product purity and recovery of magnesium hydroxide. In Phase I, the process was operated as detailed in Figure I-1. In this configuration, the separation of the by-products relied solely on the efficiency of the hydroclones. The Phase II configuration which is more complex than the Phase I operation was evaluated for its potential improvements over that which would be achieved in the first phase. This configuration involved the recycling of the gypsum-rich hydroclone underflow stream to the oxidizer and continuous filtration as shown in Figure I-2. The benefits of this configuration were the removal of magnesium hydroxide contamination in the gypsum by dissolution in the low pH regime of the oxidizer and the prevention of silica inerts from accumulating in the process due to their removal by continuous filtering.

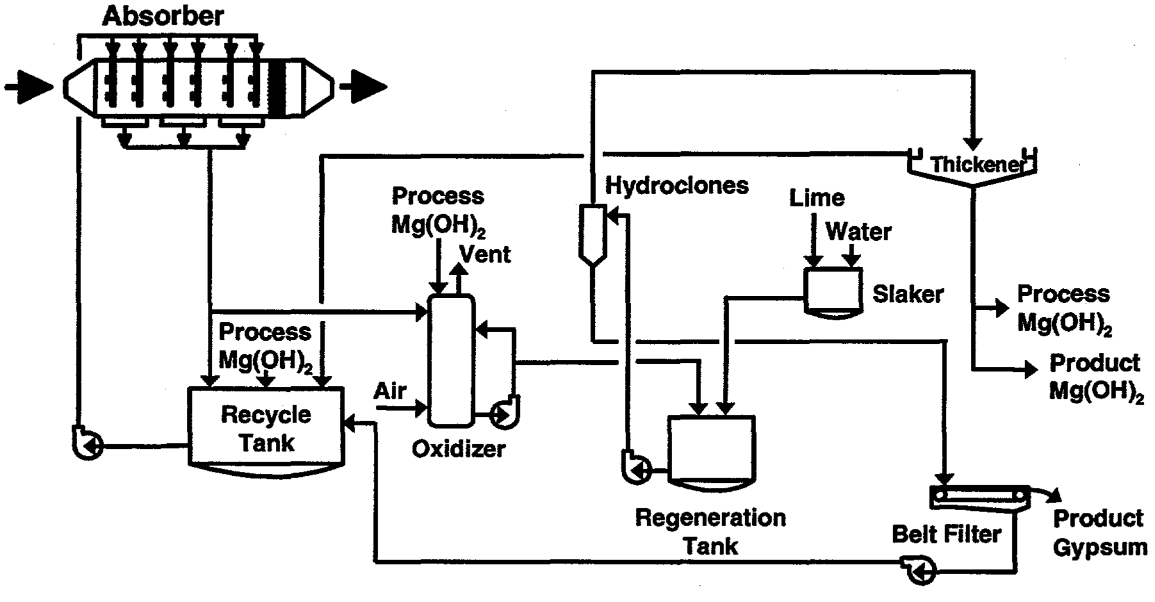


Figure I-1. Phase I ThioClear Process Flow Diagram

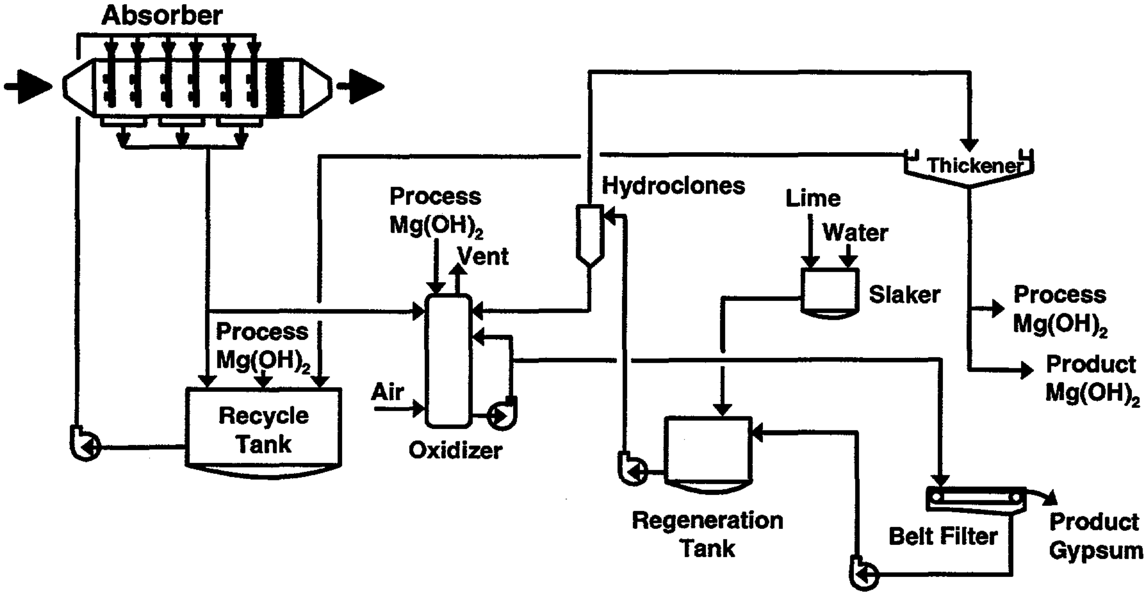


Figure I-2. Phase II ThioClear Process Flow Diagram

A. PROJECT RESULTS

1. Oxidizer Optimization

ThioClear is an ex-situ oxidation process. External oxidation allows nearly independent control of the absorber parameters of alkalinity which depend on the magnesium sulfite concentrations and the scrubbing liquor pH. Therefore, the absorber can operate at optimum scrubbing efficiency. Similarly, the separate oxidizer lends itself to greater flexibility in controlling the oxidation process. This flexibility, combined with the oxidation of the liquid phase sulfites as opposed to sulfite precipitates, minimizes the size of the oxidation vessel.

Figure I-3 details the results of the oxidizer optimization. For this study, the pH was maintained at 5.0. Vertical absorber operating parameters were 70 L/G, a gas velocity of 10 fps, and an inlet SO_2 concentration of 2000 ppm. Removals of SO_2 averaged +95% throughout the evaluation. The optimization studies showed that reduction in air requirements for oxidation of the magnesium sulfite to magnesium sulfate can be achieved by increasing the residence time of the oxidizer. To achieve an oxygen feed rate of 2 lb-mole oxygen per lb-mole SO_2 absorbed of less than 2, a residence time of approximately 1.75 hours would be required.

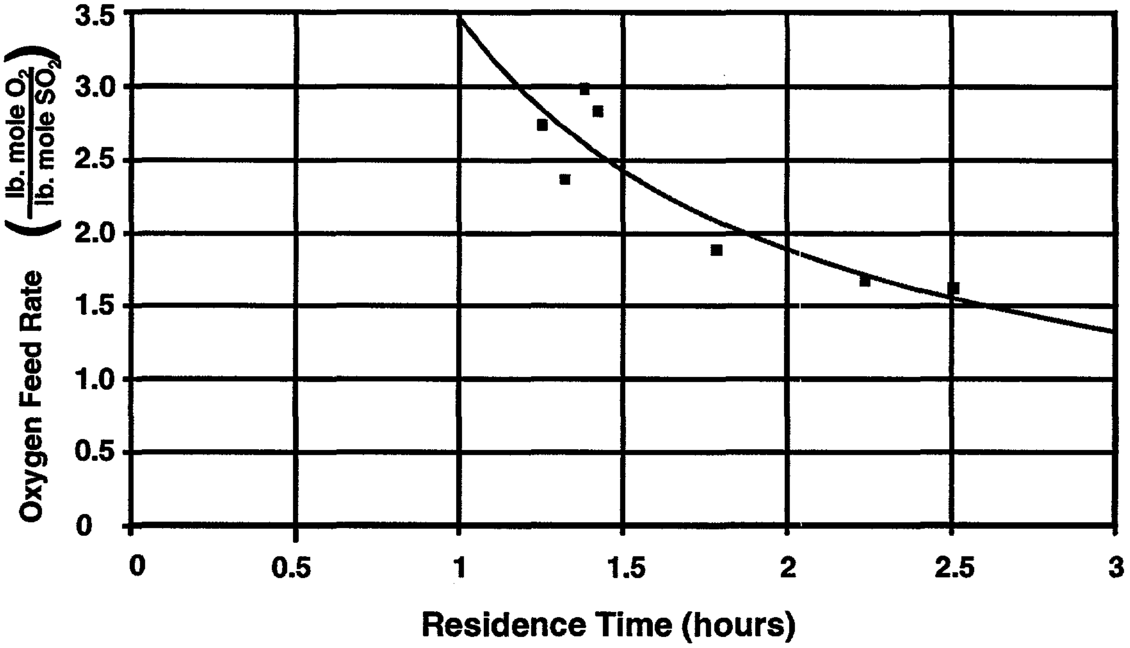


Figure I-3. Oxidizer Performance

2. Regeneration Tank Optimization

The regeneration tank is the crystallizer for the ThioClear process. It is important in the performance of this vessel that the resulting crystals of gypsum and magnesium hydroxide maintain a substantial size differential in order to undergo efficient separation by hydroclones. Economic considerations dictate limiting the size of the tank. During the optimization of the regeneration tank, the operating parameters of pH and residence time were evaluated with respect to their impact on the size of the gypsum crystal. Figure I-4 shows the results of the optimization.

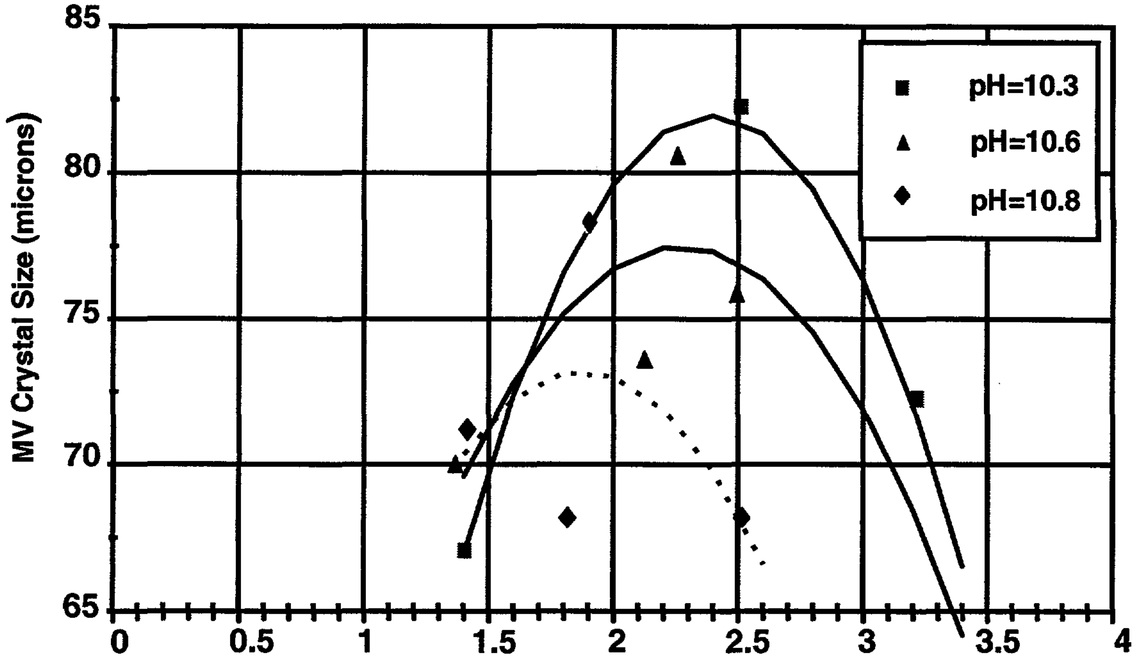


Figure I-4. Regeneration Tank Optimization

In general, as the pH of the regeneration tank was decreased, the optimal size of the gypsum crystal increased at the expense of a longer required residence time. This would indicate the slow growth of the gypsum crystal at low pH promotes a larger and less fragile crystal. The degradation of the crystal after achieving its maximum size is most likely the result of attrition caused by the agitator. The impact of the agitator is significantly less than the attrition which would be associated with gypsum crystals formed in the recycle loop of an absorber. Therefore, it is not surprising that the minimum and maximum mean values for the gypsum crystals formed in the ThioClear process were 67 microns and 82 microns, respectively. The mean value of the magnesium hydroxide crystals, which is typically less than 15 microns, was unaffected in the optimization studies.

3. Separation / Purification Optimization

For the ThioClear process to be feasible, sufficient quantities of magnesium hydroxide need to be produced and recovered to operate the facility and provide a by-product stream. Enhancing the purity of both the gypsum and the magnesium hydroxide will ease the acceptance of these by-products into their respective markets. An added benefit of improving the purity of the gypsum is the improved recovery of the magnesium hydroxide. In the ThioClear process, hydroclones and the belt filter serve to separate and purify the by-products.

Phase I of the ThioClear project focused on utilizing mechanical means, namely hydroclones, thickeners, and belt filter to separate and purify the magnesium hydroxide and gypsum by-products. Figure I-5 details the results of the by-product purities. Due to the limitations of these methods of separation, the product purity was below expectations. The overlap of the gypsum and magnesium hydroxide crystal size distribution contributed to cross contamination of each of the by-product streams. Due to the presence of magnesium hydroxide in the gypsum, the recovery of magnesium hydroxide was lower than theoretically possible which would reduce the income associated with this by-product stream and reduced the commercial value of the gypsum.

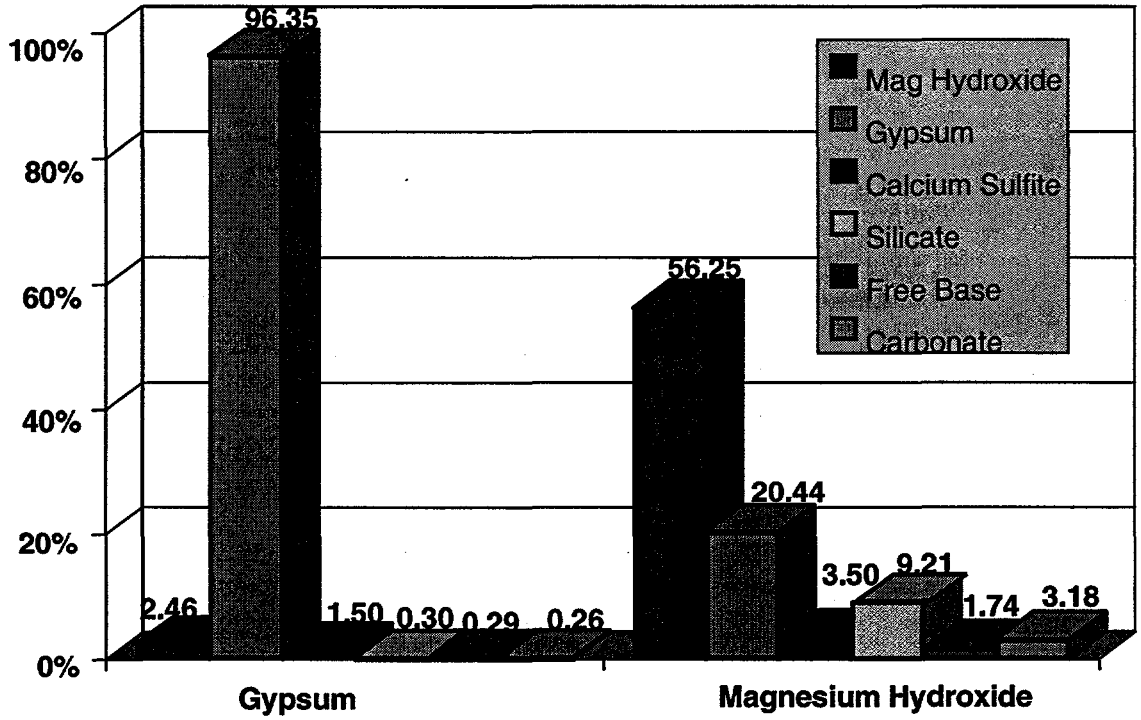


Figure I-5. Phase I By-Product Purity

Phase II utilized the chemistry of the process in addition to these mechanical means used in Phase I to improve by-product recovery and purity. The revised process configuration incorporated the recycling of the gypsum stream from the secondary hydroclones to the oxidizer. The low pH regime of the oxidizer dissolved the contaminating magnesium hydroxide. The effluent stream from the oxidizer was subjected to a desliming hydroclone which removed fines, mainly silicates, followed by a continuous filtration operation. By dissolving the magnesium hydroxide crystals in the oxidizer, the magnesium ion solution can be washed from the gypsum filter cake during the filtration operation. In increasing the purity of the gypsum, the recovery of the magnesium hydroxide was increased which improved the economics of the process as well as the acceptance of the gypsum into the commercial market. The results of the by-product purities for Phase II are shown in Figure I-6.

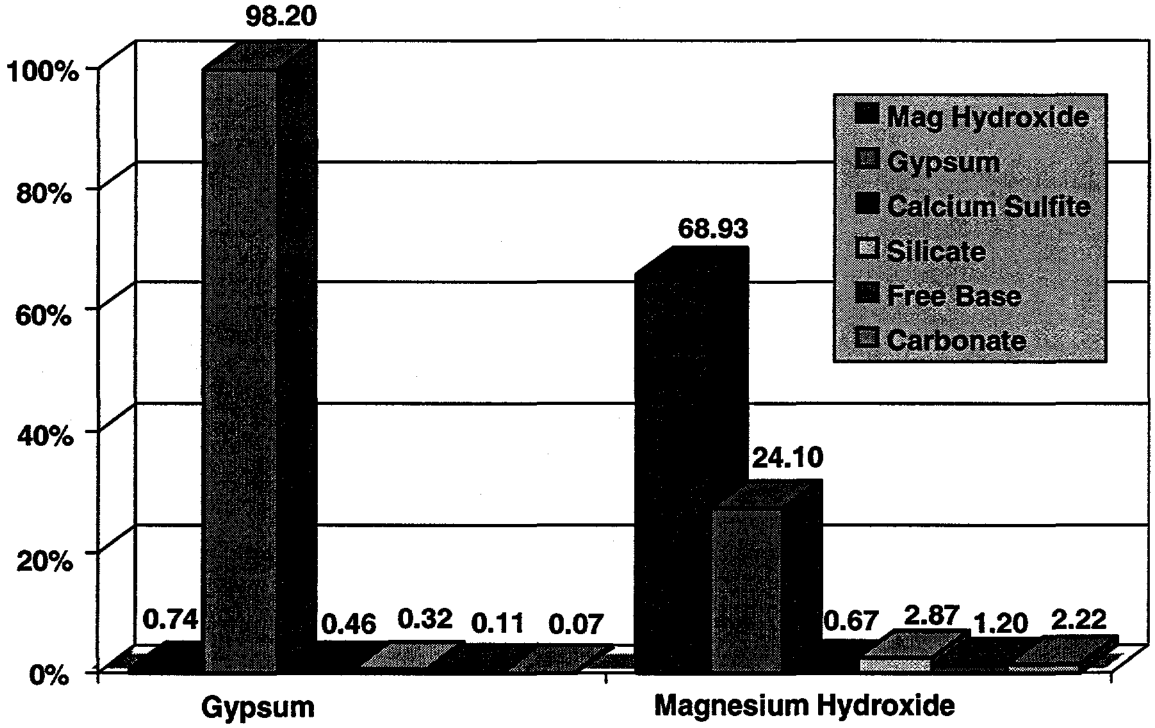


Figure I-6. Phase II By-Product Purity

4. Scrubber Performance

The Thiosorbic or magnesium-enhanced lime FGD process has been commercially available for nearly twenty years and has gained an excellent reputation for SO_2 removal capability. The development of the ThioClear process and its corresponding by-products has been successful in eliminating the disposal of the thixotropic solids generated by the prior magnesium-enhanced lime process. However, the ThioClear process has required subtle process changes to the operation and chemistry of the absorber. Utilizing magnesium hydroxide as the neutralizing agent instead of lime for the captured SO_2 has substantially reduced the quantity of calcium sulfite precipitated in the recycle tank and the resulting impact that these solids may contribute to the SO_2 removal process. Process changes affecting the operation of the ThioClear absorber included modulating the blowdown from the absorber on the basis of liquor chemistry and monitoring the pH of this stream for addition of the neutralizing agent. Whereas the Thiosorbic mode of operation focussed on the control of the percent suspended solids and pH of the recycle tank. Subsequently, evaluations of the absorber performance have been conducted in the areas of plant start-up, load-following, and high velocity scrubbing to insure the SO_2 removals are comparable to the Thiosorbic process.

One must be cautioned concerning the direct interpretation of pilot scale absorber performance to commercial size facilities. In general, the SO_2 removal achieved at the pilot plant is lower than that of a utility FGD absorber at similar operating conditions. At the pilot plant, the two absorbers utilized for the SO_2 removal studies were a 3 foot diameter vertical scrubbing tower and a horizontal absorber with length to width measurements of 51 inches by 25 inches. The droplets exiting the spray nozzles of these absorbers have a 90° spray angle which will impact the walls of the absorbers within 1 to 1.5 feet from the nozzle. The liquor lost to the walls tends to have minimal beneficial impact on SO_2 removal. This is not the case in the utility absorbers where greater utilization of the liquor is achieved due to minimal spray contacting the walls. Prior testing at the Miami Fort pilot plant has shown that up to 50% of the liquor entering the absorber does not contribute to SO_2 removal when duplicating operating conditions of commercial facilities.

a. Plant Start-up

Economic considerations require generating facilities to minimize outages and therefore be capable of full load capacity shortly after restart. It is imperative that the FGD system associated with these facilities be able to respond to the demands of the boiler start-up so as not to limit the capabilities of the boiler nor violate compliance requirements. This phase of operating a FGD facility may be further complicated when the prior FGD liquor has been dumped or the FGD system is undergoing its initial start-up. In either case, the FGD liquor chemistry necessary for SO_2 removal needs to be generated from service water and the neutralizing agent.

As a result of various process changes and parametric testing of the ThioClear process during its development at the pilot plant, multiple opportunities were available for evaluating the start-up capabilities of the ThioClear process. Figure I-7 shows a typical time sequence performance of the 3 foot diameter vertical scrubber during a "cold" start-up on service water and magnesium hydroxide slurry. As in typical scrubber operations, the recycle pumps were initiated before flue gas entered the absorber. Each data point represents an hourly average of the pertinent operational data after the booster fan was started. The inlet flue gas SO_2 concentration was 2000 ppm and the operating parameters of the absorber are as detailed in Figure I-7

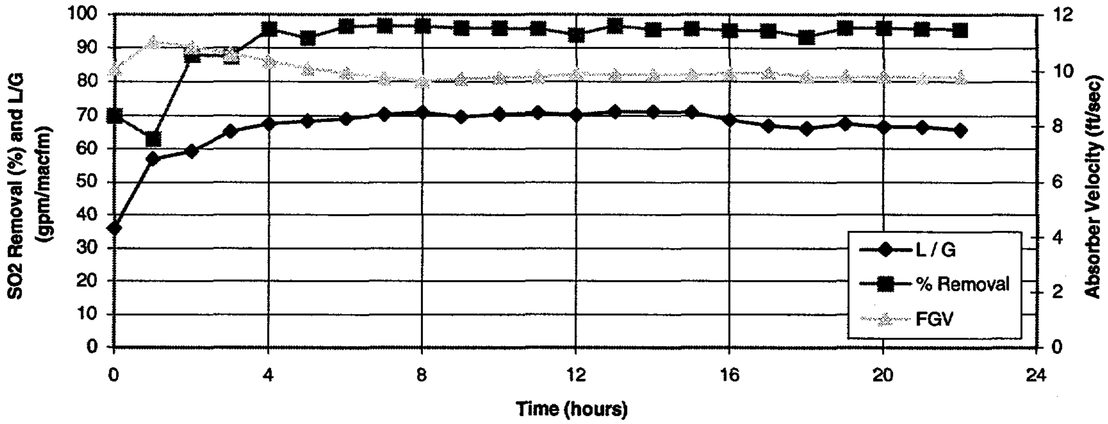


Figure I-7. Plant Start-Up

As shown on the graph, 95% SO_2 removal is achieved within 5 hours after the introduction of the gas into the absorber. These efficiencies resulted from the rapid increase of liquor alkalinity attributed to the formation of magnesium sulfite from the magnesium hydroxide additions. Since magnesium salts are soluble, the absorber blowdown was substantially reduced in order to establish a desired chemistry. Conversely, conventional non-forced oxidation calcium based FGD systems produce precipitates. Purging of the recycle tank to limit the build-up of suspended solids delays the formation of the scrubber chemistry due to dilution from make-up water.

b. Load Following

Testing of the absorber performance while simulating boiler load changes was achieved by adjusting the inlet SO_2 concentration. In this evaluation, SO_2 inlet concentrations were controlled at 1500, 2000, or 2500 ppm during predetermined times of the day. The flue gas velocity and the L/G of the 3 foot diameter vertical absorber was maintained at 10 fps and 72, respectively. In order to maintain high scrubber efficiency, the alkalinity of the absorber liquor was controlled by regulating the blowdown from the scrubber at flowrates of 10, 12.5, and 15 gpm to correspond with the above SO_2 concentrations. As in the plant start-up evaluations, the flowrate of the blowdown was reduced in response to the lower inlet SO_2 concentrations to accumulate magnesium compounds, namely magnesium sulfite, in the recycle liquor to increase its alkalinity. Due to the limited turn down of the pilot plant hydroclones for efficient magnesium hydroxide and gypsum separation, the minimal blowdown flowrates resulted in a less than optimal average alkalinity of 500 ppm. Even at this untypical alkalinity, the SO_2 removal during this week of testing averaged 95%. Figure I-8 shows a time trend of the pertinent data for the load following test.

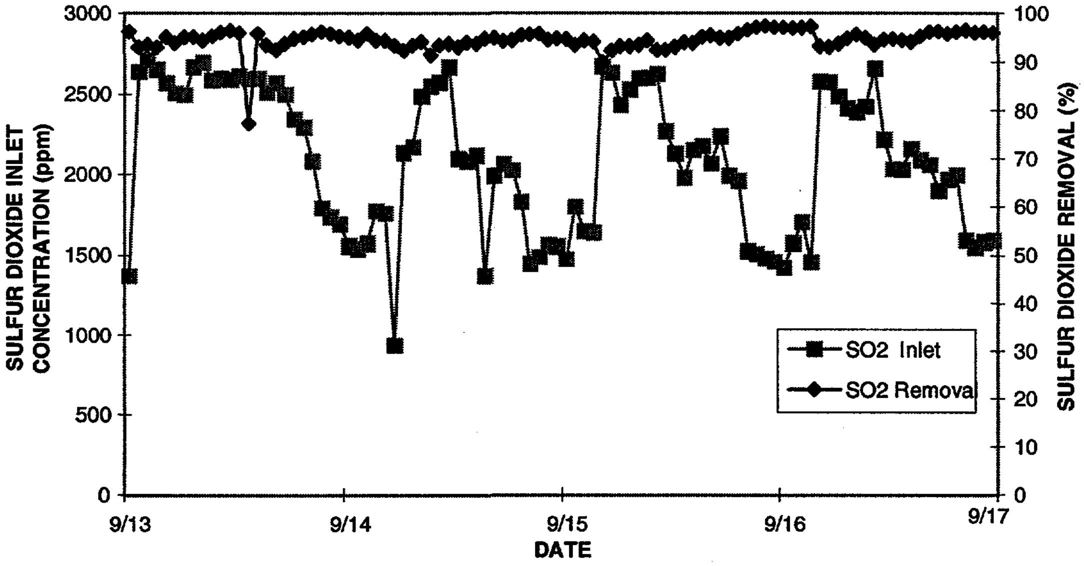


Figure I-8. Load Following

c. High Velocity Scrubbing

The purpose of this testing was to demonstrate that the ThioClear process can efficiently remove SO_2 similar to the Thiosorbic process at absorber velocities greater than the current industry design standard of 10 ft/sec. Higher design gas velocities allow a reduction in the absorber cross sectional area or the number of scrubbers to treat the same quantity of gas. For example, by increasing the design flue gas velocity to 15 ft/sec for a vertical scrubber, an 18% reduction in absorber diameter and material cost can be realized to scrub the same volume of gas.

Prior testing at the Miami Fort pilot plant has demonstrated the effectiveness of the Thiosorbic process in removing SO_2 at high absorber gas velocities in the 3 foot diameter scrubber tower. Similar tests were conducted while operating in the ThioClear mode. The results of these parametric tests in both the spray and tray tower configuration are shown on Figure I-9 and Figure I-10, respectively. The observed trends which are similar to those from Thiosorbic operation indicate that the required L/G to obtain a desired SO_2 removal decreases with increasing gas velocity. The improvement in SO_2 removal efficiencies can be attributed to increased interaction between the spray droplets and the flue gas at the higher gas velocities and an increase in the liquid residence time due to liquid holdup on the tray as well as droplet holdup within the tower.

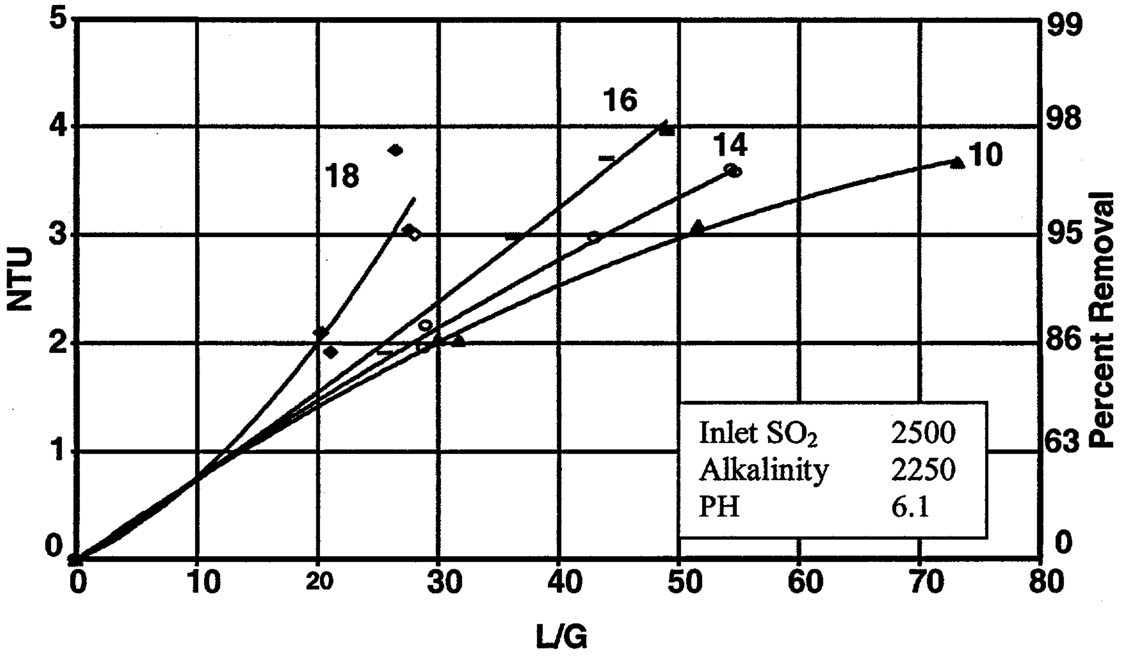


Figure I-9. Parametric Sulfur Dioxide Removal - Spray Tower

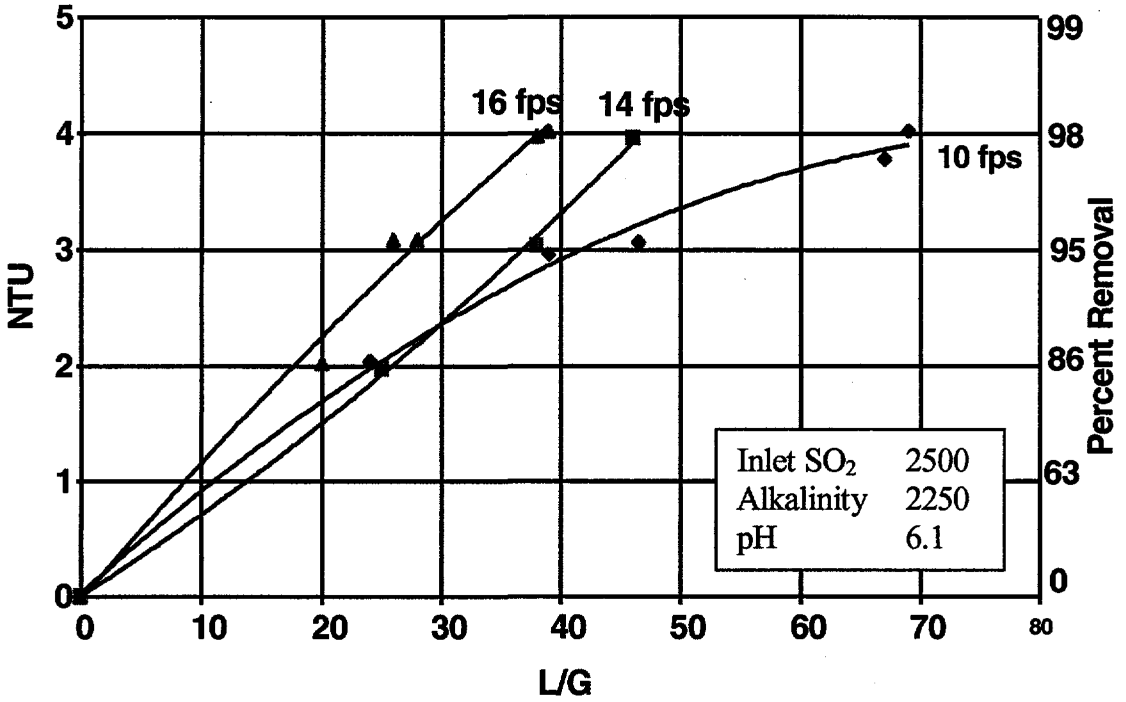


Figure I-10. Parametric Sulfur Dioxide Removal - Tray Tower

Testing in the vertical scrubber tower at higher velocities than those shown on the figures was not attempted due to re-entrainment of the accumulated liquor from the mist eliminator. The limitation of vertical demisters results from the accumulated liquor attempting to return to the scrubber with the aid of gravity while being opposed by the velocity of the flue gas which is exiting the tower. To avoid this short-coming, Dravo Lime Company installed a horizontal absorber which utilizes horizontal demisters which can effectively function at higher gas velocities than the vertical style. Additional advantages for evaluating horizontal scrubber performance include reduced height requirements when compared to vertical scrubbers and minimal impact when connecting to existing ducting. These advantages translate into greater flexibility in materials of construction, lower power consumption by pumps for meeting hydraulic head requirements, and lower inlet and outlet pressure losses.

Utilization of the horizontal absorber in the crossflow mode of gas/liquid contact is not new to the FGD industry. These FGD scrubbers, also known as Weir absorbers in reference to the inventor, are currently utilized at the Bruce Mansfield Generating Station of the Pennsylvania Power Company, the D.B. Wilson Station of Big Rivers Electric Corporation, and the Gibson Station of PSI Energy, Inc. However, performance and reliability of the absorber was adversely effected as the length of the vessel was reduced to minimize capital costs. The resulting nonuniform gas flow from compressing the gas toward the absorber floor reduced the effectiveness for SO_2 removal. The combination of the skewed velocity profile and recycle headers installed immediately in front of the demisters contributed to excessive carryover exiting the mist eliminators. To minimize these effects at the Miami Fort pilot plant, the spray headers were located within the cross sectional area of the absorber to minimize gas maldistributions. Taking advantage of the nonscaling tendencies of magnesium-enhanced lime processes, packing was installed to further reduce gas maldistributions, enhance mass transfer, and act as a predemister. Figure I-11 shows the typical configuration of the absorber as it was evaluated.

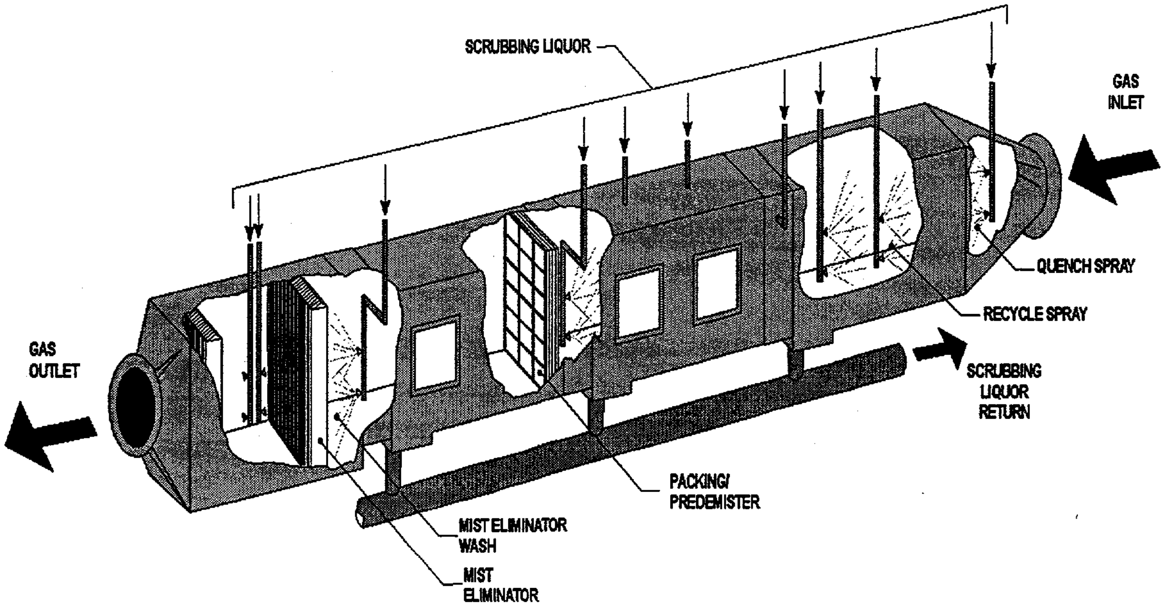


Figure I-11. Horizontal Absorber

Parametric test results for absorber velocities of 20 and 25 ft/sec in the above configuration are shown in Figure I-12. As observed in the prior vertical scrubber testing, operation at the higher velocity permits a reduction in L/G to achieve the same SO_2

removal efficiency. Although the horizontal absorber is not as efficient in gas/liquid contact as vertical absorbers, packing and counter-current nozzle orientation minimize the difference in mass transfer characteristics. This configuration was able to maintain 97% SO_2 removal at an absorber velocity of 25 fps with a L/G of 43.

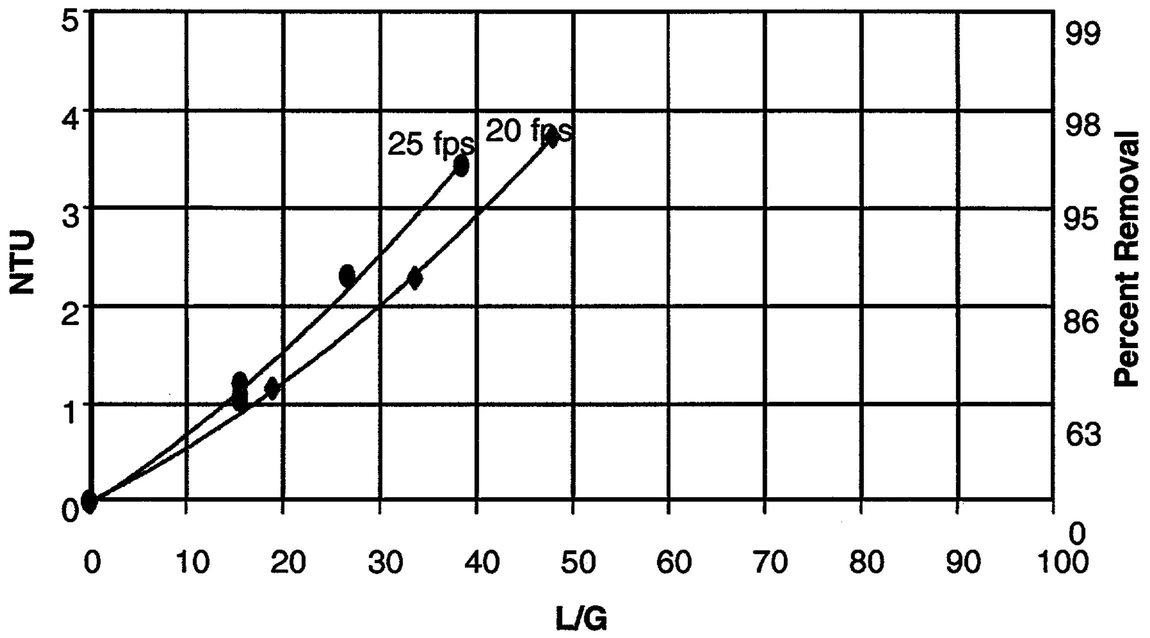


Figure I-12. Parametric Sulfur Dioxide Removal - Horizontal Absorber

Upon the completion of the parametric SO_2 removal studies, additional development work was conducted on pressure drop reduction. Cost savings in this area are realized by minimizing the power consumption costs as a result of reducing the fan requirements. The two largest contributors to the scrubber pressure drop were the packing and the demisters. Parametric evaluations involving various layers of packing, different styles of demisters, and the number of mist eliminator stages were conducted. Aside from tracking the absorber pressure drop, the flowrate of liquid in a drain downstream of the mist eliminator was monitored. These measurements insured that efforts to reduce the pressure drop did not adversely impact the performance of the demisters. As shown in Figure I-13, reductions in the number of layers of packing from four to two and the number of mist eliminator stages from two to one were able to reduce the absorber pressure drop from 10 inches of water to 6 inches of water. These changes had minimal impact on the relative carryover measurement.

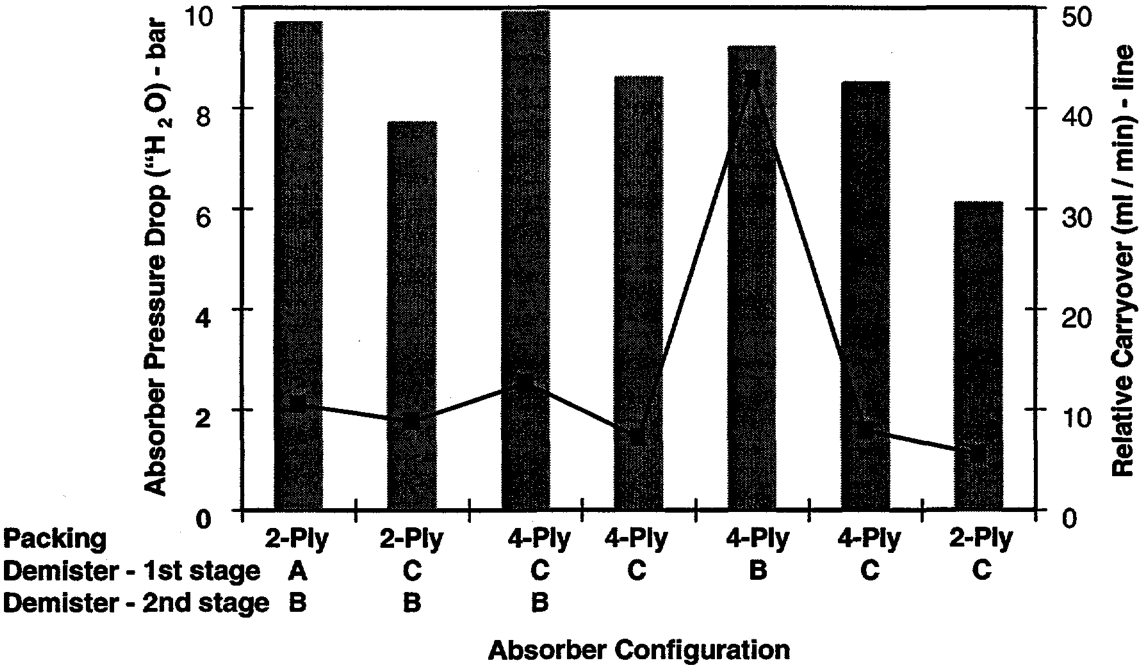


Figure I-13. Pressure Drop Reduction

B. PROGRESS OF THE PROJECT AND ACHIEVEMENT OF EXPECTED RESULTS

The project was scheduled to proceed in two phases. In the Phase I configuration, plant operation emphasized the parametric studies of the individual unit operations involving oxidation, crystallization, and by-product purification / dewatering. During the parametric studies, the pilot plant utilized the 3 foot diameter vertical scrubbing tower with a flue gas flow rate which was comparable to 1.5 MW. It was anticipated that after these optimization studies were completed, a high velocity horizontal absorber would be utilized in place of the vertical scrubber to evaluate scrubber efficiencies at velocities higher than those practical in the vertical tower. Based on a comparison of the removal efficiencies of the two absorbers, the most efficient configuration would be utilized for the Phase II testing. The second phase was to focus on the process modification which would improve the purity of the gypsum by-product and therefore increase the recovery of the process magnesium. Pilot plant testing would involve steady-state operation in order to evaluate the by-products produced by the process modification. The project timeline which was included with the Statement of Work is shown in Figure I-14.

Due to delays in designing and constructing the horizontal absorber, the Phase II testing was rescheduled to mid-1994 in which time the horizontal absorber would be available for testing. Coinciding with the design, procurement, and construction of the pilot plant for Phase II operations were the design, construction, and evaluation of the horizontal absorber with Thiosorbic chemistry. This effort to install and evaluate the horizontal scrubber was supported solely by DLC funds per the commitment in the Grant Agreement. As a result of the modifications for converting the ThioClear process into its Phase II configuration being completed before the horizontal absorber installation, three weeks of operation were devoted to evaluating the Phase II configuration while utilizing the 3 foot diameter vertical scrubber tower. These results provided baseline data for comparison to Phase I test results. After this testing and the successful operation of the horizontal absorber with the

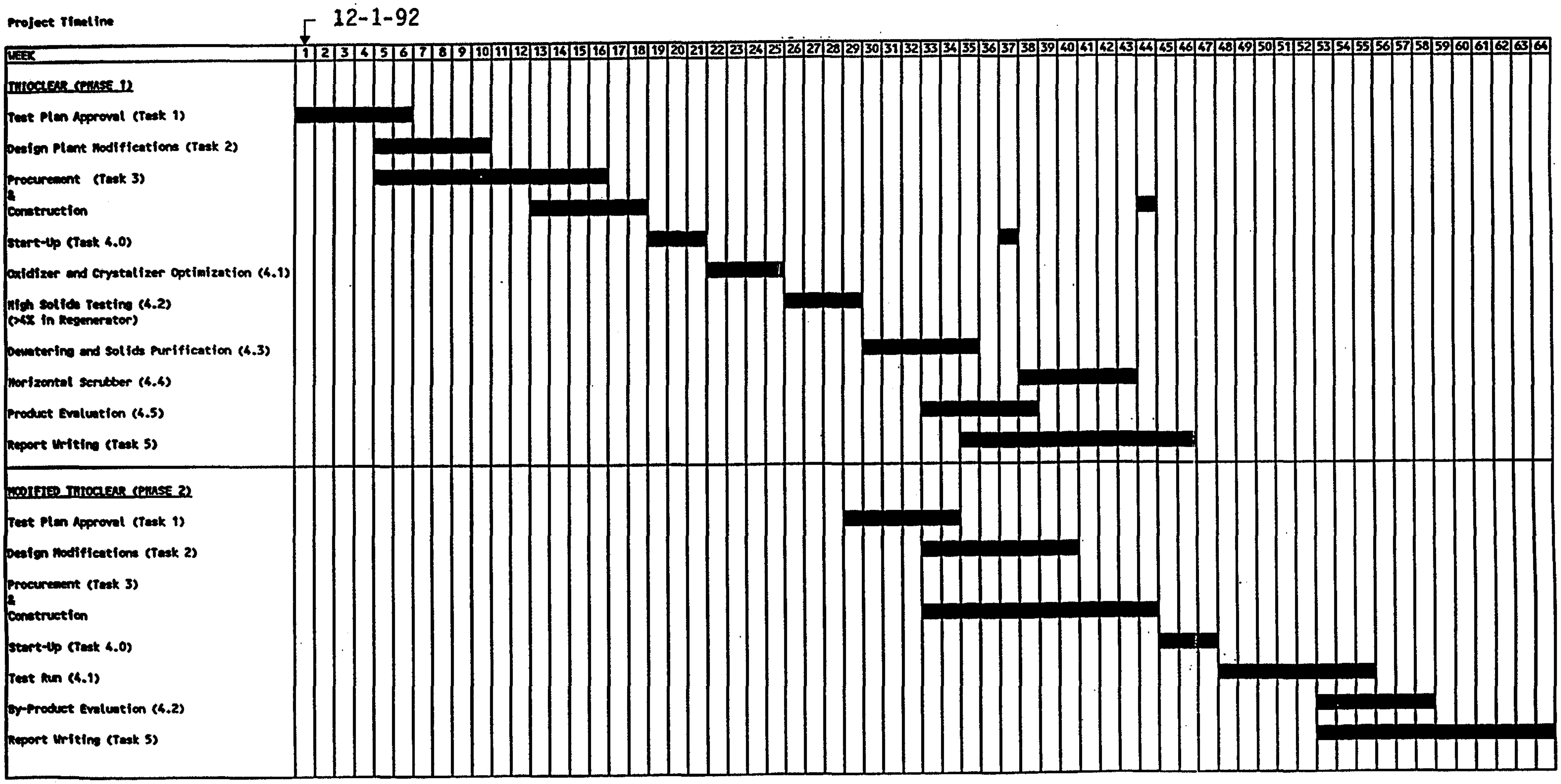


Figure I-14. Proposed Project Timeline

Thiosorbic chemistry, the remainder of the ThioClear test plan was completed utilizing the horizontal absorber. To fully evaluate the effects of horizontal scrubbing, the horizontal absorber was designed substantially larger than the vertical absorber utilized in Phase I. This was necessary to accommodate a commercial size horizontal demister module. Utilization of a mist eliminator smaller in size would enhance the retention of collected liquor and bias the carryover data from that which would be expected in commercial applications. The comparable capacity of the horizontal scrubber was 4.5 MW or 3 times the scale of the vertical absorber. Subsequently, process flow rates associated with this higher capacity required significant changes in operation from those utilized in Phase I. In particular, two oxidizers needed to be utilized in series to effectively oxidize the process liquor and additional hydroclones were placed into operation to handle the larger flowrates. These process modifications required engineering efforts beyond the installation of the horizontal absorber. The combination of the construction delays and the Thiosorbic evaluations caused the completion of the operating schedule of the pilot plant to slip approximately 10 months from that which was projected in the proposal. Figures I-15 and I-16 detail the progress of the two phases. Even though the operation of the pilot plant was extended, the costs for the project were nearly as anticipated. The only cost overruns were associated with the preparation of this report which were absorbed by DLC.

The overall objective of this project was to prepare the ThioClear process for commercialization. The objectives of the Phase I tests were to optimize the unit operations of the process. Phase I was successful in correlating the operating parameters of the oxidizer, regeneration tank, hydroclones, and scrubber with the desired outcomes of each of these unit operations which would provide an efficient and less costly FGD process. This data is useful as the design criteria for commercial scale systems. In addition to these parametric study results, the pilot plant facility demonstrated that the flexibility in controlling the process chemistry provides the ThioClear process with excellent plant start-up and load following capabilities for SO_2 removal. As was

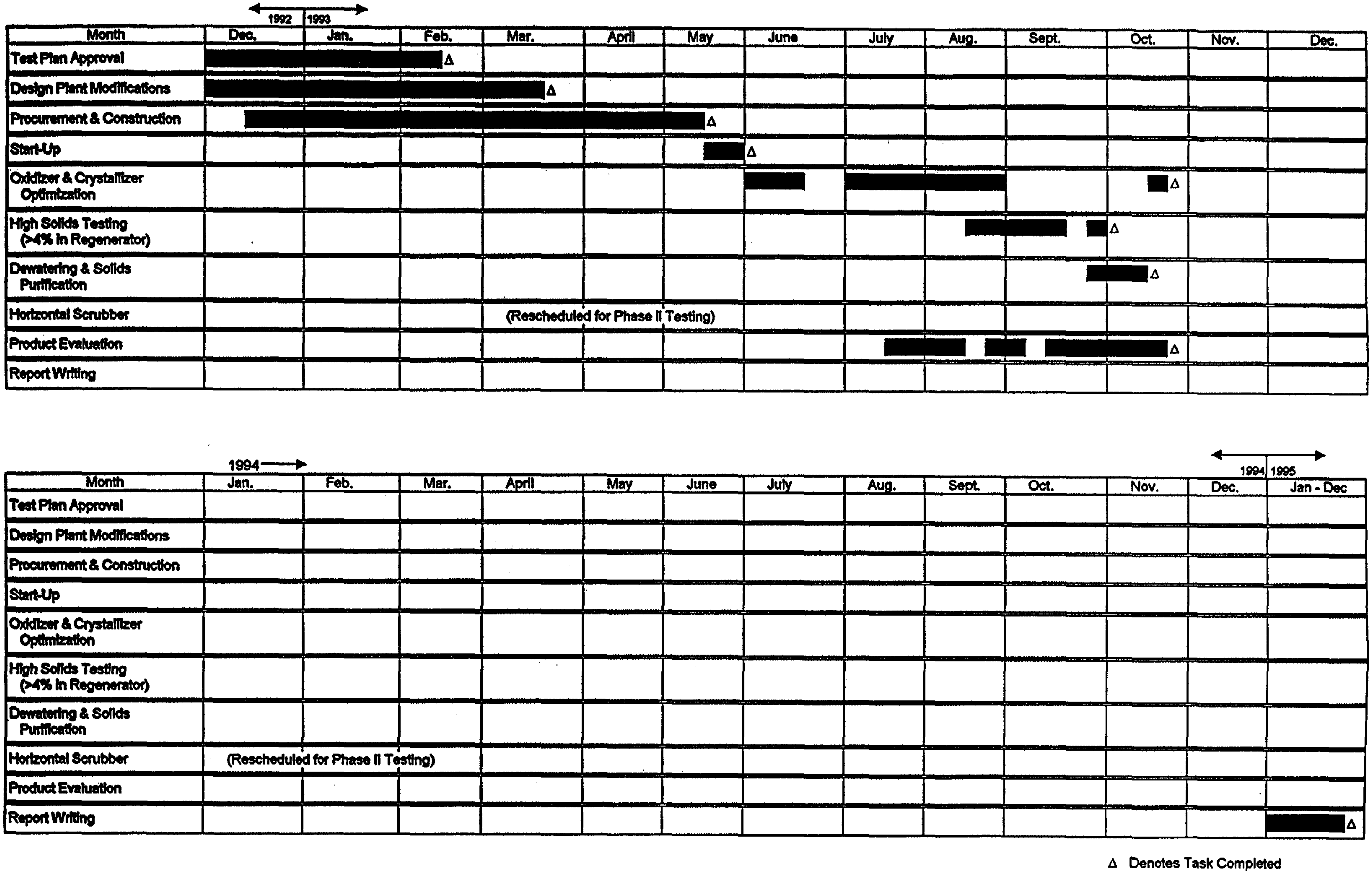


Figure I-15. Phase I Project Timeline

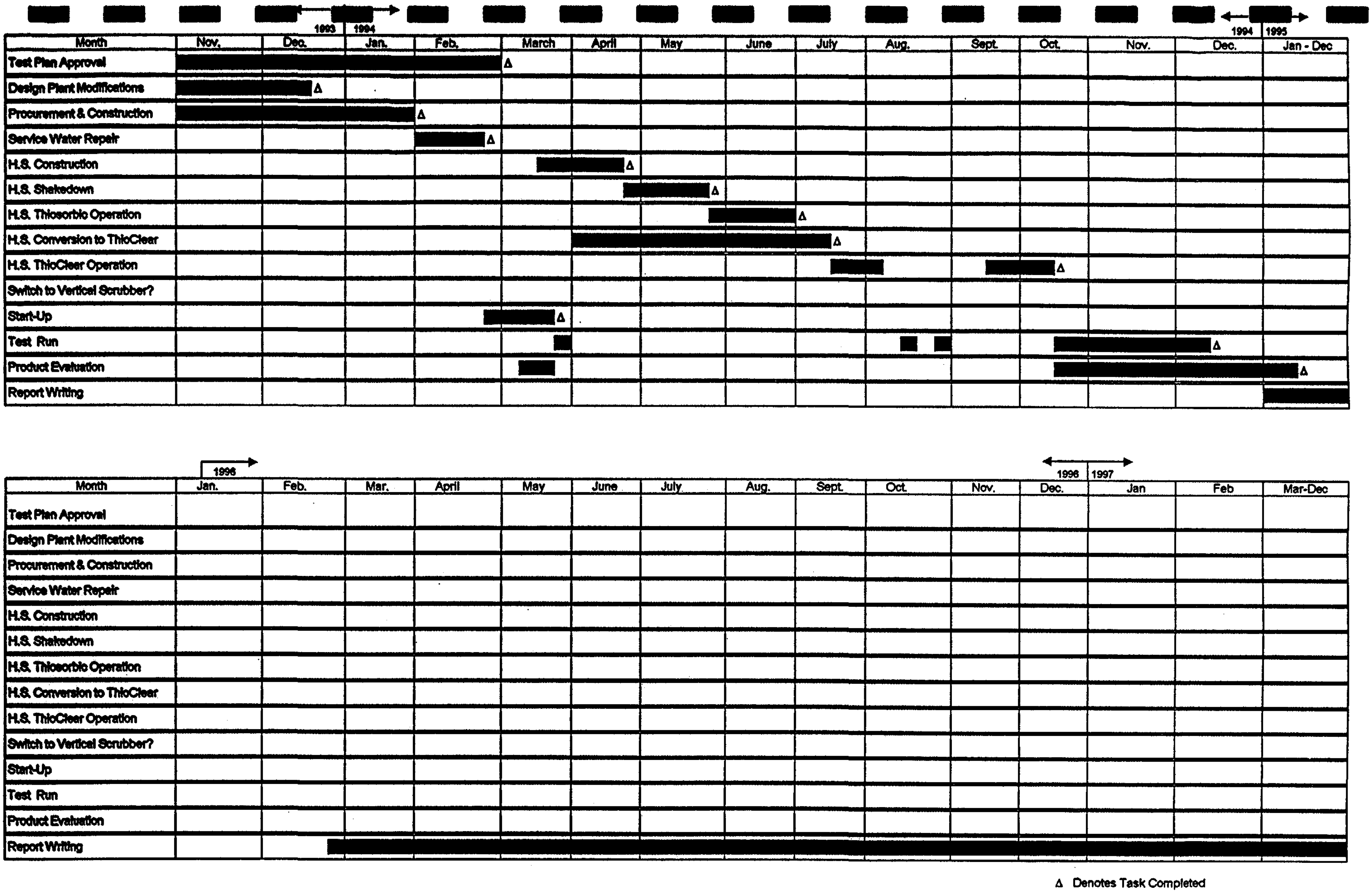


Figure I-16. Phase II Project Timeline

expected, SO_2 removals of 95% and greater were achieved in the 3 foot vertical scrubber tower.

By-product purity and efficient high velocity scrubbing were the objectives of Phase II. This phase of testing demonstrated that a gypsum by-product purity greater than 98% gypsum could be achieved with this process. By minimizing the magnesium content exiting with the gypsum, the recovery and thereby the production of by-product magnesium hydroxide was increased above Phase I results which improved the economics of the process. The efficiency of SO_2 removal in the horizontal absorber exceeded the expectations of the project. Removals exceeding 95% were achieved at a L/G of 35 at 25 ft/sec whereas commercial scale limestone forced oxidation vertical scrubber towers are designed at a L/G as high as 120 for a velocity of 10 ft/sec. At the end of this project, it had been demonstrated that the ThioClear process can produce magnesium hydroxide and an exceptionally pure gypsum by-products and operate efficiently in conjunction with a high velocity horizontal absorber, all of which contribute to substantial reductions in FGD capital and operating costs.

C. IMPLICATION OF THE PROJECT'S RESULTS ON THE NEAR FUTURE COMMERCIALIZATION

The project was successful in providing pilot plant data for the optimal design of the unit operations of the ThioClear process. Additionally, the introduction of the horizontal absorber into the process enabled design criteria to be obtained for this revised scrubber island. Each of these concepts was evaluated at a comparable 4.5 MW capacity rating. Therefore the next logical step in the commercialization of this technology would be a demonstration scale facility in the 40-160 MW capacity range.

The commercialization of the ThioClear process and the horizontal absorber can be pursued separately or jointly. Design data of the oxidizer, regeneration tank, hydroclones, and the two ThioClear configurations evaluated at the pilot plant have provided design criteria for new construction as well as retrofitting this technology to an existing FGD system. Utilities evaluating new FGD facilities would be interested in FGD processes which could provide zero discharge options such as those which would be available with the salable by-products of the ThioClear process. Additionally, magnesium hydroxide would be a commodity utilize by the utility itself in treating various acidic waste streams. (It is estimated that CG&E's Zimmer Generating Station realizes a savings of $300,000/year by recovering a portion of the magnesium hydroxide from the FGD system. This savings can substantially increase if the nearby sister plants would opt to utilize the magnesium hydroxide in the same manner.) Retrofitting of the ThioClear technology to existing operating FGD facilities would be advantageous to those systems currently utilizing technologies which produce a disposable by-product. Production of gypsum as opposed to calcium sulfite can eliminate the disposal of FGD by-products if nearby markets can absorb the gypsum by-product. However, even if the markets are not available for the gypsum, this by-product can be disposed in existing landfills at lower costs than the calcium based sulfite by-products. As in the new construction case, the magnesium hydroxide is available for on-site use. As was demonstrated in the operation of the scrubber, the ThioClear process provides optimum SO_2 removal during plant start-up and boiler load changes. This data also indicates that the utilities will have greater flexibility in sulfur contents of the coal which is purchased. As a result of the vastly superior capabilities of a magnesium-enhanced lime system to remove SO_2 when compared to limestone processes, the limestone processes can convert to this technology. Such conversions would continue to produce a gypsum by-product but reduce their parasitic power requirements as a result of the lower L/G (or pump requirements) and pressure drops (or fan requirements) without sacrificing SO_2 removal efficiencies.

Many synergies exist between the ThioClear FGD process and the utilization of a horizontal absorber which makes the installation of a horizontal absorber in new FGD facilities a serious consideration. Utilization of magnesium-enhanced lime process chemistry enables this absorber to efficiently remove SO_2 while operating at higher gas velocities and lower L/G than is commercially utilized today. The nearly clear scrubbing liquor of the ThioClear process permits the use of fine mesh mass transfer devices which enhance the SO_2 removal of the scrubber while reducing the droplet loading on the mist eliminators. These advantages greatly reduce the capital and operating costs of the absorber island.

Based on the success of this project, the ThioClear process is ready for the demonstration scale of operation. Potential utility sites for this scale will result from existing FGD facilities which are examining options to reduce landfill costs and/or have a market for the gypsum. Subsequently, retrofitting the ThioClear technology to the existing system may offer such opportunities. (As this report is in preparation, Applied Energy System's (AES) Beaver Valley Station is converting from a Thiosorbic to a ThioClear configuration to eliminate their landfill costs and profit from the salable by-products.) The installation of a new FGD facility which could include a horizontal absorber would be more capital intensive than the retrofit. Economic assistance such as that which is offered by OCDO for demonstration scale projects would be an incentive for new construction. As the utilities deregulate, minimal capital expenditures are to be expected. Therefore, a new construction demonstration site would require favorable economics resulting from the low cost of readily available high sulfur coal, markets for the by-products, and the planned dispatch of the unit's generating capacity.

As a result of the Phase II requirements of the CAAA being implemented in the year 2000, Dravo is actively pursuing sites to demonstrate all aspects of this technology evaluated at the Miami Fort pilot plant. The effort at the AES Beaver Valley Station should be completed by the end of 1997 and will demonstrate the capability of the ThioClear system to be retrofitted to an existing FGD process. As deregulation progresses and the time for implementing Phase II strategies approaches, interest in new FGD facilities should increase. Because of the vast supply of SO_2 credits available, decisions by utilities to commit to new FGD systems may be delayed until 2003 to 2005. It is prudent that the combined strategy of the horizontal absorber and the ThioClear process be demonstrated well in advance of this time frame for this technology to be commercially accepted as an alternative to existing FGD processes.

D. COST OF TECHNOLOGY

A preliminary comparative economic analysis of the limestone forced oxidation FGD process with various ThioClear options has been conducted based on criteria established in the Electric Power Research Institute (EPRI) publication, "Economic Evaluation of Flue Gas Desulfurization Systems" (EPRI GS-7193). The basis of the analysis is a 300 MW plant utilizing 2.6% sulfur coal. Limited modifications to the EPRI specifications have been made in developing the comparative economic analysis in order to incorporate current FGD design trends. Namely, the SO_2 removal efficiency was increased from 90% to 95%, operating one absorber module, and the spare scrubber module was eliminated. Annual gypsum production at this removal efficiency is approximately 89,735 tons in both the ThioClear and the limestone forced oxidation scenarios. The production of magnesium hydroxide from the ThioClear process is estimated at 2,465 tons per year base on utilization of a magnesium-enhanced lime with 6% MgO content. Pertinent process design criteria are shown in Table I-1. In this evaluation, no credit is taken for exceeding SO_2 removals of 90%.

Table. I-1

FGD Design and Economic Criteria for 300 MW Unit with a 65% Plant Capacity Factor

	LSFO	ThioClear	ThioClear Horizontal Wallboard	ThioClear Horizontal Stacking
SO_2 Removal (2.6% S Coal)	95%	95%	95%	95%
Scrubber Modules	1	1	1	1
Scrubber Type	Spray Tower	Tray Tower	Horizontal Absorber	Horizontal Absorber
L/G Ratio	120	27	35	35
Absorber Velocity	10 fps	10 fps	25 fps	25 fps
Absorber Pressure Drop	5 in H_2O	1.9 in H_2O	6 in H_2O	6 in H_2O

Table. I-1 (continued)

Plant Life Depreciation	30 years
Capital Recovery Factor	16.5%
Inflation Rate	5.0%
Real Annual Escalation Rate	0.3%
Discount Rate	11.5%
Capital Cost Retrofit Factor	1.3
Operating Labor	\$20.00/man-hour
Electricity	\$50.00/MW-HR

Figure I-17 compares the capital costs (\$/kW) and the first year operating costs (\$/ton SO_2) in 1994 dollars. Utilization of magnesium-enhanced lime as the FGD reagent substantially reduces the capital costs of the SO_2 removal and reagent feed systems. Minimal equipment is required by the utility to process the lime for introduction into the FGD application. The high SO_2 removal efficiency associated with the ThioClear process allows a reduction in the L/G required for similar removals when compared to limestone based systems. Subsequently, fewer recycle pumps and spray levels are necessary which reduce the absorber height and pressure drop requirements.

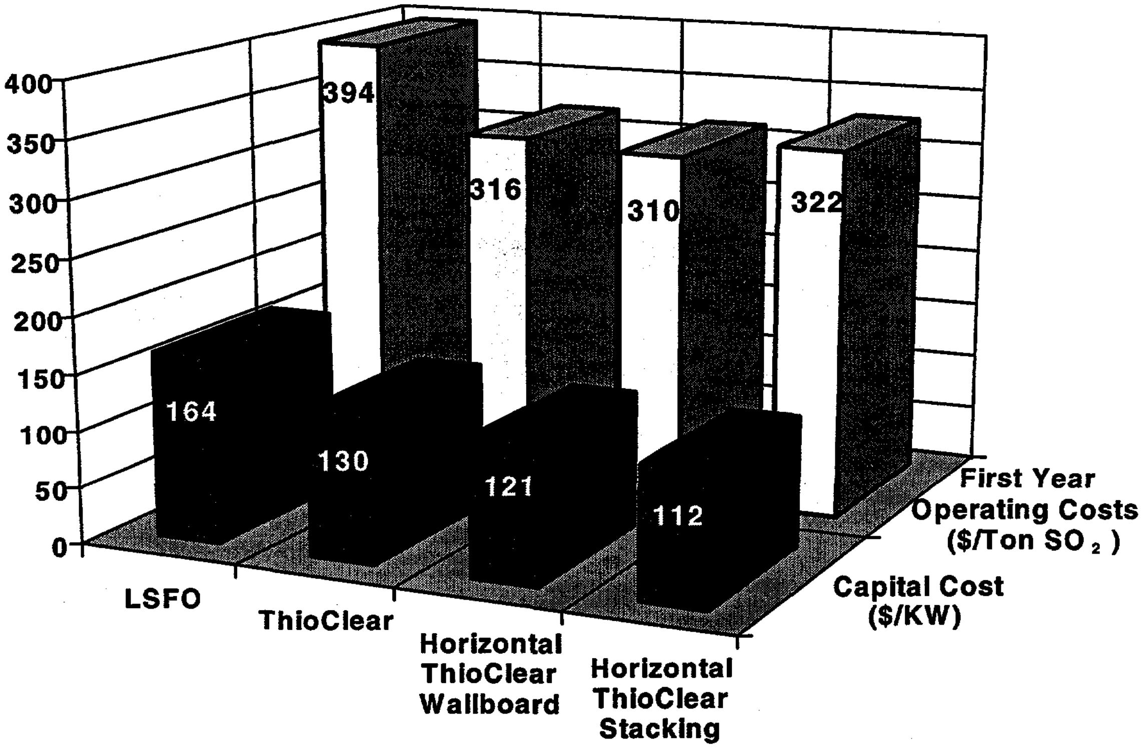


Figure I-17. Economic Comparisons

In computing the operating costs, it was assumed that the gypsum produced by the FGD facilities was of wallboard quality and provided a credit of $2/ton. The magnesium hydroxide produced by the ThioClear process provided a credit of $200/ton. Although the cost of the lime reagent, estimated at $50/ton, is significantly higher than the limestone cost at $9.50/ton, the combination of the magnesium hydroxide credit and lower parasitic load associated with a magnesium-enhanced lime process nullifies the price differential. The impact of the magnesium hydroxide credit on the cost of lime can be illustrated as follows. One ton of lime with a 6% MgO content can produce 0.078 tons of magnesium hydroxide with a credit value of $15.65. Therefore, the theoretical cost of lime as a result of the salable by-product is $34.35/ton.

E. WASTE AND BY-PRODUCTS

One of the goals in developing the ThioClear process was to generate salable by-products. By producing salable by-products, costs associated with landfilling are eliminated and the revenues from the sale of the by-products can substantially reduce the operating cost of the FGD facility. However, to insure that a ThioClear FGD facility will be a zero discharge plant, markets for the magnesium hydroxide and gypsum need to be expanded and developed.

Utilization of these by-products has been and continues to be the focus of research by Dravo Lime Company. Currently at CG&E's Zimmer Generating Station, a magnesium hydroxide recovery plant operated in conjunction with the existing magnesium-enhanced lime FGD facility is producing a magnesium hydroxide product similar to that of the ThioClear process. Preliminary evaluations of the neutralization capabilities of this by-product on bottom ash water, coal pile run-off, and plant storm collection ponds have been very favorable. Application of the magnesium hydroxide by-product will displace the annual purchase of $300,000 of commercial magnesium hydroxide. During the earlier stages of ThioClear development, gypsum produced at Pennsylvania Power Company's Bruce Mansfield Station was successfully utilized in the production of wallboard which met the quality standards of the manufacturer. Continuing studies by the U.S. Department of Agriculture - Agricultural Research Service are evaluating a gypsum/magnesium hydroxide supplement which was produced from the ThioClear process on plant growth in acid soil. Such soils are prevalent in the Appalachian region and the coastal plains of the South where many of the generating stations utilize medium and high sulfur coals. Initial tests indicate an enhancement in plant growth which was attributed not only to the calcium and sulfur nutrients from the gypsum but also to the magnesium from the magnesium hydroxide which can be a limiting nutrient for plants grown in acid soils. Future testing supported by Ohio Coal Development Office, Cincinnati Gas and Electric Company and Dravo Lime Company will evaluate various technologies to enhance the purity of the magnesium hydroxide and to ease the handling of the gypsum in order to expand these by-products into typical commercial markets.

1. Gypsum

One of the most likely markets for gypsum produced from the ThioClear process is the wallboard industry. However, based upon market needs, it appears that the most realistic option for gypsum sales is a localized "niche" market. In order to overcome the primary obstacle of selling such a high volume, low value commodity, it will be necessary to keep transportation costs to a minimum. Wallboard manufacturers will need to be located near the power plant or induced to relocate nearby to realize a low cost source of gypsum raw material.

Other potential markets for gypsum include the cement manufacturing industry where gypsum can be utilized to control the setting properties, soil conditioning for agriculture, and mineland reclamation and civil engineering applications as a structural fill. Not all of these applications are as advanced as gypsum use in wallboard manufacturing and are still subject to the aforementioned transportation cost problems.

The difficult problems of overproduction of gypsum for local wallboard market needs coupled with transportation costs for this relatively low value commodity make disposal of gypsum an alternative option. There are still advantages to be gained by producing calcium sulfate rather than calcium sulfite even in the absence of the wallboard market. Gypsum produced by the ThioClear process lowers capital costs by eliminating the thickener and greatly reducing the belt filter requirements. In addition, disposal costs may be further reduced if the gypsum by-product is stacked in an impoundment eliminating the need for dewatering equipment.

2. Magnesium Hydroxide

As opposed to gypsum, magnesium hydroxide is a low volume, high value commodity and therefore is not as subject to the market saturation and transportation limitations imposed on gypsum. Magnesium hydroxide is a major consumptive product in itself and is also an intermediate product for producing most magnesium compounds including magnesium metal. The world from its seawater, brine, and natural mineral magnesite (magnesium carbonate) has a vast supply of magnesium. However, it is very costly and energy intensive to produce from these relatively cheap natural sources.

Commercially, magnesium hydroxide is available in a slurry form at 57.5% dry solids content which sells for about $200 per short ton and as a dry solid in 50 pound bags which is sold for nearly $1,000 per ton at a minimum purity of 95%. Processing the magnesium hydroxide to yield magnesium metal produces a product which is valued over $1,500 per ton. It thus becomes very easy to see how attractive the by-product production of magnesium hydroxide is, especially considering that the energy cost of its production from the ThioClear process is a fraction of today's conventional methods.

The major markets for magnesium hydroxide, aside from its intermediate functions, include pulp and paper, chemical industries, and water treatment applications. The environmental applications which typically utilize a magnesium hydroxide slurry similar to that generated from the ThioClear process are envisioned to be a growth market as a result of the advantages magnesium hydroxide has over other alkalis, caustic soda, and lime. These advantages include:

- Buffer capability which limits effluent pH to 9.5 when overdoses occur and therefore eliminates the need for back additions of acid.

- Reduced metal hydroxide sludge volume due to formation of larger crystals.

- Improved metal removal of lead and chrome III from wastewater due to their minimal solubilities near the buffered pH of magnesium hydroxide.

- Reduced quantities are required when compared to caustic soda (0.72 tons of magnesium hydroxide has the same neutralizing capability as 1 ton of caustic soda).

- Relative safer material to handle.

The potential exists due to these advantages to displace 75% of the caustic soda market for environmental applications which equates to 651,000 TPY of magnesium hydroxide or nearly twice the current production.

F. IMPACT OF THIS PROJECT ON OHIO COAL USE

In order to predict the impact of the ThioClear process on the usage of Ohio mined coal, one must review Ohio Coal's current status and other contributing factors which would influence its usage. Ohio coals range from 4 to 20% ash, from 2 to 6% sulfur, and from 10,000 to just over 12,500 BTU/lb, making it a highly volatile fuel which is desirable as a steam coal for utilities. The decline of the heavy industrial sector coupled with the enactment of the Clean Air Act Amendments (CAAA) of 1990 have depressed the market for Ohio high sulfur coal. In 1980, 40,672,771 tons of coal were mined in Ohio. In 1995, which was the first year of compliance for the CAAA, the production rate dropped to 25,538,935 tons, nearly a 37% decline in production.

Aside from the economic impact of complying with the federal clean air regulations on the usage of Ohio coal, a second major influence is the cost of the fuel itself. The cost of Ohio coal in 1995 averaged $26.49/ton whereas low sulfur compliance western coal was being shipped to states east of the Mississippi River at a cost of $28/ton on a comparable BTU content. As deregulation of the utility industry unfolds, greater pressure will be placed on utilities, including those in Ohio, to maintain and even reduce the cost of their product in order to maintain market share and be profitable. In 1995, the production costs of electricity for the twenty lowest cost fossil fuel generating facilities ranged between 9.73 to 12.80 $/MWH for an average cost of 11.47 $/MWH. This average production cost was composed of 8.36 $/MWH for fuel and 3.10 $/MWH for operation and maintenance. As can be seen, fuel costs account for nearly 75% of the costs of electricity generation and therefore has a major influence in the competitiveness of particular generating station. Of the twenty low cost generating stations, nineteen were west of the Mississippi River where low cost compliance fuel is readily available. It is therefore not surprising that the opportunity for utilities to utilize a fuel of comparable price which does not require the substantial costs in capital and O&M of environmental equipment was a compelling reason to fuel switch. Over 62% of the affected CAAA Phase I generating stations chose low sulfur coal as their environmental strategy.

CG&E's Zimmer Generating Station provides an excellent example to illustrate the influence of clean air regulations and fuel costs on an Ohio generating facility. The 1995 cost of producing electricity at Zimmer was 9.75 $/MWH for fuel costs and 5.04 $/MWH for operation and maintenance costs for a total cost of 14.79 $/MWH. Zimmer is one of the newer generating stations in Ohio which utilizes over 85% high sulfur Ohio coal and is equipped with some of the latest commercial magnesium-enhanced lime technology for wet scrubbing to meet clean air regulations. When compared to the average costs of the twenty lowest producers of electricity, Zimmer's costs are 16.6% and 62.6% higher in fuel and O&M costs, respectively.

The objectives of this project in developing the ThioClear process were to bring to the commercialized market a FGD process with low capital cost, high SO_2 removal efficiency, low parasitic load requirements, and production of salable by-products. By demonstrating all of these traits of ThioClear at the Miami Fort pilot plant, this process has been shown to be the lowest cost method of wet scrubbing. To illustrate the impact of this technology on Ohio coal usage, the projected effect of the ThioClear process when compared to the existing Thiosorbic process at Zimmer would be to reduce the O&M costs by 1$/MWH, a 20% reduction in these costs. If these gains can be coupled with a 10% decrease in fuel costs which would reduce the fuel costs to 8.74 $/MWH, the Zimmer Generating Station, burning high sulfur Ohio coal would be one of the twenty lowest cost fossil fuel generation stations in the United States.

The relationship between Ohio coal usage and FGD processes can be expanded beyond Zimmer. In 1995, 25,538,935 tons of coal were mined in Ohio and of this quantity, 17,334,157 tons were utilized by Ohio utilities. In this same year, the three utility stations equipped with magnesium-enhanced lime scrubbing technology, Conesville Units 5 and 6, Zimmer Unit 1, and Gavin Units 1 and 2 burned Ohio coal in the respective quantities of 1,672,475 tons, 2,581,450 tons, and 6,151,596 tons. Thus, these three stations accounted for the consumption of 40% of all coal mined in Ohio and 60% of all Ohio coal utilized by Ohio utilities.

Because of the CAAA of 1990, the utilization of high sulfur Ohio coal will require the use of environmental controls such as wet scrubbing. Today the current generation of magnesium-enhanced lime FGD technology is being utilized by Ohio utilities effectively and permitting the utilization of Ohio coal. The recently developed ThioClear process has the advantage of reducing the costs associated with meeting the clean air regulations which will enable utilities to substantially reduce their O & M costs. The economics of the ThioClear process alone will not assure the economic generation of power from Ohio coals. However, this new FGD technology will expand the local markets for the low cost miners of Ohio coal.

G. NEXT STEPS, TECHNICAL AND COMMERCIAL, AND PARTICIPANTS

The successful pilot scale testing of the ThioClear process and the horizontal absorber has validated the goals of the project and prepared these technologies for the next level of commercialization. Commercial demonstration of these two technologies can be accomplished separately or together. The ThioClear process can be retrofitted to an existing FGD facility. The second option would be the installation of both the horizontal scrubber and the ThioClear process to a generating station which does not have an FGD system. The technical data gained through this project will be utilized to define the design criteria for these installations.

As of this report writing, the first option of demonstration has been initiated at Applied Energy System's Beaver Valley Generating Station in Monaca, PA. This facility is a four unit boiler generating station with a combined steam and electrical production capacity of 140 MW which has existing Thiosorbic scrubbers. DLC has provided the process design and financing of the project, managed the construction, and participated in various critical areas of engineering design. Outside engineering consultants for engineering design and structural erection were utilized to complete the design of the facility. Operation of the ThioClear process is targeted for the third quarter of 1997. The overall cost of this project is approximately $4.0 million.

The second option of demonstrating a horizontal scrubber with the ThioClear process will require substantial effort and resources if this task is to be accomplished in the near future. As a result of deregulation, utilities who have met their Phase I requirements and are banking SO_2 removal credits will be noncommittal on undertaking a capital investment in SO_2 removal technology at this time. However joint financial support from one or more of the following group which includes but is not limited to the Ohio Coal Development Office, U.S. Department of Energy, Dravo Lime Company, the recipient utility, the coal supplier, and the engineering and construction firm will reduce the initial capital investment and may entice a prospective utility. DLC continues to pursue demonstration opportunities with existing utility customers, through contacts at OCDO, and by presentations to potential users group.

II. INTRODUCTION

A. PROBLEM STATEMENT

Wet scrubbing is the leading proven commercial post-combustion FGD technology available today to meet the SO_2 reductions required by The Clean Air Act Amendments (CAAA). The Thiosorbic or magnesium-enhanced lime FGD process with its capability to efficiently scrub flue gases generated from the combustion of high sulfur coals have a strong position in the market. Currently 27 electric utility units with a combined generating capacity of 13,500 MW utilize magnesium-enhanced lime FGD scrubbers to meet or exceed the requirements of the CAAA.

The drawbacks of the conventional Thiosorbic FGD process include significant capital and operating costs resulting from:

- Large thickeners and filters to dewater the calcium sulfite sludge.
- Pug mills and associated fixation equipment required to prepare the sludge for disposal.
- Transportation of the sludge, property procurement, operation and maintenance of the landfill while complying with ever increasing environmental restrictions and limitations.
- Scrubber vessels overdesign for the reagent being utilized.

To remedy the above drawbacks, Dravo Lime Company (DLC) has utilized this project to continue the development of the ThioClear process in conjunction with the testing of a high velocity horizontal absorber. The ThioClear process unlike the conventional Thiosorbic process utilizes a recycle liquor with minimal suspended solids and produces the salable by-products, gypsum, and magnesium hydroxide. Production of salable by-products eliminate the need for landfills and their associated operating costs. Gypsum crystals settle and dewater at a faster rate than calcium sulfite. Thus, the size of the thickeners and belt filters can be significantly reduced and potentially eliminated. As a result of the ThioClear recycle scrubbing liquor having minimal suspended solids and high alkalinity, capital and operating costs associated with the scrubber can be reduced by operating at higher absorber gas velocities and utilizing mass transfer devices. A horizontal absorber which has the capability to operate at gas velocities above 20 ft/sec (which is twice the conventional design velocity) was the logical choice to fully investigate the limits of an advanced FGD wet scrubbing process.

B. PROGRAM OBJECTIVES

The overall objective of this project was to develop an alternative FGD wet scrubbing technology for commercialization. This technology consisted of the ThioClear process and a high velocity gas absorber. Upon the completion of this project, it has been demonstrated that the cost of wet scrubbing flue gas desulfurization, especially in high sulfur coal applications, can be substantially reduced.

The focus of Phase I was to continue the development of the ThioClear process evaluated in the proof of concept testing conducted at the Miami Fort pilot plant in 1991. Engineering review of this prior work has led to process enhancements to improve process control, by-product purity, and scrubber efficiency. To improve on the process economics, optimization studies evaluated each of the unit operations pertinent to the process. These studies involved the performance of the oxidation tank, crystallizer or regeneration tank, hydroclones, by-product purification methods, and to a lesser extent, the scrubber efficiency. (Note: the terms crystallizer and regeneration tank are utilized synonymously within this report.) These efforts were conducted as separate tasks in Phase I.

The objective of Phase I was to incorporate design modifications into the pilot plant based on analysis of the proof of concept testing conducted in 1991 and requirements for the optimization studies to be conducted in Task 4. Short comings noted in the proof of concept testing needed to be addressed in order to provide a reliable and efficient operating process as well as insure the economics of this process for commercialization were viable. Flexibility in the key unit operations equipment was necessary so that optimization studies could be conducted to further improve the economics and the by-product purity of this process.

Development work for the ThioClear process that was identified in the proof of concept testing which required additional engineering effort for this phase of testing included:

- Enhancements to the oxidizer were required to reduce the quantity of air utilized to oxidize the sulfites to sulfates. In order to supply a large quantity of air, multiple compressors that consume enormous amounts of electricity which have a negative impact on both the capital and operating economics are required. The prior tests needed nearly three times the amount of air for oxidation than had been anticipated.

- Increasing the volume of the crystallizer/regeneration tank to provide for extended residence times and to improve the capability to control the percent suspended solids within this vessel were required to minimize scale formation and improve crystal growth. The inability to control gypsum supersaturation during the proof of concept testing resulted in 1/2-inch of scale formation over the six week period of operation and periodically hindered flow through the hydroclones.

- A system of process control for tank levels, liquid flowrates, and pH modulation needed to be developed which would be viable for a commercialized process. The initial control system developed for the ThioClear process utilized manual operation and a co-current pH / tank level control scheme which could not readily respond to process variables such as boiler load fluctuations or system upsets.

- Improvements in the equipment responsible for the purity and recovery of the by-products were required to produce commercial grade gypsum and magnesium-hydroxide. The by-product gypsum contained between 2-3% magnesium hydroxide and the by-product magnesium hydroxide contained 15-20% gypsum during the operation of the proof of concept testing.

- A separate tank would be utilized to store concentrated magnesium hydroxide from the thickener for controlling the pH of the absorber as opposed to utilizing thickener underflow directly. This philosophy improved the pH control system, prevented thickener upsets from affecting absorber operation, and enabled control of pH and liquid level to the recycle tank to be conducted as separate control loops.

- The feedrate to the secondary hydroclone would be modulated in order to provide level control to the recycle tank. The hydroclone overflow would be fed directly to the recycle tank whereas the underflow would be pumped to the filter feed tank for eventual filtration.

- Magnesium hydroxide and sulfuric acid storage tanks have been added to assist in pH control of the oxidizer during start-up and parametric studies. Maintaining the proper operating conditions in the oxidizer is necessary in preventing calcium sulfite precipitation in the regeneration tank. The formation of solid phase calcium sulfite would decrease the purity of the by-products and increase the difficulty of the oxidation process.

Once the above deficiencies from the proof of concept testing were addressed, equipment requirements were defined for providing flexibility of operation in order to optimize various unit operations. These modifications included the capability to vary tank volume in both the oxidizer and crystallizer/regeneration tanks, provided separate pH control loops for the oxidizer, crystallizer/regeneration tank, and the scrubber, and utilized variable speed agitators for mixing of the tanks. The combination of these efforts were required for the process optimization that was conducted in Phase I.

The objectives of Phase II were to incorporate a process modification of continuous filtering and to optimize the scrubbing efficiency in a horizontal absorber. Once each of the unit operations were optimized in Phase I, process modifications such as gypsum recycle to the oxidizer with continuous filtering and an alternate scrubbing vessel to the vertical spray / tray tower could be fully evaluated. These two modifications demonstrated the capability to further reduce the costs of the ThioClear FGD process.

The limitations of the hydroclones for physically separating the gypsum and magnesium hydroxide crystals prevented maximizing the purity of the gypsum and the recovery of the magnesium compounds. Improvements in this area would permit the gypsum to command top value in wallboard applications and would enable this by-product entry into other high end-use applications of gypsum where high purity is a necessity. By improving the purity of the gypsum, the recovery of magnesium was increased which translates into additional magnesium hydroxide available for sale.

In order to fully realize the advantages of high velocity scrubbing, a horizontal scrubber was required. Typical vertical scrubbing towers are designed for operation at a gas velocity of 10 ft/sec. Advanced vertical absorber towers are currently operating at ~20 ft/sec. However, horizontal absorbers with efficient demisters can operate at velocities in excess of 20 ft/sec. Operating at a higher velocity reduces the size of the scrubbing vessel and can improve the scrubbing efficiency. Both improvements aid in the reduction of capital and operating costs.

Special goals which were established for the Phase II testing included:

- Improvements in the gypsum purity and recovery of the magnesium compounds beyond that which was demonstrated during the first phase of this project were required. Limitations to the physical separation of the gypsum and magnesium hydroxide crystals dictated that the magnesium hydroxide contaminating the gypsum would need to be dissolved and removed during the filtering operation.

- Demonstration of SO_2 removals above 95% could be achieved at gas velocities greater than 20 ft/sec. Re-entrainment of accumulated liquor on vertical flow demisters prohibited gas velocities above 20 ft/sec in a vertical scrubber tower. Utilization of a horizontal absorber with horizontal flow demisters avoided this problem.

- Utilization of advanced mass transfer devices to maximize the SO_2 removal efficiency to take advantage of the minimal solids in the recycle liquor associated with the ThioClear process was demonstrated.

After establishing the above goals for Phase II, the appropriate process flow modifications were made to incorporate the continuous filtering concept. Additionally, a pilot plant scale horizontal absorber was designed, constructed, and test operated at DLC's expense before the ThioClear parametric SO_2 removal studies were initiated. These efforts were required to build on to the successes of the first phase of testing.

C. INVOLVEMENT AND CONTRIBUTION OF CO-SPONSORS

The co-sponsors of this project were Cincinnati Gas and Electric Company (CG&E) and Dravo Lime Company (DLC). The respective contributions of each were as follows:

CG&E was the host site at its Miami Fort Station, Unit 7, for the Miami Fort pilot plant where this ThioClear process evaluation was conducted. During pilot plant operations, CG&E supplied flue gas, electrical power, and service water for pilot plant operations. Disposal sites for the liquid waste at the Miami Fort Station and solid waste at the East Bend Station were made available to DLC. Additionally, CG&E provided maintenance and instrumentation personnel on an as needed basis in support of the pilot plant activities.

DLC was responsible for managing, scheduling, and budgeting the project, developing the test plans, and engineering and construction of the pilot plant modifications. During pilot plant evaluations, DLC personnel operated the pilot plant, analyzed the chemistry of the process, and generated weekly technical reports on the status of the pilot plant. OCDO contractual reports such as the Milestone Report, Monthly Status Report, and Final Report were completed by DLC.

III. TECHNICAL DISCUSSION – PHASE I

A. TECHNOLOGY DESCRIPTION

Figure III-1 details the conventional ThioClear process evaluated during Phase I testing. The chemistry of the ThioClear process takes advantage of the catalytic effect of magnesium to increase the alkalinity of the scrubbing liquor. Magnesium hydroxide ($Mg(OH)_2$) is introduced to the recycle tank where the pH may range between 6.0-6.5. The hydroxide reacts with dissolved sulfur dioxide (SO_2) in either the recycle tank or the absorber to form the soluble alkaline salt, magnesium sulfite ($MgSO_3$). This species rapidly neutralizes additional absorbed SO_2 by forming magnesium bisulfite ($Mg(HSO_3)_2$) and thereby provides the scrubbing liquor additional capacity in absorbing SO_2 compared to systems where magnesium sulfite is not present.

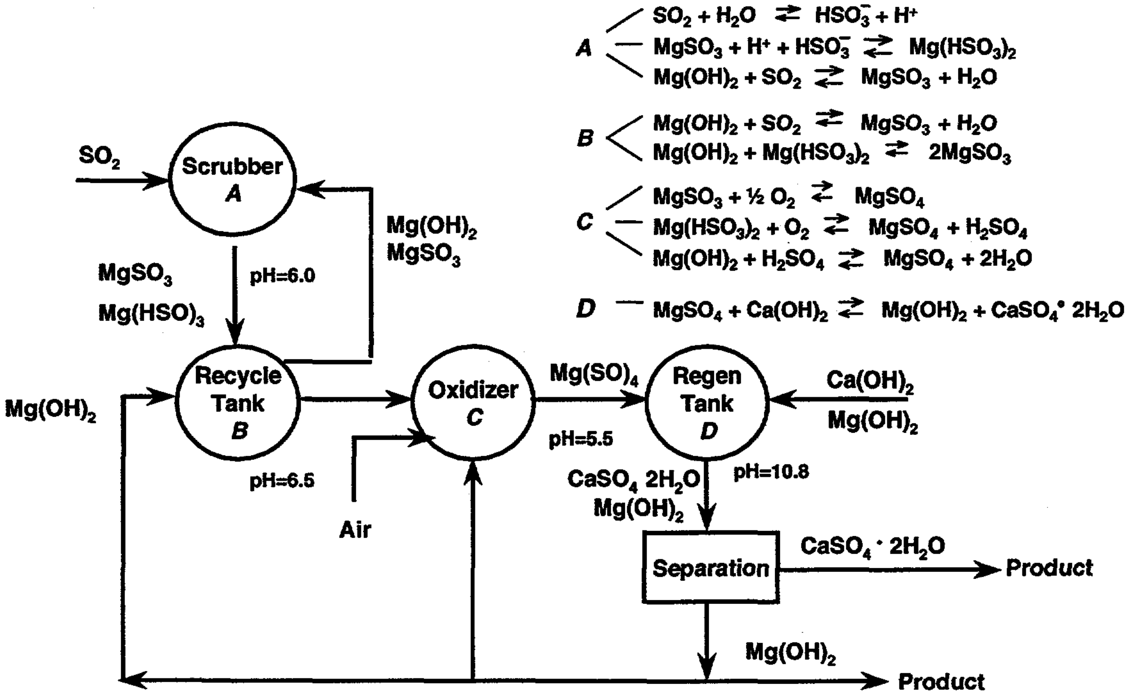


Figure III-1. ThioClear Chemistry

The scrubber effluent feeds low pH liquor in the range of 5.5-6.0 to the oxidizer. Oxidation of the liquid phase magnesium sulfites and bisulfites produces magnesium sulfate ($MgSO_4$). Due to formation of sulfuric acid (H_2SO_4) from the oxidation of the bisulfites, magnesium hydroxide additions are required to maintain the pH of the oxidizer between 4.5-5.5

The oxidized liquid is bled to the regeneration tank. Slaked magnesium-enhanced lime which is composed of +90% calcium oxide (CaO) and 4 to 8% magnesium oxide (MgO), is added to the regeneration tank to maintain the pH between 10.0-10.8. The resulting mixture precipitates the sulfates as gypsum ($CaSO_4 \cdot 2\,H_2O$) and regenerates the magnesium species to magnesium hydroxide.

B. PILOT PLANT DESCRIPTION

The flow diagram of the ThioClear process as installed at the Miami Fort pilot plant for Phase I is shown in Figure III-2. A slipstream from CG&E's Miami Fort Unit No. 7 downstream of the precipitator supplies the flue gas to the pilot plant. The volume of flue gas to the absorber is controlled by a booster fan with an inlet damper capable of delivering 2000 to 15000 acfm at 300°F. This gas flow is measured by a venturi flow meter installed immediately downstream of the fan. As a result of boiler load changes, the composition of the flue gas with respect to oxygen and sulfur dioxide will vary. An on-site SO_2 spiking system, capable of vaporizing up to 150 lb SO_2/hour, enables control of the SO_2 concentration to the inlet of the absorber. During testing, this concentration is typically maintained at 2000 ppm.

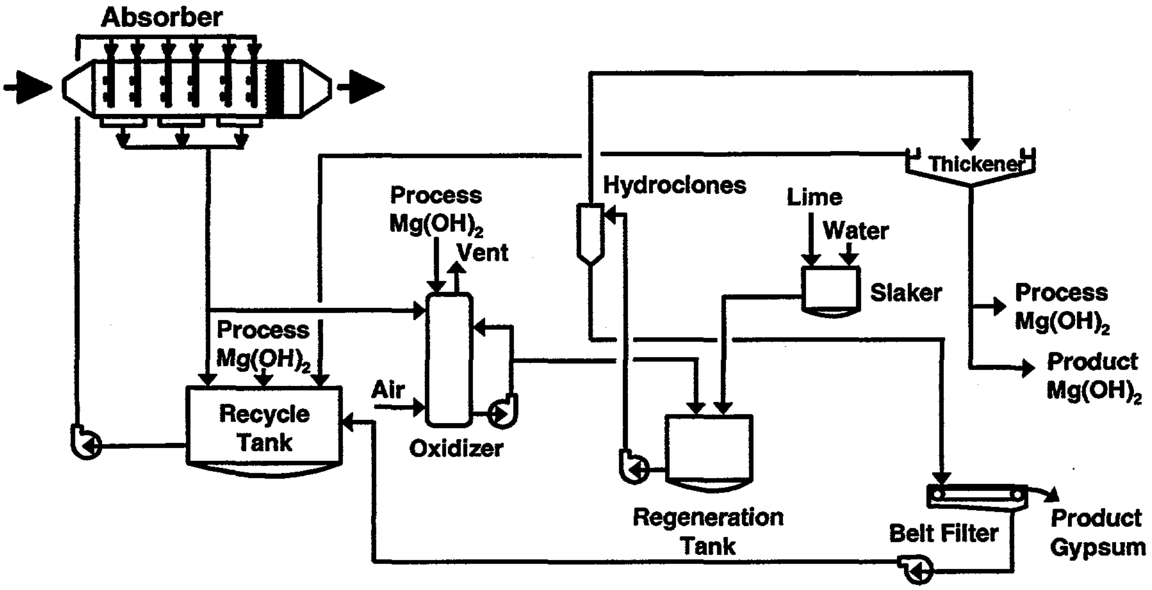


Figure III-2. ThioClear Process Flow Diagram

Typically, the flue gas enters the bottom of either of the two 40 foot tall scrubbing towers, one 4 foot and the other 3 foot in diameter. Aside from controlling the absorber gas velocity by the inlet damper, multiple liquid to gas ratios (L/G) at a given absorber velocity can be achieved by operating any number of the three variable speed recycle pumps that are each capable of delivering a maximum flow rate of 125 gpm. Each of the three spray levels within the tower is equipped with a typical FGD spray nozzle. Provisions within the scrubber permit the installation of trays or packing to enhance mass transfer between the gas and the liquor. Each scrubber has a two stage mist eliminator section to remove entrained liquor droplets from the exiting gas.

The 3 foot diameter scrubber tower was utilized during the initial phase of ThioClear testing. The configuration of the scrubber was in the counter-current mode of gas-liquid contact with a 40% open area tray installed below the lowest spray level. Absorber gas velocities of 10 and 15 ft/sec were evaluated.

Unlike typical FGD operations, the blowdown from the absorber in the ThioClear process is extracted from the scrubber sump and fed to the oxidizer. The control of the effluent flowrate and pH is important to the ThioClear process. Modulating the blowdown flowrate provides control of the scrubber alkalinity and thereby provides excellent boiler load following capabilities. The lower pH associated with the blowdown improves the rate of oxidation. Subsequently, magnesium hydroxide additions to the recycle tank are controlled by the desired pH of the blowdown to the oxidizer. The oxidizer is a 1600 gallon FRP tank containing a 5-hp drive agitator and an air sparging system capable of delivering 200 scfm. Control of the oxidizer pH is accomplished by either the addition of magnesium hydroxide or sulfuric acid via chemical metering pumps, depending upon the control setpoint. Typically, magnesium hydroxide is required to neutralize the acid produced from bisulfite oxidation. Gypsum seed crystals for the crystallization process, which takes place within the regeneration tank, are introduced through the oxidizer.

The oxidized liquor with seed crystals is pumped to the regeneration tank. The regeneration tank is a 7280 gallon vessel. Magnesium-enhanced lime is added as required for pH control. A high speed turbine agitator provides for good mixing between the lime and oxidized liquor to produce magnesium hydroxide and gypsum. During testing, the volume of this vessel varied between 1500 to 4500 gallons in order to evaluate the effect of residence times on the crystallization process.

Separation of the magnesium hydroxide and gypsum crystals from the regeneration tank slurry is achieved by the use of two hydroclones in series. Commercially available 2 inch and 3 inch hydroclones were utilized. The magnesium hydroxide rich overflow from the first hydroclone is delivered to an 8 foot diameter thickener for settling and thickening. The thickened magnesium hydroxide is used for pH control in the absorber and the oxidizer. The excess production is stored in an available 12 foot diameter thickener. The hydroclone underflow is supplied to the thickener overflow (water management) tank and is diluted with the clear liquor leaving the thickener. The resulting slurry is fed to the second hydroclone for final separation. The liquor from the overflow of the second hydroclone returns to the recycle tank to maintain liquid level. The gypsum-rich underflow stream is stored in the filter feed tank for eventual dewatering on a belt filter with an active filter area of 10 ft^2. The filter has provisions for three counter-current cake washes which were evaluated during the purification phase of testing. The gypsum cake is deposited on a lay-down area for removal to disposal while the filtrate is returned to the process.

C. OBJECTIVES

The focus of Phase I was to initiate pilot plant operation, conduct parametric studies of the pertinent unit operations of the conventional ThioClear process, and analyze the resulting data. The facility was typically operated twenty-four hours per day, five days per week. The addition of the computer/PLC control and data acquisition system enabled the operators of the facility to make on line process changes as well as automatically control the operation. Process parameters such as flue gas emissions, liquid flowrates, tank levels, and pH's were continuously monitored and recorded. The on-site laboratory was constantly staffed during facility operation so as to monitor process chemistry. Analysis which could not be performed in the field and QA/QC of the field analysis was accomplished by overnight shipping of samples from the pilot plant to the Research Center in Pittsburgh where the appropriate laboratory instrumentation was available.

Analysis of the pilot plant performance was conducted by the staff of the Research Center. Both the laboratory and process data bases were transferred electronically to the Research Center for detailed evaluation and report preparation.

Five subtasks which encompass facility operation and process optimization were completed during the first phase of ThioClear testing. These subtasks were start-up, oxidizer and crystallizer/regeneration tank optimization, high solids testing, dewatering and solids purification, high velocity horizontal scrubbing testing, and product evaluation.

1. Start-up

The initial period of operation was devoted to development of procedures for operation, operator training, and facility start-up. Individual unit operations were operated on service water to evaluate procedures and operation of equipment. Modifications were made as required. When the evaluation of the individual unit operations had been completed, operation of the overall system on service water was initiated to evaluate the by-product recovery flow loop and its corresponding control strategy. This mode of operation facilitated the training of the operating personnel.

After system verification and operator training on service water had been completed, commercial magnesium hydroxide was utilized as the neutralization reagent for initiating absorber operation. Flue gas was permitted to enter the 3 foot vertical tray absorber to initiate the establishment of process chemistry. As the chemistry matured, pump performance, hydroclone operation, belt filter operation, thickener performance, scrubber sulfur dioxide removal capability, and the control systems for pH, level, and flow were observed and modified as required. When the process chemistry achieved steady state and process control could be maintained in automatic, the facility commenced optimization studies.

2. Oxidizer and Crystallizer / Regeneration Tank Optimization

Due to economic considerations, one of the primary objectives of oxidizer and crystallizer/regeneration tank optimization studies was to minimize the size (or residence time) of these vessels and thereby their associated capital costs. Parametric residence time studies were accomplished in two ways. The first was to maintain a set flowrate within the by-product recovery loop and reduce the level in the tankage. The second method was to maintain a desired liquid level and adjust the by-product recovery loop flowrate to achieve a desired residence time. Controlling the absorber blowdown or the flowrate of the by-product recovery loop dictates the liquid phase chemistry of the absorber and the oxidizer as well as the percent solids produced in the regeneration tank. Reducing the flowrate of the by-product recovery loop creates a proportional increase in the dissolved and suspended solids of the respective vessels. Subtask 4.1 investigated residence time effects of the former method. These parametric studies were conducted at low dissolved and suspended solids in which the typical flowrates were 20 gpm and the liquid phase magnesium concentration was 2000 mg/l. Subtask 4.2 studied the latter method of altering residence time. Optimum operating parameters established in Subtask 4.1 were evaluated at a reduced flowrate of 10 gpm which corresponded to an average liquid phase magnesium concentration of 4000 mg/l.

a. Oxidizer Optimization

The oxidation step of ThioClear is an ex-situ process. External oxidation allows nearly independent control of the absorber alkalinity which results from the magnesium sulfite and pH of the scrubbing liquor. Therefore, the absorber can operate at optimum scrubbing efficiency with low recycle ratios. Similarly, the separate oxidizer lends itself to greater flexibility in controlling the oxidation process. This flexibility combined with the oxidation of liquid phase sulfites as opposed to sulfite precipitates aids in the performance of the oxidizer.

Optimization of the oxidizer was conducted while maintaining 95% sulfur dioxide removal in the 3 foot diameter vertical tray tower. Objectives of the optimization studies were the reduction of the vessel size (residence time) and the air requirements for oxidation. Minimizing the size of the oxidizer and the amount of air required for oxidation will reduce the capital costs associated with the vessel and the compressor. Additionally, the energy needed to produce compressed air for oxidation of the liquid phase sulfites is one of the most expensive contributions to the process. Subsequently, lower air demands will also reduce the operating costs of the compressor. To further improve the process economics of the oxidation process, the need for supplemental sulfuric acid additions must be reduced by promoting the production of natural acid from the oxidation of bisulfites. Therefore, parametric studies were conducted to determine the optimum liquid height, residence time, pH, and recirculated gypsum content.

b. Crystallizer / Regeneration Tank Optimization

The crystallizer or regeneration tank of the ThioClear process is the vessel where magnesium hydroxide is regenerated from the oxidized magnesium sulfate liquor and the gypsum is precipitated. It is important in the performance of this vessel that the resulting crystals of gypsum and magnesium hydroxide maintain a substantial size differential in order to undergo efficient separation by hydroclones. Also, the larger gypsum crystals improve dewatering and therefore reduce transportation and/or disposal costs. As with all capital equipment, economic considerations dictate minimizing the size of the tank. However, insufficient residence time within this vessel will produce a supersaturated gypsum effluent stream which will create scale formations downstream of the regeneration tank. It is important to minimize the amount of scaling in the process so as to maintain a reliable operating system and reduce maintenance costs.

Parametric studies for the regeneration tank focussed on improving the gypsum crystal size and minimizing scale formation downstream of the vessel. Parameters adjusted during these studies included flowrate of gypsum seed crystals to the regeneration tank, residence time, and pH.

3. High Solids Testing

An alternative method for reducing the size of the majority of the vessels and pumps and the related capital costs associated with the ThioClear process was evaluated by increasing the concentration of dissolved solids within the process liquor. This task was accomplished by reducing the flowrate of the liquor in the by-products recovery flow loop. A set reduction in this flowrate initiated a proportional increase in the dissolved solids concentration.

Therefore to double the dissolved solids in the absorber, the absorber bleed flowrate is reduced by one half. This translates into doubling of the magnesium ion concentration in the scrubbing liquor and conversely the magnesium sulfite. The associated increase in the alkalinity of the absorber liquor, permits reductions in the flowrate of recycle liquor and the pump size for efficient sulfur dioxide removal. Additionally, the volume requirements of the oxidizer, regeneration tank and thickener and the number of required hydroclones will be reduced by the same factor. An additional benefit is that the increase in solids within the regeneration tank may assist in reducing the gypsum saturation which can allow further reduction in the size of this vessel or eliminate the need for supplemental seed crystal additions.

4. Dewatering and Solids Purification

For the ThioClear process to be feasible, sufficient quantities of magnesium hydroxide need to be produced and recovered to operate the facility and provide a by-product stream. Emphasis is also required on producing a purer gypsum filter cake which relates directly to improved magnesium hydroxide recovery and an improved material for gypsum markets. These objectives were attempted by optimizing hydroclone operation, water washing of the by-products, and improved dewatering methods.

The operation of the hydroclones provides the initial method of separating gypsum and magnesium hydroxide crystals from the slurry exiting the regeneration tank. The hydroclones provide the first and low cost options for improving by-product purity and recovery. Therefore, parametric testing was performed on the hydroclones once operation of the ThioClear process was initiated and continued during Subtask 4.1 to insure optimization of their operation. Performance of the hydroclones during Subtask 4.2 was paramount to the success of high solids testing. If high by-product purities and recovery rates are maintained, the economics of the process will be vastly improved. Subsequently, additional parametric testing needed to be performed on the hydroclones. Variables to be investigated included various sizes of hydroclones and their corresponding apexes and vortexes. After the hydroclone separation process had been optimized, the next phase of this subtask investigated dewatering techniques and additional purification processes for the gypsum and magnesium hydroxide by-products.

Gypsum dewatering and purity are important in wallboard manufacturing. In the production of wallboard, the gypsum is calcined. Therefore, the percent moisture in the gypsum is critical to the economics of wallboard production due to the energy requirements to dry the feedstock. A goal of 10% moisture in the cake was targeted.

Aside from the moisture content of the gypsum, the concentration of the chloride and magnesium ions are important due to their impact on the drying time of the gypsum board. Drying time influences the board strength and the adhesion of the paper cover to the wallboard. Counter-current water wash on the belt filter was investigated to remove these ions.

As with the gypsum, the magnesium hydroxide by-product needed to be purified and dewatered. Improving the purity of this commodity to that of commercial grade magnesium hydroxide will increase the value and potential markets for this by-product. Reducing the moisture content of the magnesium hydroxide will reduce the transportation and handling costs associated with marketing this material. Water washing was investigated as a means to remove gypsum contamination from the magnesium hydroxide. The solubility of gypsum in water is 2400 mg/l as compared to 8 mg/l for magnesium hydroxide. Methods investigated to concentrate this material included filtering, centrifuging, and utilization of a bag filter.

5. High Velocity Horizontal Scrubber Testing

The purpose of this testing was to demonstrate that the ThioClear process can efficiently remove sulfur dioxide similar to the Thiosorbic process at absorber velocities greater than the current industry standard of 10 ft/sec. Higher design gas velocities would allow a reduction in the absorber cross sectional area or reduce the number of scrubbers to treat the same quantity of gas. A reduction in absorber size or numbers will translate into lower capital costs.

Operation of vertical scrubber towers at high gas velocities is limited due to re-entrainment of accumulated liquor from the mist eliminator. The limitation of vertical demisters results from the accumulated liquor attempting to return to the scrubber with the aid of gravity while being opposed by the velocity of the flue gas which is exiting the tower. To avoid this short-coming, a horizontal absorber which utilizes horizontal demisters which can effectively function at higher gas velocities was integrated and evaluated with the ThioClear process. In addition to the capability to operate at higher gas velocities, advantages of reduced height requirements and minimal impact when connecting to existing ducting can be realized when compared to vertical style towers in the commercial FGD applications. These advantages translate into greater flexibility in materials of construction, lower power consumption by pumps for meeting hydraulic head requirements, and lower inlet and outlet pressure losses.

Sulfur dioxide removal evaluations of the horizontal absorber included parametric testing of velocity, L/G ratios, pH effects, blow down rate, and internal absorber configuration changes of nozzles and packing.

6. Product Evaluation

When optimum process conditions were achieved and the dewatering and purification processes optimized, samples of the by-products were collected. These samples were provided to magnesium hydroxide and gypsum end-users for evaluation. The magnesium hydroxide was tested for purity and possible uses. The gypsum was tested for calcination properties and wallboard manufacturing possibilities.

D. PILOT PLANT OPERATING DESCRIPTION

1. Start-up

As in all new pilot plant process start-ups, the objectives of the initial weeks are multifaceted but generally involve three areas. These are training of the plant personnel, evaluating and troubleshooting the process and its equipment, and finally, operating in a steady state mode. Start-up of the ThioClear process at Miami Fort was conducted in a two step process. The first required the utilization of service water to verify the process flow loop by evaluating pump performances and the liquid flow and level control loops. The second step entailed the operation of the scrubber and the establishing of process chemistry in order to conduct a comprehensive evaluation of the unit operations.

The ThioClear process is composed of multiple unit operations such as absorption, oxidation, crystallization, and separation. Each of these functions is conducted in its separate vessel which can have multiple control loops. The process and instrumentation diagram is shown in Figure III-3. Initial operation on service water provided the opportunity for the operators to start-up and shut-down the flow loop as part of their training without concern to the process chemistry. Multiple interruptions that occurred during this step of operation had the potential to create scaling conditions if the FGD system was fully operational.

After completing operator training on service water, operation of the pilot plant on the ThioClear process was initiated the week of May 17th. The configuration of the scrubber for start-up entailed the 3 foot diameter absorber tower with a 40% open area tray. Bete MP1125 60° spray nozzles were installed on each of the three recycle headers. Operating conditions of the absorber included a gas velocity of 10 ft/sec and a L/G of 72 resulting from the use of two recycle pumps operating at 125 gpm each. The liquid flow in the by-product recovery loop was targeted at 20 gpm which would provide a liquid phase magnesium ion concentration of 2000 mg/l. The level in the oxidizer was maintained at 90% and that of the regeneration tank at 65% which corresponded to residence times of

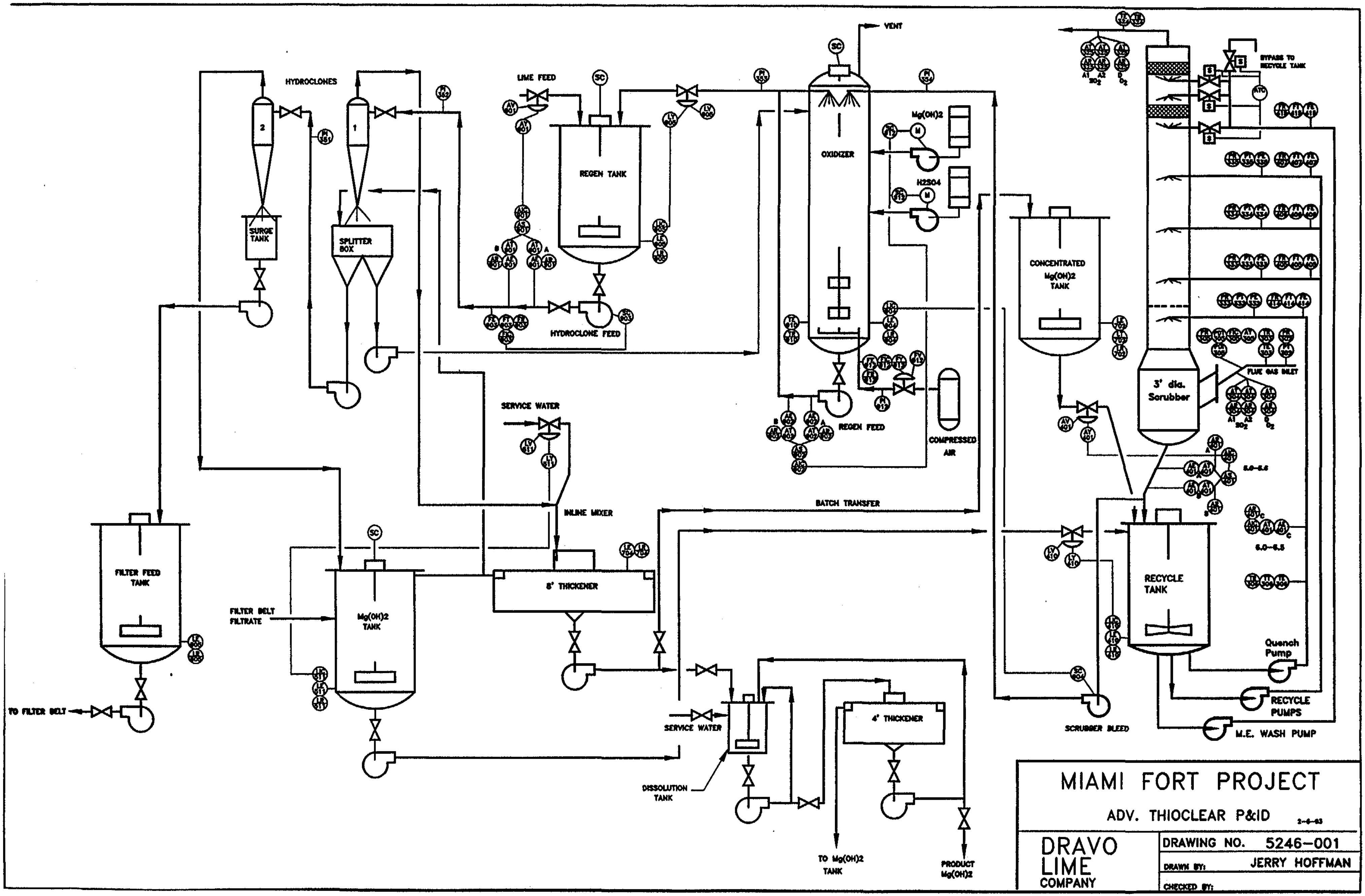


Figure III-3. ThioClear P&ID

1.2 and 3.75 hours respectively. Two tons of commercial magnesium hydroxide were utilized as the neutralizing reagent for initiating absorber operation.

2. Oxidizer and Crystallizer / Regeneration Tank Optimization

a. Oxidizer Optimization

Once operator training was accomplished and the impact of mechanical problems was minimized, focus of testing was placed on the optimization of the oxidizer. The oxidizer utilized for testing was a 1600 gallon tank with an agitator and an air sparger. The agitator was a top mount design whose shaft contained two sets of turbine blades to recirculate the entrained air within the liquor and a set of paddle blades for air bubble dispersion. The turbine blades were located at approximate tank levels of 30% and 60% whereas the paddle blades were located on the bottom of the tank. Compressed air was introduced through sparger pipes directly below the lower paddle blades.

The sulfur dioxide absorbed in the scrubber is present in the scrubbing liquor as liquid phase magnesium sulfites and bisulfites. Oxidation which occurs in the absorber as a result of the oxygen present in the flue gas converts a portion of these sulfites to sulfates. Due to the alkalinity contributed by the sulfites for an efficient scrubbing process, it is desirable to have minimal oxidation in the absorber. Therefore, the oxidation process in the ThioClear process is external from the scrubber recirculation loop.

As described in the test objectives, optimization of the oxidizer is critical in reducing the tankage size and air requirements for oxidation. Subsequently, the capital and operating costs of the vessel and air compressors would be reduced accordingly. Additionally, the complete conversion of sulfites to sulfates is an important aspect in the production of commercial quality gypsum and magnesium hydroxide. Sulfites which exit the oxidizer precipitate as calcium sulfite in the crystallizer/regeneration tank. The purity of both the magnesium hydroxide and gypsum are adversely impacted by this contaminant. These sulfites become incorporated into the gypsum crystal lattice generating smaller and more fragile gypsum crystals. Such crystals tend to be more difficult to separate from the magnesium hydroxide in the hydroclones and produce a gypsum filter cake which generally has poorer dewatering capabilities.

In order to maintain consistent sulfite loading to the oxidizer during optimization studies, the absorber was operated at a set of standard conditions. These typical operating conditions were a gas velocity of 10 ft/sec with a recycle flowrate that provided a L/G of 70. The inlet concentration of sulfur dioxide to the absorber was 2000 ppm and the removal efficiency was maintained above 95%. The feed flowrate to the oxidizer from the absorber averaged 20 gpm which corresponded to a liquid phase magnesium ion concentration of 2200 mg/l.

Optimization studies entailed improving the utilization of air supplied to the oxidizer and limiting the formation of scale. Air minimizing evaluations investigated oxidizer operating parameter changes which would permit reductions in the air supplied to the oxidizer while the exiting magnesium sulfite concentrations remained below 100 mg/l. Parameters which were changed during these studies included air flowrate to the oxidizer, pH, agitator speed, and catalyst additions. Evaluations involving the rate of scale formation required variations in the gypsum seed crystal recycle rate to the oxidizer in order to monitor the impact of the suspended solids concentrations on scaling rate. These oxidizer optimization studies were conducted from May 31st to July 26th.

b. Crystallizer / Regeneration Tank Optimization

Upon completion of the optimization studies of the oxidizer which assured a consistent concentration of low sulfite liquor exiting the vessel, the crystallizer/regeneration tank optimization was initiated. The regeneration tank has a maximum volume of 7280 gallons, but was typically operated at a level of 65% or less. A variable speed turbine agitator provided the energy for mixing of the oxidized liquor and the magnesium-enhanced lime slurry. The lime additions maintained the slurry pH at the desired pH between 10.0 to 10.8. The resulting mixture precipitated the sulfates as gypsum and regenerated the magnesium species to magnesium hydroxide.

The objectives of the regeneration tank optimization studies were to maximize the size differential between the gypsum and magnesium hydroxide crystals, minimize the tank size, enhance the gypsum crystal shape, and reduce the scaling potential of the process. Encouraging the growth of large gypsum crystals aids in the separation of the gypsum from magnesium hydroxide via hydroclones and has the potential to improve the dewatering of the resulting gypsum filter cake. As with the oxidizer, capital cost considerations dictate that the vessel be as compact as possible in order to provide a low cost FGD process. Crystal structure modifications that may be achieved during the crystallization process can produce by-product gypsum solids which may easily be substituted for natural gypsum rock. As in the oxidizer, scale formation needs to be minimized to insure a reliable and low maintenance FGD process.

The achieve these objectives, the regeneration tank's operating parameters of pH and level were varied to evaluate the impact on gypsum size and scale formation. Utilization of a crystal modifier which was added directly to the regeneration tank was investigated for effects on the gypsum crystal structure. Aside from pH and level, the relationship between percent suspended solids in the regeneration tank to the rate of scale formation on a metal test coupon was monitored.

As in the oxidizer studies, the absorber was maintained at steady state conditions with a gas velocity of 10 ft/sec and a L/G of 70. Removals averaged greater than 95% of the 2000 ppm inlet sulfur dioxide concentration. The flowrate within the by-product generation flow loop was typically 20 gpm and had an average of magnesium ion concentration of 2400 mg/l. The regeneration tank parametric studies were conducted from July 19th to July 31st.

3. High Solids Testing

The efforts of the prior subtask involved optimization of the oxidizer and regeneration tank while the concentration of dissolved solids within the scrubbing liquor was low. The dissolved magnesium ion concentration which is an excellent barometer of the dissolved solids concentration averaged 2200 mg/l when the by-product recovery flow loop flowrate was 20 gpm. Due to the minimal volume of the oxidizer during these studies, all optimization studies were conducted with a full tank volume (residence time of 1.2 hours) to insure complete oxidation of the sulfites to sulfates. The larger volume of the regeneration tank enabled multiple residence times to be evaluated due to level changes.

In this subtask, a second method of altering the residence times of these two vessels for optimization studies was accomplished by reducing the flowrate of the by-product recovery loop. By reducing this flowrate by 50 percent, the effective residence times at a defined tank level are doubled. Accordingly, the dissolved solids entering each of these two vessels also doubled.

The positive impact of decreasing the flowrate of the by-product recovery flow loop is not restricted to minimizing the tank volumes required for the oxidizer and regeneration tanks. As a result of decreasing flowrates, the size of pumps in the flow loop can be decreased. Lower flowrates translate into a reduction in the number of required hydroclones for separating gypsum from magnesium hydroxide and a reduction in the size of the thickener utilized for magnesium hydroxide.

Decreasing this flowrate also improves absorber performance. The increase in the magnesium concentration of the liquor permits a corresponding increase in the sulfite concentration. Subsequently, the alkalinity of the absorber increases accordingly which enables a unit volume of scrubbing liquor to neutralize additional captured sulfur dioxide. Improving the efficiency of the scrubbing liquor correlates with reducing the absorber size and the number of pumps required to remove sulfur dioxide.

These potential reductions in capital and operating costs which can be achieved by operating at a higher concentration of dissolved solids warranted additional optimization studies of the ThioClear process during this subtask. As in the prior optimization studies, the operation of the absorber was maintained at a gas velocity of 10 ft/sec with a L/G of 70. As has been typical with the operation of the absorber, these conditions insured that +95% of the inlet sulfur dioxide concentration of 2000 ppm was captured. The by-product recovery flow loop flowrate was reduced to a low of 10 gpm which corresponded to a liquid phase magnesium ion concentration of 3500 mg/l in the liquor of the scrubber, oxidizer, and entering the regeneration tank. As the flowrate was reduced, the impact on both the absorber alkalinity and sulfur dioxide was monitored. The longer residence time achieved at the same liquid level in the oxidizer allowed additional parametric studies concerning the reductions of the air flowrate. Investigations pertaining to the sulfuric acid requirements of the oxidizer were also conducted. Regeneration optimization studies reinvestigated the impact of the higher solids concentration on gypsum crystal size and scale formation. These tests were conducted from August 2nd to August 27th.

4. Dewatering and Solids Purification

The hydroclones and belt filter serve to separate, purify, and dewater the magnesium hydroxide and gypsum by-products. Hydroclone performance, belt filter wash, magnesium hydroxide purification, belt filter percent solids, and centrifuge tests were explored to examine solids purification and dewatering.

Hydroclone parametric tests were conducted to determine the conditions which would result in high magnesium hydroxide recovery from the hydroclone overflow. In addition to this, high gypsum purity was essential to recover the maximum amount of magnesium hydroxide possible. This ensures that sufficient magnesium hydroxide is available to operate the process.

The basis for hydroclone separation is the size differential of the magnesium hydroxide and gypsum. During the precipitation process, small magnesium hydroxide (6-12 microns) and large gypsum (greater than 60 microns) crystals are produced. This size differential allows for the concentration of the two streams by hydrocloning. In the hydroclone shown in Figure III-4, centrifugal force sends the larger heavier particles down the hydroclone while the lighter particles report to the overflow. The size differential is presented for a typical particle size analysis of the two product streams in Figure III-5. The efficiency of the separation is based on particle size and density, liquid flowrate through the hydroclone, operating pressure of the hydroclone, apex/vortex configuration, percent solids in the feed solution, viscosity of the feed solution, and the ratio of the two solid phases entering the hydroclone.

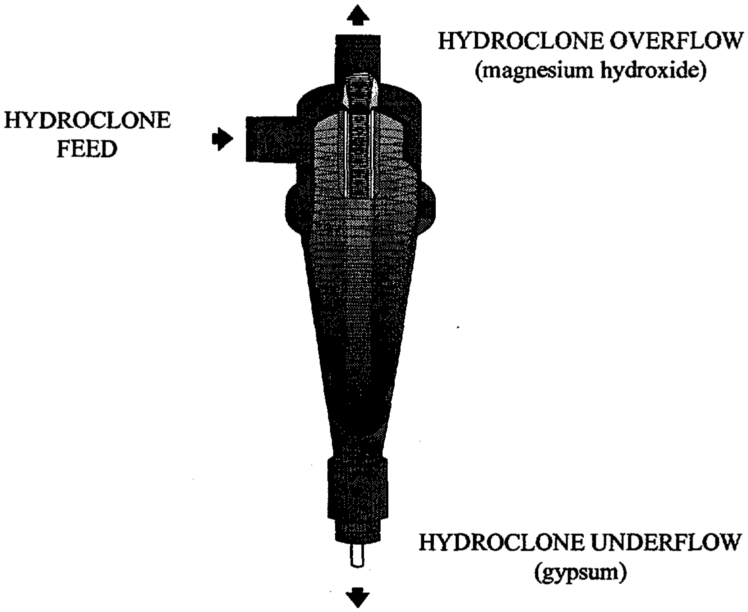


Figure III-4. Hydroclone Cross Section

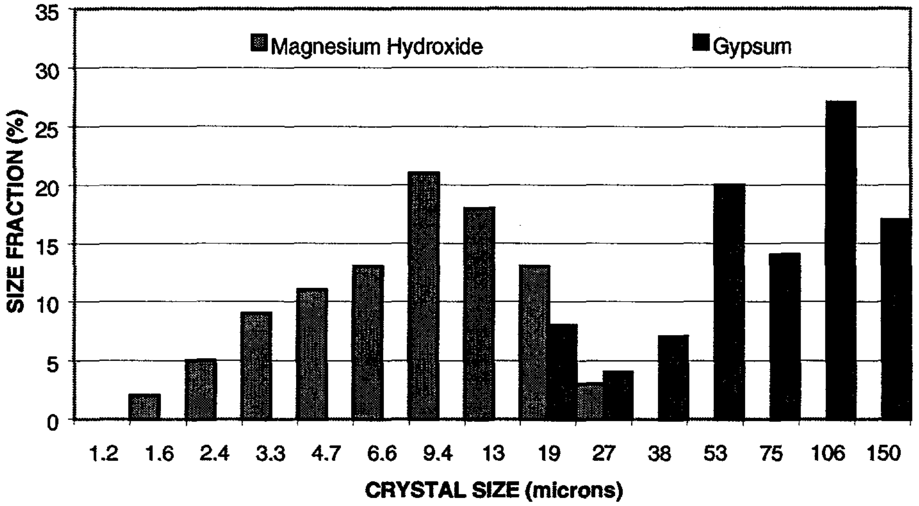


Figure III-5. Crystal Size Analysis of By-Products

During this subtask of the test program, two types of hydroclones were evaluated, a 2" Krebs hydroclone and a 3" Dorr-Oliver hydroclone. These hydroclones were different in size and shape and exhibit different separation characteristics.

Hydroclone operations were very dependent upon the operation of the regeneration tank. Poor crystal formation in the regeneration tank ultimately led to poor hydroclone performance. A shift in the ratio of magnesium hydroxide to gypsum by excessive gypsum seeding also produced undesirable effects.

Solids purification testing involved measuring the chloride concentration of the gypsum product with and without washing to determine the effectiveness of washing. Calcination properties of gypsum are dependent upon chloride levels with too high a concentration having a long set time. Therefore, it is desirable to have a gypsum product with as low a chloride level as possible. To lower the chloride concentration, service water was sprayed over the gypsum filter cake to remove the chloride which leaves with the filtrate. The project's target was to achieve less than 100 mg chloride ion/kg gypsum filter cake.

A short study was made to improve the product purity of magnesium hydroxide by dissolving the gypsum phase. Gypsum is soluble in water up to 2400 mg/l while magnesium hydroxide solubility is only 8 mg/l. Lab tests confirmed the viability of this concept. The study utilized a purification subsystem composed of an agitated tank for mixing water and magnesium hydroxide by-product and a 4 foot diameter thickener. The underflow of the thickener would be stored and analyzed for magnesium hydroxide purity.

The solids content of the filter cake was measured during testing along with the mean volume diameter of gypsum particles reporting to the secondary hydroclone underflow. Typically, large gypsum crystals have better dewatering characteristics than smaller gypsum crystals. Therefore the relationship between gypsum crystal size and filter cake solids was examined to determine whether a correlation existed. In addition to this, the percentage of crystals below 11 microns was measured to determine if a correlation existed in this parameter with the filter cake solids content. The percentage of crystals below 11 microns represents the presence of magnesium hydroxide impurity and attrition of gypsum particles.

Bird Machine Company performed centrifuge tests on a magnesium hydroxide slurry and mixture of gypsum and magnesium hydroxide slurry. Samples from these tests were further analyzed by Dravo's laboratory. For the mixture of gypsum and magnesium hydroxide slurry, the centrate and dried cake were measured for weight percent MgO. For the magnesium hydroxide slurry, the total suspended solids weight percent was measured for the feed, cake, and effluent. The purpose of these tests was to compare the ability of a centrifuge to separate magnesium hydroxide from gypsum and to investigate improved dewatering of the magnesium hydroxide by-product.

5. High Velocity Horizontal Scrubber Testing

The horizontal scrubber enables high sulfur dioxide removals at gas velocities greater than 10 ft/sec. Higher gas velocities correspond to smaller absorber cross-sectional area or a reduction in the number of scrubbers to treat the same volume of gas. The smaller absorber or number of absorbers implies less capital cost. Horizontal absorbers can operate at higher gas velocities than vertical absorbers because horizontal demisters prevent reentrainment of liquor at higher gas velocities than vertical demisters. The horizontal scrubber possesses lower inlet and outlet pressure losses as a result of eliminating gas directional changes associated with vertical absorbers. Lower power consumption by pumps is realized because of the reduced hydraulic head required to supply the spray nozzles. Due to delays in construction, the horizontal scrubber was not completed by the end of Phase I testing. Therefore, horizontal absorber parametric studies of sulfur dioxide removal with gas velocity, L/G, pH, and internal absorber configuration could not be attempted. Testing of the horizontal absorber was conducted in Phase II.

Vertical absorber studies were made to characterize sulfur dioxide removal of the ThioClear process. In this study, sulfur dioxide removal was investigated as a function of L/G at 10 ft/sec. High velocity testing at 15 ft/sec was conducted to examine the sulfur dioxide removal. Finally load following was investigated. Load following involved changing the absorber bleed in accordance with changes in the sulfur dioxide inlet concentration.

6. Product Evaluation

Gypsum and magnesium hydroxide samples were obtained and analyzed. Gold Bond Building Products evaluated the gypsum while Premier Services Group analyzed the samples of magnesium hydroxide. Quantitative and qualitative analysis of gypsum and magnesium hydroxide were also performed by Dravo's laboratory. A detailed account of Dravo's analysis is provided in Subtask 4.3.

E. RESULTS AND ANALYSIS

1. Start-Up

Test Results

Flow testing of the pilot plant on service water insured the integrity of the system, verified the flow loop control strategies, and assisted in training the operators on the new process and operator/computer interface. Also accomplished during this period was the calibration of the liquid level and flow instrumentation. This effort required two weeks to complete.

Start-up of the ThioClear process was planned in a cascading fashion of the individual unit operations. The operation of the absorber was the first subsystem initiated. Service water was recirculated through the recycle pumps to quench and scrub the incoming flue gas. The commercial magnesium hydroxide was added to control the recycle tank pH, neutralize the absorbed sulfur dioxide, and form magnesium sulfite which began the process of establishing chemistry. When the desired magnesium ion concentration was established in the recycle tank, the feed to the oxidizer was initiated. As the oxidizer filled, the agitator and air supply were initiated to convert the magnesium sulfite to magnesium sulfate. Upon achieving a full oxidizer, the oxidized liquor was bled to the regeneration tank where the pH was increased to 10.8 with magnesium-enhanced lime slurry additions. The elevated pH precipitated the magnesium hydroxide and gypsum products. After the regeneration tank reached the 65% level, flow was initiated to the hydroclones. The hydroclones separated the gypsum from the magnesium hydroxide. The gypsum slurry was stored in the filter feed tank for eventual filtration. The magnesium hydroxide slurry was thickened in the 8 foot diameter thickener. As magnesium hydroxide was recovered, it was utilized in place of the commercial magnesium hydroxide for pH control of the oxidizer and absorber.

The establishing of the process flows and chemistry was accomplished with minimal difficulty. Approximately 12 hours were required from initiating flue gas into the absorber until flow from the secondary hydroclone overflow was returned to the recycle tank for level control. Although the initial start-up proceeded as planned, steady state operation was elusive during the first week designated for start-up as a result of various mechanical problems. These problems which are outlined in the significant problems encounter section were gradually resolved over the course of this week.

Although these problems occurred, the long residence time established in the regeneration tank minimized scale formation and plugging of the hydroclones from that observed in the prior proof of concept test. The dewatering of the gypsum varied from 55 to 77% solids. The magnesium hydroxide recovered in the thickener achieved a slurry concentration of 14% solids. The purity of the magnesium hydroxide varied between 50-80%.

Smoother operation of the system was achieved during the second week of the process start-up. Tuning of the controllers and automatic control of the process was initiated. Air flowrates to the oxidizer averaged over 100 scfm resulting in an oxygen to absorbed sulfur dioxide molar ratio of 6.0. At mid-week, Miami Fort Station's Unit 7 shut down preventing further testing.

Sulfur dioxide removals during the second week averaged in the low 90's. The product gypsum averaged 75% solids. Minimal scaling was noted in the oxidizer, but significant scale was discovered in the scrubber bleed line to the oxidizer.

Analysis

Data analysis for the start-up of the ThioClear process was minimal as a result of focusing on operator training and mechanical trouble-shooting. However, review of sulfur dioxide removal data associated with this and many of the subsequent start-ups of the process provided insight into one of the many advantages of the ThioClear process. This advantage is the rapid response of this process to achieve high sulfur dioxide removal shortly after start-up.

As shown in Figure III-6, 95% sulfur dioxide removal was achieved within 5 hours after the introduction of the gas into the absorber. These efficiencies resulted from the rapid increase of liquor alkalinity attributed to the formation of magnesium sulfite from the magnesium hydroxide additions. Since the magnesium salts are generally soluble, the absorber blowdown can be substantially reduced in order to establish a desired chemistry whereas calcium based neutralizing reagents would produce precipitates. Therefore, the purging of the recycle tank to limit the concentration of suspended solids as practiced in conventional wet FGD systems is not a limiting factor in the ThioClear process.

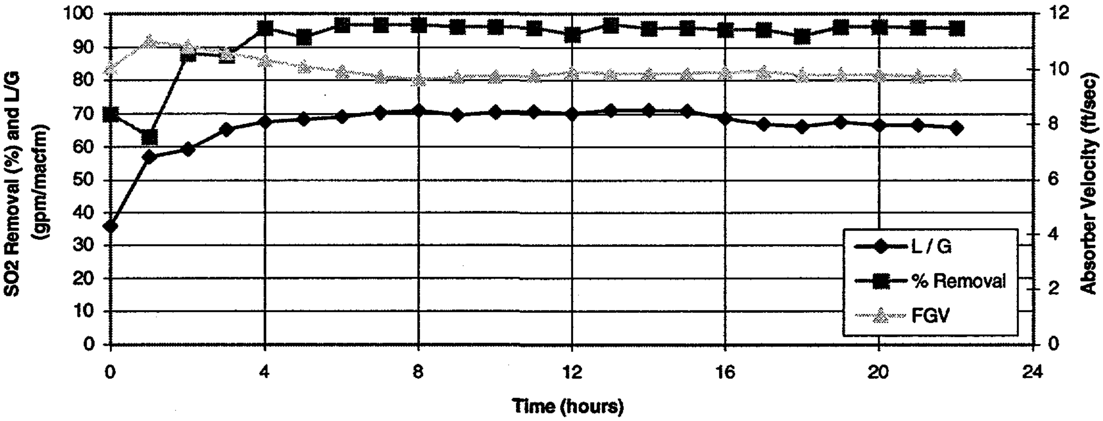


Figure III-6. Plant Start-Up

2. Oxidizer

Test Results

Figure III-7 depicts the typical relationship observed between the concentration of sulfites exiting the oxidizer and the quantity of air supplied expressed in a molar ratio of oxygen to absorbed sulfur dioxide. The operating conditions for this data were an oxidizer pH of 5.0 and a residence time of 1.2 hours. As the air flowrate to the oxidizer was reduced, the exiting sulfites increased exponentially. In this case, the exiting sulfite increased from a concentration of 150 mg/l to 650 mg/l as the oxygen supply ratio was reduced from 2.0 to 1.5.

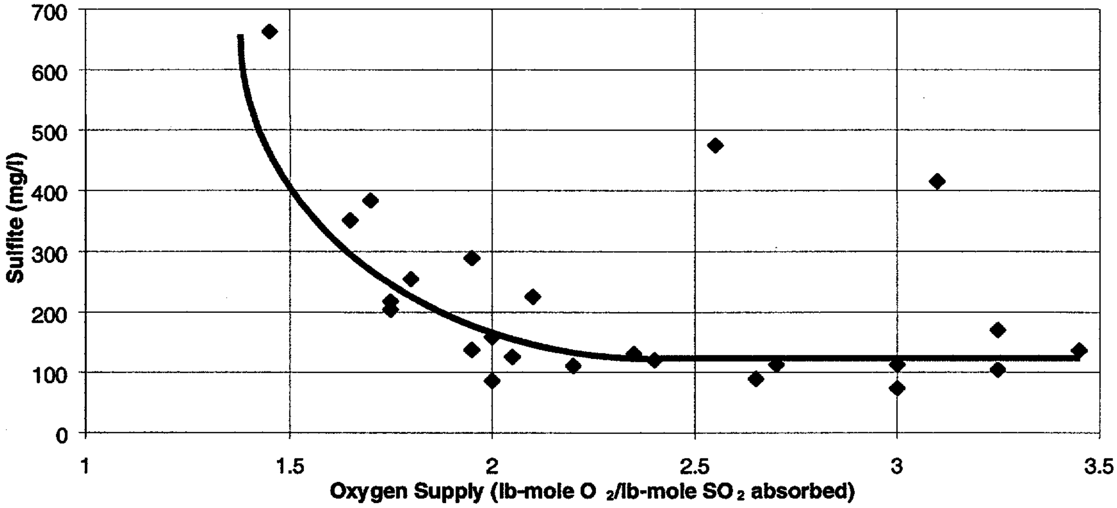


Figure III-7. Effect of Oxidizer Oxygen Supply vs Exiting Sulfites

Labeling the data points on Figure III-7 with the percent of full agitation speed that the agitator was operating provides insight into the effects of agitation on oxidation. Figure III-8 shows that increasing the speed of the agitator from 70% to 75% permits the oxygen supply ratio to be reduced from 2.5 to 2.0 while maintaining the same average exiting sulfite concentrations. However, further decreases in the air flowrate could not be compensated by agitation speed increases as a result of insufficient motor horsepower to prevent the agitator from stalling at low air flowrates. Subsequently, lower air flowrates were accompanied by lower agitation speeds.

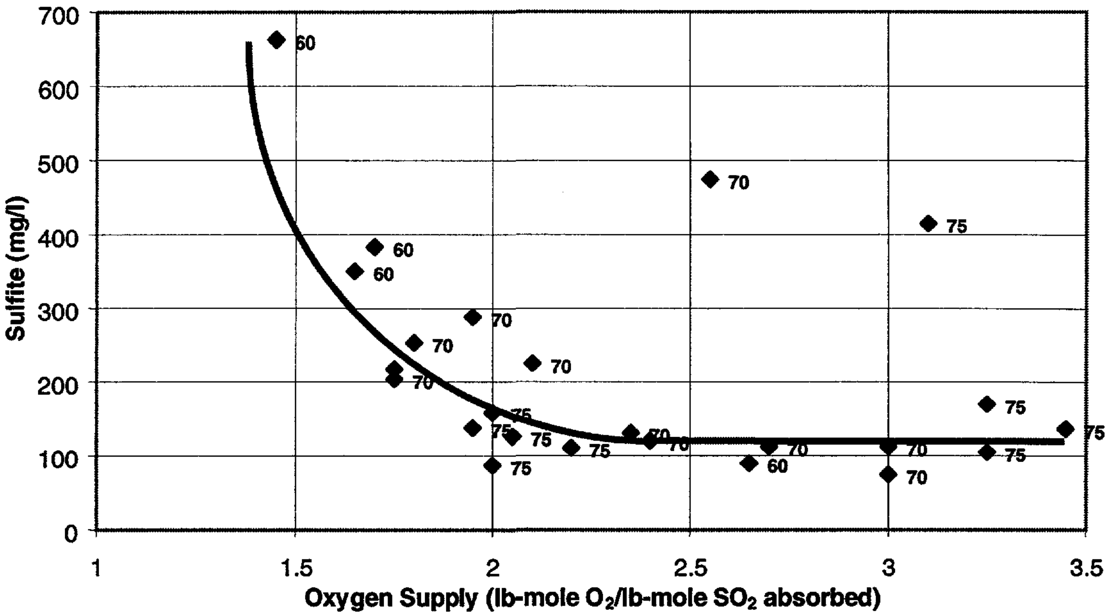


Figure III-8. Effect of Percent Agitator Speed on Exiting Sulfites

The effect of pH on the utilization of air in the oxidizer was evaluated by operating the oxidizer at pH's of 4.4 and 5.3 as opposed to the baseline of 5.0. The pH of the liquor determines the ratio of sulfite to bisulfite in the liquor. Altering the sulfite/bisulfite ratio can provide insights into the oxidation mechanism as to which chemical species may be more readily oxidized. The results of these evaluations are displayed in Table III-1. As shown, minimal improvement was achieved with respect to residence time at similar oxygen supply ratios at the lower pH

Table III-1

Effect of pH on Oxidation

pH	Oxygen Supply $\left(\frac{lb\text{-}mole\ O_2}{lb\text{-}mole\ SO_2\ absorbed}\right)$	Residence Time (hour)
4.4	3.15	1.21
5.0	3.03	1.29
5.3	3.10	1.34

A second method to enhance the oxidation process is through the addition of metal catalysts. The catalytic affect of metals ions in mg/l concentrations can accelerate the oxidation process and aid in the reduction of residence time and possibly improve the utilization of oxygen. For these studies, the impact of iron, copper, and manganese metal ions was investigated. These metals were added directly to the oxidizer in the form of a solution which was generated by dissolving the sulfate compounds of the respective metals in water. Utilizing standard procedures for optimizing the oxidizer air usage, the air flowrate to the oxidizer was reduced until the exiting sulfites exceeded 100 mg/l. The results of this testing in comparison to comparable data from non-catalyst testing is shown in Table III-2.

Table III-2

Comparison of Catalytic and Non-Catalytic Oxidation Evaluations

	Catalyst		Non-Catalyst	
Catalyst	Residence Time-Hrs	lb-mole O_2 Supplied / lb-mole SO_2 Absorbed	Residence Time-Hrs.	lb-mole O_2 Supplied / lb-mole SO_2 Absorbed
Iron	1.33	3.0	1.35	2.9
Copper	1.33	3.0	1.35	2.9
Manganese	2.45	2.0	2.43	1.6

Although not directly calculated as an operating cost, the impact of scale formation within the oxidizer on process downtime and poor operating conditions can be significant. Scale can reduce the cross-sectional area of the piping which increases pumping costs or coat the air spargers which restricts the flow of air into the oxidizer. Therefore it is prudent to minimize unscheduled downtime and maintenance of the oxidizer by limiting scale growth.

The formation of scale within the oxidizer results from the dissolution of calcium solids within the oxidizer and the subsequent crystal nucleation of the calcium sulfate. A larger loading of these calcium solids into the oxidizer increases the relative saturation of the gypsum which results in excessive nucleation or scaling. At steady state with regards to a constant uptake of SO_2 in the absorber, the rate of crystal formation within the oxidizer is constant and proportional to the volume, suspended solids content, and relative saturation of gypsum of the slurry in the oxidizer. Subsequently, increasing the volume and/or suspended solids content of the oxidizer will decrease the gypsum relative saturation and promote crystal growth as opposed to scaling.

Therefore the parameter of percent suspended solids in the oxidizer liquor was investigated to minimize scale formation.. The flowrate of the gypsum seed crystals to the oxidizer provided the control of this parameter. Increasing this flowrate increased the percent solids in the slurry. The data produced by these evaluations is depicted in Figure III-9. Low percent solids (<1.5%) exhibited a significant increase in scaling rate of over 1.0 grams/day as measured accumulation on a submerged metal test coupon. Operating in a range of 2.0-3.0% suspended solids reduced this scaling rate by a factor of five.

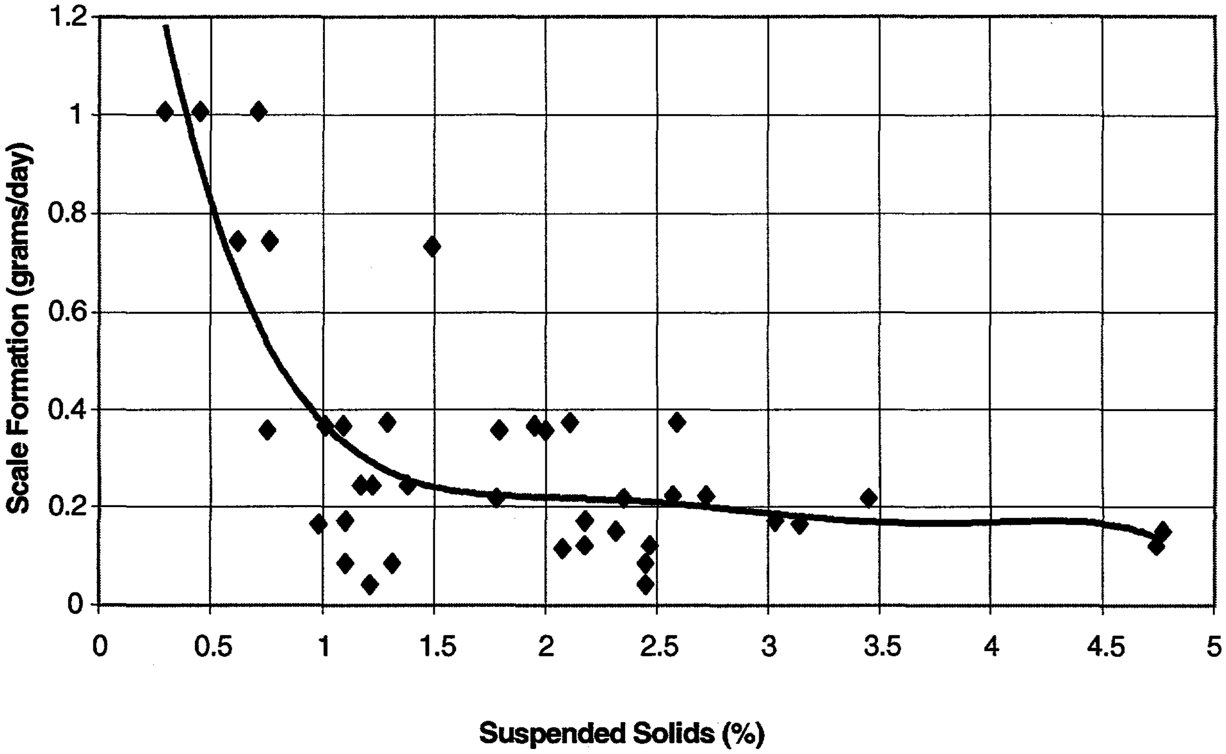


Figure III-9. Effect of Suspended Solids on Oxidizer Scale Formation

<u>Analysis</u>

The curve shown in Figure III-7, which was constructed by plotting the concentration of exiting sulfites from the oxidizer versus the molar ratio of oxygen supplied per the absorbed sulfur dioxide, highlights the two regimes which influence the oxidation reaction of sulfites. The first regime at the higher supplied air ratios is a regime that is reaction limited. In this region, there is an over abundance of oxygen and therefore the oxidation process is limited by the rate of reaction. However, as the flowrate of oxygen is reduced, the limitation becomes the rate at which oxygen diffuses into the liquid. As less and less oxygen is available to satisfy the oxidation reaction at a set residence time, the concentration of exiting sulfites increased.

For the agitated oxidizer tank evaluated in these studies, the amount of agitation impacted the oxidation process in two ways. The paddle blades at the bottom of the tank were responsible for producing small air bubbles from the incoming air sparger and dispersing these bubbles throughout the zone surrounding the paddle blades. Increasing the agitator speed assisted in producing smaller bubbles with greater surface area which improved the diffusion into the liquid phase as well as improved the gas/liquid mixing in this zone. The two sets of turbine blades generated recirculation zones which increased both the residence time of the air bubble in the liquid and the mixing of the gas and liquid. All of these factors improved air utilization within the oxidizer.

As shown in Figure III-8, increasing the agitation speed at decreasing air flowrates improved the air utilization as would be expected by the function of the agitator. However, the agitator tests at the pilot plant were limited by the horsepower of the agitator drive motor. At higher air flowrates, the liquid density surrounding the paddle blades was lowered due to the fluidization from the air. This permitted the agitator to operate at lower speeds. Conversely, at low air flowrates, the liquid density surrounding the paddle blades increased as a result of less fluidization. The agitator would stall due to insufficient horsepower to overcome the drag of the paddle blades in this denser zone. Subsequently, testing which required reducing air flowrate below 70 scfm needed to be accomplished while reducing the agitator speed. Therefore, it is not surprising that the exiting sulfites increased rapidly as the air flowrate was lowered due to the impact of both the lower available oxygen and the reductions in the efficiency the agitator has on the oxidation process.

Parametric oxidizer pH testing at control setpoints of 4.4 and 5.3 resulted in minimal differences of the residence time with respect to similar oxygen feed ratios at a pH of 5.0. The gains exhibited at the lower pH could be the result of the effects of solid phase calcium sulfite on the oxidation process. Solid phase calcium sulfite forms in two ways. The first is the result of chlorides absorbed in the scrubber from incoming flue gas. These chlorides result in soluble calcium chloride in the regeneration tank which forms calcium sulfite and magnesium chloride upon re-entering the absorber. The second mode of calcium sulfite formation is from high sulfite concentrations exiting the oxidizer due to poor oxidation. These sulfites form calcium sulfite in the regeneration tank which contaminate the magnesium hydroxide utilized for pH control of the absorber and oxidizer as well as the liquid returned to the recycle tank for level control. In either case, the oxidizer is required to dissolve this solid phase calcium sulfite before it can be oxidized. Subsequently, the higher pH which hinders the dissolution of calcium sulfite and requires additions of potentially contaminated magnesium hydroxide to maintain the higher pH, under-performed the lower pH. However, observations during the proof of concept testing determined that low pH operation increased the potential for scale formation. Therefore, the operation of the oxidizer in the pH range of 5.0 was determined to be optimal.

Attempts to increase the reaction rate of oxidation process by utilizing catalysts were not as successful as anticipated. As shown on Table III-2, the residence time required for achieving an exiting concentration of 100 mg/l sulfites or less was similar for both the catalyst and the non-catalyst oxidation evaluations at the same oxygen to absorbed sulfur dioxide molar ratios. The rational behind these outcomes can be traced to the interaction of magnesium hydroxide with the metal ions in solution. Localized high pH regions near undissolved magnesium hydroxide precipitated the metals as metal hydroxides. Additionally, metal ions in solution exiting the oxidizer entered the high pH regime of the regeneration tank where the same phenomena occurs. In either case, once these metals precipitated from the solution, they no longer exhibited catalytic behavior. This once through potential is inefficient and increases the costs of commercial oxidizer operations due to the continuing consumption of the metal sulfates. Also, the metal hydroxide precipitate becomes a contaminate to the magnesium hydroxide and reduces the value of this by-product.

Scale formation on process equipment is the result of crystal precipitation from a supersaturated solution which typically does not have a sufficient quantity of nucleation sites or seed crystals. In the ThioClear process, scaling of the oxidizer was minimized by operating at a pH of 5.0 and recycling gypsum solids for seed crystals from the hydroclone underflow to the oxidizer. The parameter of percent suspended gypsum solids in the oxidizer slurry was control by the flowrate of this recycle stream. As detailed in Figure III-9, the quantity of suspended solids must exceed a threshold value before the scaling process is minimized. In this evaluation, the threshold value was approximately 1.5%. When the oxidizer's percent suspended solids was below this value, the scaling rate measured on a test coupon significantly increased to a rate exceeding 1 gram of accumulation per day of operation. By increasing the gypsum seed flowrate to achieve a percent suspended solids concentration of 2 to 3%, the scaling rate was reduced below 0.2 grams per day.

b. Crystallatizer / Regeneration Tank Optimization

Test Results

In evaluating parametric changes in the regeneration tank level (or residence time) and pH, particle size analysis of the gypsum crystals exiting the secondary hydroclone was conducted utilizing a Leeds and Northrup Microtrac. The mean particle size data as a function of pH and residence time is as shown in Figure III-10. The trends indicated by these tests show that in general as the pH increases (10.0 to 10.8) or as the residence time increases (1.9 to 3.75 hours), the size of the gypsum crystal decreases. The exception to this rule was at the shortest residence time of 1.4 hours which provided gypsum crystals smaller than the residence time of 3.2 hours and exhibited a trend of increasing crystal size as the pH was increased.

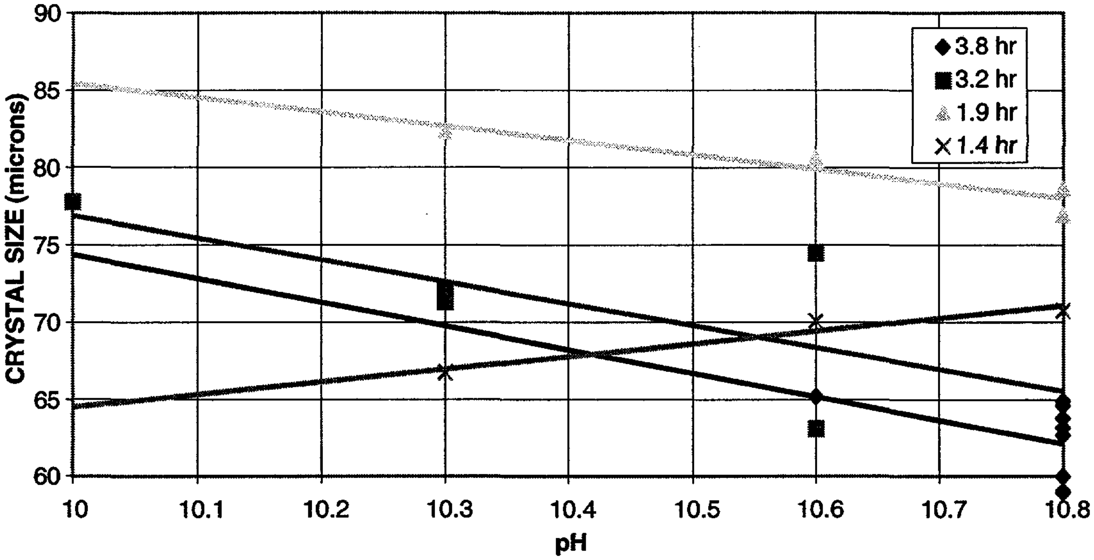
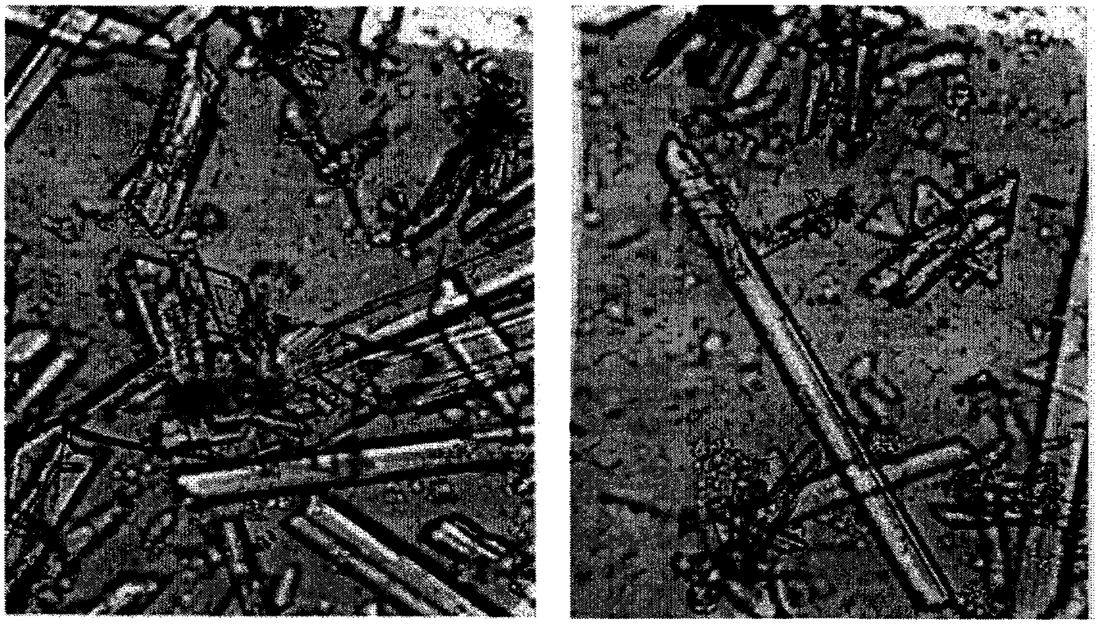


Figure III-10. Effect of pH and Residence Time on Gypsum Crystal Size

Aside from changing the conditions of the crystallizer to enhance the crystal formation of the gypsum particles, a second method would be to introduce an additive which would alter the crystal structure. Such an additive which has commonly been utilized in the gypsum industry is succinic acid. An inexpensive source of succinic acid is the waste by-product of nylon production know as dibasic acid (DBA) which is composed of succinic, adipic and glutaric acids. The method of addition consisted of 0.3 gpm flow of 25% DBA to the regeneration tank. The photomicrographs shown in Figure III-11 provide a comparison between gypsum crystals formed with and without DBA, respectively. In reviewing these photographs and the corresponding particle size analysis, no physical change in the crystal structure was noted.



Crystals Formed with DBA Crystals Formed without DBA

Figure III-11. Gypsum Crystal Modification Evaluation

As with the oxidizer, scale formation as a result of the regeneration tank's operating conditions can lead to substantial down time of the process and increased operating costs. A metal coupon was inserted into the regeneration tank to accumulate scale. On a daily basis, the coupon was weighed to determine the rate of scale formation. The average rate of scale formation as a function of residence time and pH is detailed in Table III-3. Although there is significant scatter in the data, a general trend of lower scaling rates at lower pH can be noted. The impact of residence time is unclear in that at a pH of 10.8 the scaling rate was virtually unchanged from a residence time of 1.4 to 3.8 hours but showed substantial increases at a pH of 10.6 as the residence time increased.

Table III-3

Effect of Residence Time on Scale Formation (gm/day x 1000)

Residence Time (Hours)	pH 10.0	10.3	10.6	10.8
1.4	---	0.67	0.54	3.58
1.9	---	5.46	3.00	2.38
3.2	1.66	0.77	4.25	---
3.8	---	---	---	3.06

Table III-4 shows the influence of the percent suspended solids and pH on the rate of scale formation. The general trend of decreasing scaling rate with decreasing pH holds true in this parametric testing. As with the prior table, significant scatter masks the trends. It can be postulated that as observed in the oxidizer scaling studies, when the percent solids in the slurry exceeds a minimal threshold, the variance in this parameter has minimal impact. Thus other parameters which were not controlled during these studies became more influential on the rate of scale formation.

Table III-4

Effect of Suspended Solids on Scale Formation (gm/day x 1000)

Suspend Solids (%)	pH 10.0	10.3	10.6	10.8
<4	1.66	----	1.77	3.66
4-6	----	1.92	----	2.71
5-6	----	----	4.25	2.81

Analysis

Figure III-10 provides multiple insights into the influence of gypsum crystal growth by pH and residence time. When operating the regeneration tank at higher pH's, excessive nucleation of gypsum crystals occurred creating smaller crystals. This resulted from the low pH liquor from the oxidizer mixing with the high pH regeneration tank slurry.

Such crystals also tend to be more fragile. Hence, attrition may have played a secondary role in forming smaller crystals. In the regeneration tank, the agitator was the main cause of attrition. After a set residence time in which maximum crystal growth has occurred, a longer residence time only provided additional interaction between the agitator and the crystals. The "needle-shaped" gypsum crystals formed in the ThioClear process can easily break during these extended residence times.

The negative influences of the small crystals formed from the high pH environment and attrition of the fragile crystals can have synergistic effects. Poorly formed crystals which act as seed crystals tend to promote the formation of similar crystals. Therefore, new crystals precipitated from the supersaturated liquor would also be small and fragile.

The above trends were observed for residence times of 1.9, 3.2 and 3.75 hours. However, a reversal in these observations was noted at a residence time of 1.4 hours. At this shorter time the crystal growth increased as the pH increased. Such a trend indicated that insufficient residence time was available for maximum crystal growth. Therefore, increasing the pH, which was the driving force for crystal growth, produced the largest crystals as it increased. However, the higher pH does not compensate for the longer residence time required for crystal growth which can be seen by comparing the 70 micron average crystal size produced at 1.4 hours against an average size 79 micron at 1.9 hours.

Utilization of DBA in limestone FGD processes has provided additional buffering capacity which enables these systems to improve their sulfur dioxide removal. However, in the case of ThioClear, DBA was utilized for its content of succinic acid. The gypsum industry utilizes succinic acid to modify the shape of the gypsum crystals to a "block-shaped" structure. These "block-shaped" crystals tend to have improved handling and dewatering characteristics than the "needle-shaped" crystals typical of the ThioClear process. The photomicrographs in Figure III-11 from the Miami Fort pilot plant evaluations show no changes in the shape of the crystal. Inhibiting effects of the high pH regime in which the precipitation process occurs or the abundance of dissolved magnesium in the liquor may have limited the effectiveness of this crystal modifier in the regeneration tank.

Analysis of the rate of scale formation as a function of pH, residence time, and percent suspended solids in the liquor detailed in Table III-3 and Table III-4 was difficult due to the scatter of data. Standard methods to reduce the rate of scale formation included increasing the residence time and/or the percent suspended solids of the crystallizer. Each of these methods involved desaturating the solution by either providing sufficient time for the supersaturated liquor to interact with the available crystals or adding additional crystals to enhance the interaction. Therefore, crystal formation on equipment surfaces was discouraged. These expected trends were not observed during the parametric studies of Subtask 4.1. Both residence time and the percent solids in the slurry had minimal impact on the scaling rate. However, the trend of increasing pH, which coincides with increasing relative saturation of calcium compounds, did produce corresponding increases in the rate of scale formation.

3. High Solids Testing

Test Results

Figure III-12 details the influence of reducing the absorber blowdown (or by-product recovery flow loop) flowrate on the scrubbing liquor alkalinity measured as a concentration of carbonate. At the high flowrate/low dissolved solids testing, the effective alkalinity was 625 mg/l. The result of reducing the flowrate from 20 gpm to 10 gpm doubled the alkalinity to an average measured value of 1300 mg/l.

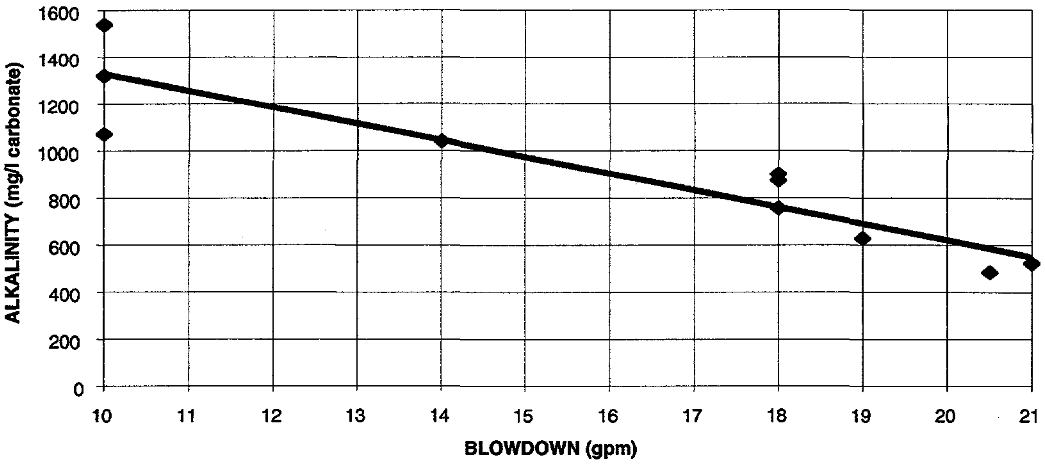


Figure III-12. Effect of Absorber Blowdown on Alkalinity

Corresponding with the monitoring of the alkalinity, the efficiency of the sulfur dioxide removal process was also investigated. The results of these studies are shown in Figure III-13. The sulfur dioxide removals are reported as transfer units (NTU), a logritamic scale, so as to clearly differentiate improvements at these high removals above 95%. At a blowdown flowrate of 20 gpm, the removal achieved in the absorber was 3 NTU's or 95%. The removals increased steadily to 4 NTU's or 98% as the blowdown flowrate was decreased to 14 gpm. Further decreasing the blowdown flowrate to 10 gpm had nominal improvement of the sulfur dioxide removal.

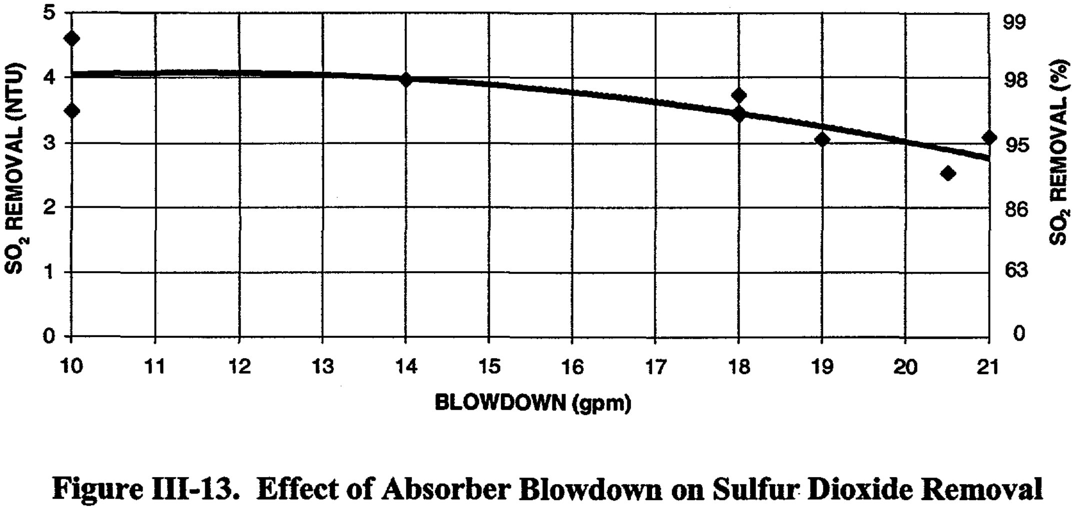


Figure III-13. Effect of Absorber Blowdown on Sulfur Dioxide Removal

The parameter of residence time which was changed by the reductions in the liquid flow in the by-product recovery flow loop did have a major influence on the oxygen requirements of the oxidizer. These results are detailed in Figure III-14. For this study, the pH was controlled at the optimum pH of 5.0 and a full tank level was maintained. As was conducted in the prior oxidizer optimization studies of Subtask 4.1, the air flowrate was lowered at each residence time to determine the minimum flowrate required to maintain exiting sulfites below 100 mg/l. The lowest achieved air flowrates for each test are depicted in Figure III-14. As can be seen from the graph, to achieve the goal of a 2.0 molar ratio of oxygen supplied to sulfur dioxide absorbed requires a residence time of 1.9 hours.

An alternative method of varying the residence time of the oxidizer is to change the liquid level within the oxidizer. The data point designated by the 50% label on Figure III-14 shows the results of operating the oxidizer at a liquid level of 50% and an absorber blowdown flowrate of 10 gpm. Although the residence time of 1.33 hours is similar to other data points, the air required was much greater. In fact, the exiting sulfites from the oxidizer exceeded 500 mg/l while the air flowrate to the oxidizer was at its maximum of 100 scfm.

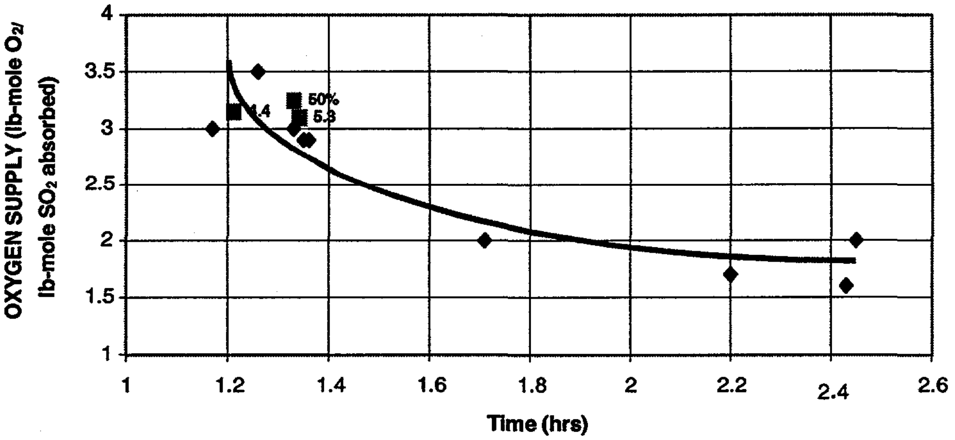


Figure III-14. Effect of Residence Time on Oxidizer Air Requirements

Aside from minimizing the costs associated with the tankage and air supply, it is important to reduce the cost of sulfuric acid consumption required to maintain the pH of the oxidizer. Acid additions are required when insufficient acid is produced from the oxidation of bisulfites to neutralize magnesium hydroxide which may enter the oxidizer through the absorber downcomer or the gypsum seed crystal streams. In this evaluation, the usage of the sulfuric acid was monitored while the pH of the feed to the oxidizer and the operating pH of the oxidizer were varied. The results displayed in Table III-5 show that the minimum consumption of acid was obtained at an absorber downcomer pH of 5.5 and an oxidizer pH of 5.0.

Table III-5

Effect of Absorber Downcomer pH and Oxidizer pH on Sulfuric Acid Consumption

Absorber Downcomer pH	Oxidizer pH	Acid Consumption - lb/hr
5.5	5.0	1.26
6.0	5.0	1.59
6.0	4.5	4.92
5.5	4.5	4.56

The influence of increasing the concentration of dissolved solids at various pH control setpoints on gypsum crystal size is shown in Figure III-15. The data from these studies was superimposed onto the regressions developed from regeneration tank optimization studies conducted in Subtask 4.1. This test was conducted at the minimum tank volume utilized in the prior tests. As with the prior data, the average gypsum crystal size was determined from particle size analysis of the gypsum exiting the secondary hydroclone. A similar trend in the average crystal size was noted with respect to a maximum of 82 microns being achieved at a pH of 10.3 and the average size decreasing to a minimum of 70 microns as the pH is increased to 10.8. As can be seen, the slope of this regression is much sharper than that of the previous results.

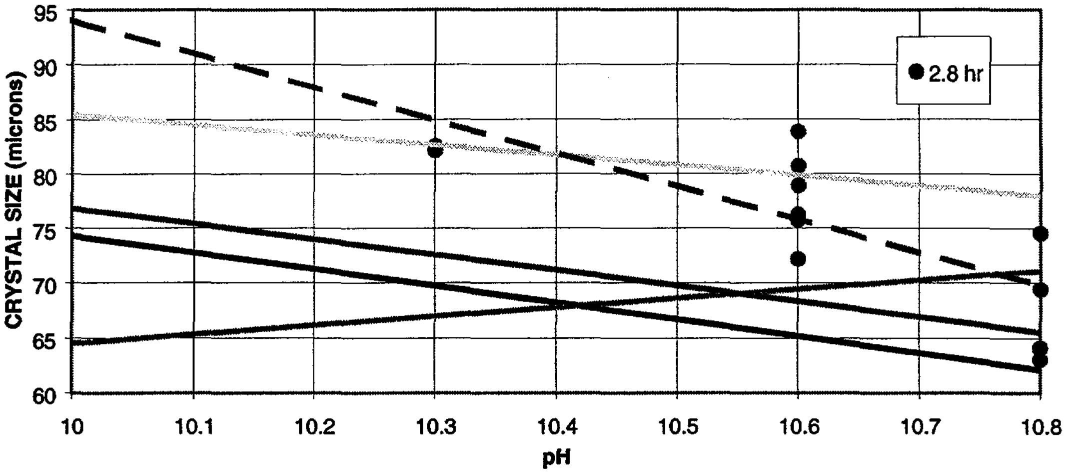


Figure III-15. Effect of High Dissolved Solids on Gypsum Crystal Size

Scale deposition on the metal test coupon was monitored in conjunction with the regeneration optimization studies. During these tests, the percent suspended solids averaged 6% as a result of the higher concentration of dissolved solids entering the regeneration tank. The results of these measurements are detailed in Table III-6. As observed in the prior tests, the pH of 10.8 had the largest rate of scale formation. However, all deposition rates were significantly less than those of the low solids testing.

Table III-6

Effect of High Dissolved Solids on Regeneration Tank Scale Deposition

(gm/day x 1000)

pH:	10.3	10.6	10.8
Scaling Rate:	.75	.01	1.6

Analysis

As anticipated, a reduction in the absorber blowdown flowrate increased the dissolved solids concentration in the absorber liquor. Figure III-12 shows the impact of the decreased flow on the alkalinity of the absorber scrubbing liquor. At an absorber blowdown of 20 gpm, the dissolved magnesium ion concentration was 2200 mg/l. By reducing the flowrate to 10 gpm, the ion concentration increased above 3500 mg/l. The increase in magnesium concentration permitted the sulfite concentration to increase from 2400 mg/l to over 3800 mg/l. Magnesium sulfite is a soluble alkaline salt whose increase is reflected by significant increases in the effective alkalinity measured as a carbonate concentration on Figure III-12.

Corresponding to the increase in the effective alkalinity of the scrubbing liquor was an increase in the sulfur dioxide removal efficiency of the absorber. As shown in Figure III-13, sulfur dioxide removal increases until a blowdown flowrate of 14 gpm is achieved. This flowrate coincides with an alkalinity of approximately 1100 mg/l on Figure III-12. These results show, as expected, that increasing the neutralizing capability of the scrubbing liquor increased the sulfur dioxide removals for low levels of alkalinity. Further increases in alkalinity did not increase sulfur dioxide removals. Above an alkalinity of 1100 mg/l, the sulfur dioxide removal process became gas-film limited. This means removals no longer depend upon the neutralizing capability of the liquor, but on the degree of contact between the gas and the liquor. Since all these tests were conducted with the same absorber configuration and operating conditions, the degree of contact was unchanged and no further increases were noted at the higher alkalinity.

In reviewing the data between the oxygen supplied to the oxidizer and the liquor residence time, it was not surprising to have the relationship depicted on Figure III-14 to occur. During long residence times, the sulfites within the liquor have sufficient time to react with the available oxygen entering the oxidizer. The flattening of the curve at the higher residence times indicates the oxidation process is in a reaction rate limited regime. Conversely at low residence times, the diffusion of the oxygen into the liquor becomes the limiting step. Therefore, the oxygen required by the oxidizer increases exponentially to provide the driving force for maintaining a desirable level of dissolved oxygen in the oxidizer.

The data point labeled 50% represents the results of reducing the oxidizer tank level as opposed to lowering the absorber feed rate to the oxidizer for reducing the residence time. A significant increase in the oxygen feed rate was required while attempting to maintain the exiting sulfite concentration at 100 mg/l. However, the necessary amount of air exceeded the compressor capacity and the sulfite concentration exceeded five times the target value. These results illustrate the reduction in the solubility of oxygen into the liquor as a result of decreasing the hydraulic head. The decrease in the hydraulic head of the oxidizer reduced the solubility by proportionately the same value. The resistance for the diffusion of the oxygen into the liquor would translate into nearly a six fold increase as represented by the mass transfer coefficient.

Analysis of the acid consumption trends of the oxidizer shown in Table III-5 was as anticipated. Operating conditions of the absorber and the oxidizer which required higher pH in the former and lower pH in the latter had the largest consumption rates of acid in the oxidizer. This trend results from a larger quantity of undissolved magnesium hydroxide entering the oxidizer from the absorber when it was operating at a higher pH. This added burden coupled with less sulfuric acid production resulting from the oxidation of a lower bisulfite concentration associated with the higher pH of the incoming liquor increased acid utilization, especially at lower oxidizer operating pH's. Conversely, a lower absorber operating pH with a higher oxidizer operating pH required the minimal amount of acid additions.

Analysis of the gypsum crystal sizes resulting from operating at a higher concentration of dissolved solids indicated that reducing the recycle of the gypsum seed crystals to the regeneration tank and operating at a low pH enhances the growth of large crystals. As the concentration of dissolved solids is increased in the feed to the regeneration tank, the suspended solids in this tank increased accordingly due to the precipitation of the higher concentration of sulfate ions in the dissolved solids. Therefore, the amount of recycle can be reduced which alleviates the effects of attrition which occurred at high recycle rates. Additionally, the lower concentration of seed crystal promoted growth of a smaller number of crystals which enhances the mean value crystal size.

As the pH was increased which results in excessive nucleation, the crystal size decreased as previously discussed in Subtask 4.1. The higher concentration of magnesium ion which was present in the liquor at the lower flowrates played a larger role in precipitating fragile crystals due to its contamination of the crystal lattice. These effects contributed to the sharp decline in the crystal size as observed in Figure III-15.

As discussed in the earlier section on regeneration tank optimization, standard methods to reduce scale deposition included increasing the residence time and increasing the percent suspended solids. Although clear trends were not observed in the prior data, the data on Table III-6 in comparison to the data on Table III-3 and Table III-4 showed a significant decrease as a result of desaturating the liquor by operating at higher solids with a longer residence time. The trend of increasing scale deposition at the higher pH which coincides with increasing the relative saturation of the calcium compounds held true in these studies also.

4. Dewatering and Solids Purification

Test Results

From Table III-7, it is evident that at higher hydroclone feed flowrates the gypsum purity is higher than at lower hydroclone feed flowrates. The gypsum purity is an indication of the amount of magnesium hydroxide being recovered in the process. The gypsum purities resulting from the different hydroclone configurations operating at the 20 gpm flowrate were all above 95%. This is contrasted by the hydroclone configurations at the 10 gpm feed flowrate where the gypsum purities never exceeded 95%. The 3" Dorr-Oliver hydroclones with 5/8" vortex and 1/4" apex as well as the 1" vortex and 1/4" apex performed well giving higher than 98% gypsum purity at 20 gpm feed flow. These two hydroclone configurations also provided suitable magnesium hydroxide purities in the overflow of 37% and 33%, respectively. The magnesium hydroxide purities for the primary hydroclone overflow only exceeded 40% for one test run using a 5/8" vortex and

1/4" apex at 10 gpm as illustrated in Table III-7. There was no discernible trend in the gypsum purity with feed percent solids. For instance, the 5/8" vortex and 1/4" apex configuration at 20 gpm did not exhibit higher or lower gypsum purity with increasing feed percent solids. As the feed percent solids increased, the gypsum purity first increased then decreased. For some configurations, the gypsum purity decreased for increasing feed percent solids while for other configurations the gypsum purity increased for increasing feed percent solids. One trend that was observed was that the magnesium hydroxide purity in the primary hydroclone overflow decreased with increasing gypsum purity. For the 5/8" vortex and 1/4" apex configuration at 20 gpm, 37% magnesium hydroxide purity was achieved with 95.4% gypsum purity for one test run. However, only 32.2% magnesium hydroxide purity with accompanying 96.4% gypsum purity was achieved with another test run with the same hydroclone configuration and feed flowrate. At 10 gpm with 5/8" vortex and 1/4" apex, the gypsum purity was 91.2% with magnesium hydroxide purity of 47%. Another test run with the same hydroclone configuration and feed flowrate had 95% gypsum purity and 32% magnesium hydroxide purity.

Table III-7

Hydroclone Parametric Evaluations

Vortex Size (in)	Apex Size (in)	Feed Flow-rate (gpm)	Feed Suspended Solids (%)	Gypsum (%)	Magnesium Hydroxide (%)
5/8	1/4	10	4.80	94.8	29.2
			5.35	86.8	27.4
			7.44	93.2	47.7
			9.50	92.5	32.0
1	1/4	10	7.44	93.7	33.3
			9.50	92.2	38.1
5/8	1/4	20	4.80	96.4	32.2
			5.03	98.6	12.0
			5.35	95.4	37.0
1	1/4	20	5.03	98.3	13.7
			5.35	96.0	33.0

Comparative studies with and without belt filter washings were performed to examine the change in chloride ion concentration in the filter cake. Without belt filter washings, the chloride ion concentration in the gypsum by-product reached values above 1000 mg/kg filter cake. For instance, analysis on September 29th revealed 1415 mg/kg chloride ion concentration in the cake. It was found that washings of the filter cake with service water could reduce the chloride ion concentration. On October 19th, analysis showed the chloride ion concentration in the cake to be 47 mg/kg. This was achieved with a 3 gpm counter-current washing on the belt filter. The purity of the unwashed and washed samples is shown in Table III-8.

Table III-8

Gypsum Wash Results

Sample	Chloride (mg/kg)	Gypsum (%)	Magnesium Hydroxide(%)	Calcium Sulfite(%)	Silicate (%)	Free Base(%)	Carbonate (%)
Unwashed	1415	97.65	1.36	1.41	0.32	0.20	0.24
Washed	47	99.80	1.14	0.97	0.32	0.13	0.18

The purification subsystem did not produce a higher purity magnesium hydroxide by-product compared to that which was found from the primary hydroclone overflow. The purity of magnesium hydroxide over the period of purification for the primary hydroclone overflow was 55.14% while the purity of magnesium hydroxide after passing through the purification system was 58.17%. These results differ by less than the experimental error associated with the measurement. The complete purity of the magnesium hydroxide by-product after passing through the purification system and that of the source from the primary hydroclone overflow are given below in Table III-9.

Table III-9

Magnesium Hydroxide Wash Results

Sample	Magnesium Hydroxide(%)	Gypsum (%)	Calcium Sulfite (%)	Silicate (%)	Free Base (%)	Carbonate (%)
Unwashed	55.14	22.17	1.09	12.83	1.24	4.30
Washed	58.17	23.62	0.58	12.54	1.19	3.60

The mean volume diameter of the gypsum crystals reporting to the secondary hydroclone underflow was compared with the filter cake solids content as shown in Table III-10. The filter cake solids content did not correlate directly to the gypsum particle size. With a gypsum particle size of 81 microns, the filter cake solids was 79.2%. This solids content is less than a sample with average gypsum particle size of 64.3 microns. Conversely, another analysis revealed an 80.6% solids content with an average gypsum particle size of less than 72.5 microns. Because the scatter in the points does not show a correlation between average gypsum particle size and the filter cake solids content, the percentage of particles below 11 microns was investigated to determine influences on the filter cake solids content. As in the particle size analysis, no trend was evident as shown in Table III-10. One interesting result is that the sample with the lowest average gypsum particle size (47.19 microns) also exhibits the lowest filter cake solids content of 69%. The cut less than 11 microns of 16.61% is also the highest of all samples measured. Perhaps over a large range of gypsum particle size, a correlation of percent solids of the filter cake and average gypsum particle size does exist.

Table III-10

Comparison of Gypsum Particle Size Analysis and Filter Cake Solids

Filter Cake Solids (%)	Volume Mean Diameter (microns)	Cumulative Smaller Than 11 microns(%)
69.20	47.19	16.61
71.20	74.52	3.07
72.49	70.71	8.75
74.67	78.21	6.49
76.36	86.03	---
76.85	78.44	2.52
77.76	72.77	4.25
78.49	78.66	2.31
79.11	80.72	2.13
80.16	64.08	11.32
80.86	72.17	6.80
84.88	78.22	---

The analysis of the centrifuge tests for the gypsum and magnesium hydroxide mixture shows the lowest magnesium hydroxide weight percent in the dried cake to be 4.35%. Magnesium hydroxide recovery was poor and much less than the 1.5 weight percent magnesium hydroxide reporting to the secondary hydroclone underflow. The corresponding weight percent of magnesium hydroxide in the centrate was 56.36% and is comparable to the magnesium hydroxide purity in the primary hydroclone overflow. The average weight percent of magnesium hydroxide in the dried cake was 8.7%. Dewatering tests were conducted with magnesium hydroxide slurry utilizing a decanter centrifuge. These tests showed no improvement over vacuum filtration in that the cake could only achieve 24% solids.

The settling properties of the magnesium hydroxide by-product material were also of importance. The primary hydroclone overflow reported to the center well of an 8 foot diameter thickener. These solids typically settled in the 12-20% range as shown in Figure III-16. Filter cakes generated on laboratory apparatus produced solid contents in the 20-30% range with 25% being normal.

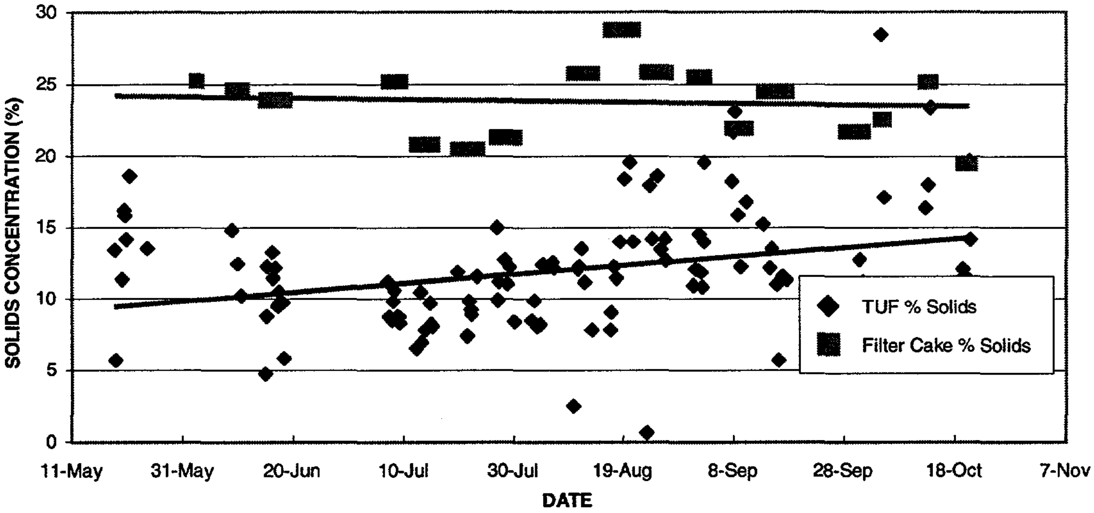


Figure III-16. Settling and Dewatering Properties of Magnesium Hydroxide

The nature of the magnesium hydroxide crystal and the impurities were very important in the settling rate and the final settled solids of the by-product. Settling and filtration tests were performed weekly to follow the changes in thickening properties. It was found that as the concentration of contaminates increased, the thickener area required to obtain adequate percent solids also increased. This indicates that the impurities are gelatinous colloidal. Hydroxides of iron, aluminum and silica exhibit properties such as this and dewatering difficulties are generally associated with poor settling ability.

Analysis

The primary objective of the hydroclones is to recover the magnesium hydroxide in the process. This is necessary to neutralize captured sulfur dioxide in the absorber and sulfuric acid in the oxidizer. If this is not achieved, an outside source of magnesium hydroxide will be required. The recovery of magnesium hydroxide is reflected in the purity of the gypsum. Sufficient gypsum purity is achieved at a feed flowrate of 20 gpm such that the process does not require an outside source of magnesium hydroxide. At 15 and 10 gpm, the gypsum purity falls below 95% and magnesium hydroxide recovery decreases. For the percent suspended solids evaluated in the range of 5 to 9%, hydroclone performance was not effected. It is possible that at much lower percent solids that the gypsum purity is adversely affected. The magnesium hydroxide purity in the primary hydroclone overflow also decreases with increasing gypsum purity. This suggests that a trade-off exists where magnesium hydroxide purity is sacrificed to maintain high magnesium hydroxide recovery. The average analysis of the magnesium hydroxide and gypsum from Phase I of ThioClear testing is shown in Figure III-17.

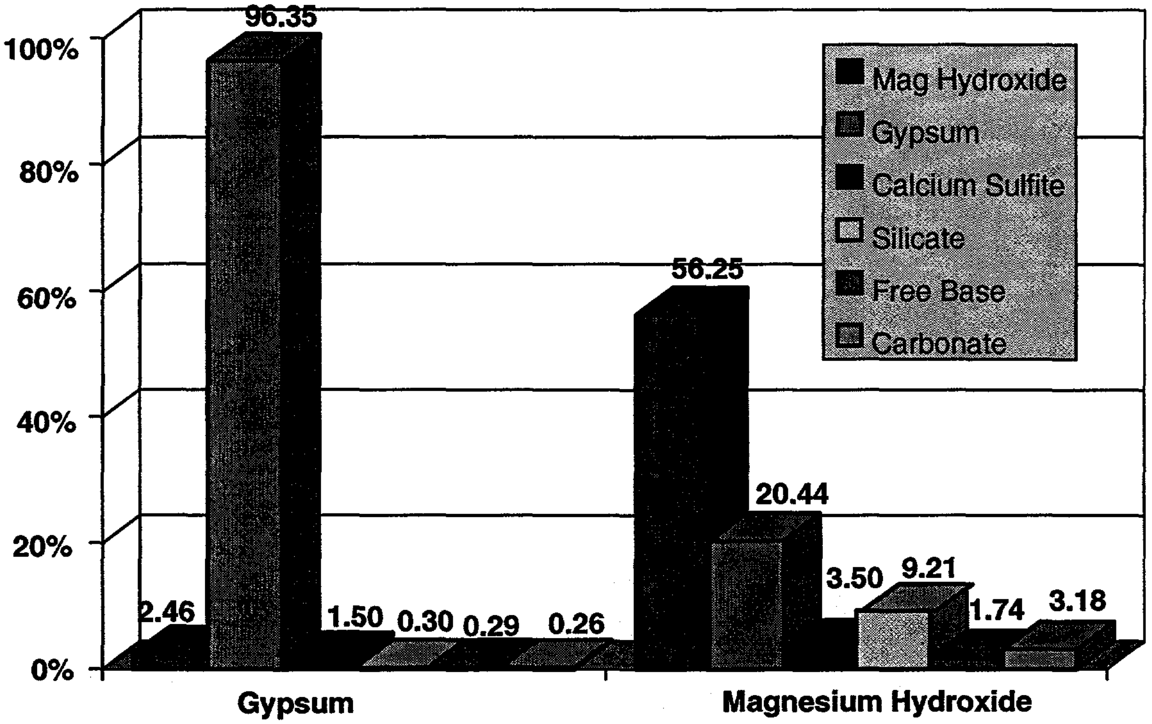


Figure III-17. Phase I By-Product Purity

The by-product magnesium hydroxide contains nearly 40% impurities in the form of calcium sulfite, silicates, free base and calcium carbonate. These impurities limit the markets for the by-product magnesium hydroxide. The calcium sulfite impurities are formed from incomplete oxidation. The free base is formed from excessive lime addition to the regeneration tank. The silicates come from fly ash particles and impurities in the lime. The calcium carbonate is precipitated from solution when dissolved carbon dioxide reacts with lime slurry in the regeneration tank. The contribution of these species to decreases in magnesium hydroxide quality is of concern. Data shows that the calcium sulfite and free base can be controlled by proper operation of oxidation and regeneration parameters. The silicates and calcium carbonate problems are much bigger. Data shows that these two species continued to build throughout the project until an equilibrium level was reached. Silicate contamination reached as high as 13%. The reason for this continuous increase in silica and calcium carbonate lies in the recirculation of fines. The fine magnesium hydroxide is deliberately recovered. This allows the build-up of other fines and impurities in the by-product recovery flow loop. These fines which never leave the system act to decrease the by-product purity. For this reason a modified version of the ThioClear process was developed for testing in Phase II. The modified version removes these fines before they buildup by continuously filtering the by-product flow loop stream at the point of gypsum discharge. This introduces a slight impurity to the gypsum, but removes it from the magnesium hydroxide.

Belt washing has proven to be effective for the removal of chloride ions from the gypsum by-product. Chloride is undesirable because of its impact on the set time and cohesive strength of wallboard. It was found that the ions were washable to a level of less than 100 mg/kg, the industry standard for FGD gypsum.

The magnesium hydroxide purification system consisted of a 4 foot diameter thickener, mixer, rotameter, and four pumps. A slurry pump was utilized for feeding the mix tank. The rotameter maintained the correct flow of wash water to the mix tank which was 5 to 15 times greater than the slurry flow from the 8 foot diameter thickener underflow. The mix tank possessed a volume of 30 gallons providing a residence time of 1 hour for maximum flow conditions. A barrel was also required for magnesium hydroxide storage resulting from the magnesium hydroxide bed of the 4 foot diameter thickener. The results showed that the purity of the solids of the slurry exiting the wash system did not improve over the slurry entering the mix tank. For a slurry which consisted of 50% magnesium hydroxide, 15% gypsum, and 35% inerts, the maximum dissolution of the gypsum would permit removal of 15 lb. of gypsum per 100 lbs. of feed. This would therefore improve magnesium hydroxide purity from 50% to 58%,. Improvements in purity in the actual testing did not reach the 8% change expected.

The underflow from the secondary hydroclone contains the gypsum by-product. This stream was typically 20-30% solids and reported to the filter feed holding tank. For the filtering operation, the slurry in the holding tank was pumped to the belt filter. The belt filter removed the excess water from the gypsum. Although mean gypsum particle diameter was found not to effect the filter cake solids content, other properties of the solids and operation of the belt filter do determine the dryness of the gypsum filter cake. Gypsum product dewatered to 70-81% solids. It has been shown that small amount of fines in the gypsum had drastic effects on the dewatering. The 1-1.5% magnesium hydroxide can contributed to the poorer dewatering.

A second reason for high moisture content of the filter cake has to do with the stripping velocity of the air that passes through the gypsum particles. A high air flowrate through the belt will remove more water than low air flowrates. As long as the pores of the belt are kept clean, this stripping velocity is high. Generally filter belts are changed when they become clogged. The gypsum slurry that was fed to the belt had a pH of 10.5 - 11.0. At these high pH's, there was dissolved calcium (greater than 800 mg/l) in the filtrate. The calcium and high pH allow for a carbonation reaction to occur.

$$Ca(OH)_{2(\mathrm{l})} + CO_{2(\mathrm{air})} \rightarrow CaCO_{3(s)} + H_2O$$

Liquid phase calcium hydroxide reacts with carbon dioxide in the stripping air to form solid phase calcium carbonate. This solid phase calcium carbonate can crystallize in the pores of the belt and eventually seal it completely. With no air flow through the belt, the percent moisture in the product rises considerably. To minimize this sealing effect, the belt was washed periodically with hydrochloric acid. The calcium carbonate dissolved and the pores were opened.

The mean volume gypsum crystal size may affect the filter cake solids content over large ranges in mean volume diameter. The majority of samples taken extended from 64.2 microns to 86.1 microns. At much lower gypsum mean volume diameters, the filter cake solids content may decrease appreciably. This is illustrated by a sample with 46.8 microns gypsum particle size which also possessed a low filter cake solids content of 69%.

The analysis of the centrifuge samples generated by Bird Machine Company showed that a centrifuge is not as effective as the hydroclones at magnesium hydroxide recovery. The dried cakes possessed much higher weight percent of magnesium hydroxide than the secondary hydroclone underflow. In addition, the magnesium hydroxide purity resulting from the centrifuge was not significantly higher than the magnesium hydroxide purity from the primary hydroclone overflow.

5. High Velocity Horizontal Scrubber Testing

Test Results

At 10 ft/sec, the sulfur dioxide removal increased from 89.9% to 97.6% as the L/G was increased from 38.5 to 69.2. This is shown in Figure III-18 where sulfur dioxide removal increases with L/G. Inlet sulfur dioxide concentrations averaged 2000 ppm in all cases. The pH of the absorber liquor varied between 6.0 - 6.4 while alkalinities measured in comparable mg/l of carbonate ranged from 1100 to 2900. The high velocity test at 15 ft/sec showed 98.1% sulfur dioxide removal at L/G of 45.6. At 10 ft/sec and L/G of 45.6, the sulfur dioxide removal is 92.5%. To achieve an equivalent removal at 10 ft/sec requires an L/G of 69 as shown on Figure III-18.

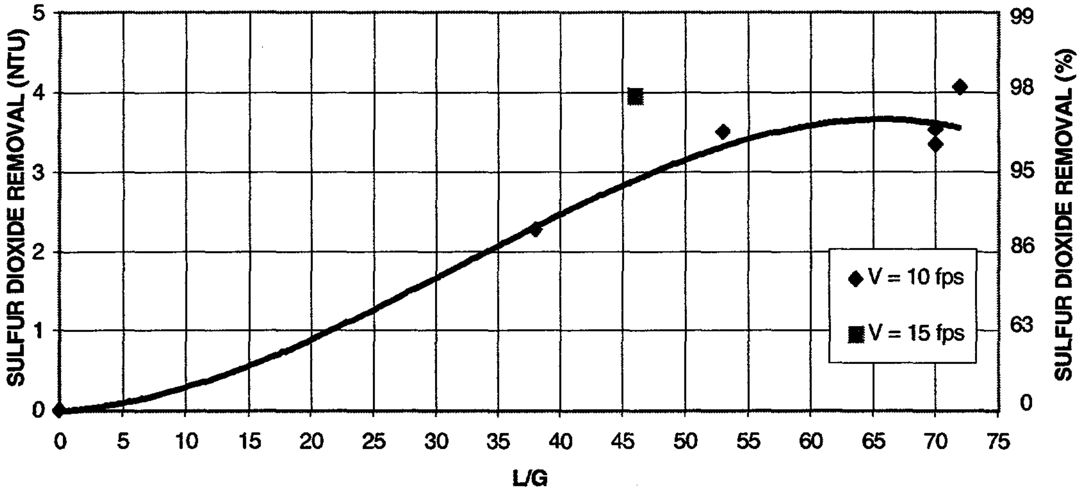


Figure III-18. Parametric Sulfur Dioxide Removal Testing

During the week of September 13th, the inlet sulfur dioxide concentration was changed at eight hour intervals along with a change in absorber bleed flowrate to maintain high removals of 95% and 3000 mg/l magnesium ion concentration in the recycle tank. During 0000-0800 interval, the inlet sulfur dioxide concentration was spiked to 1500 ppm with a blowdown flowrate of 10 gpm. At the 0800-1600 interval, the inlet sulfur dioxide concentration was raised to 2500 ppm with a blowdown flowrate of 17 gpm and during the 1600-0000 interval, the inlet sulfur dioxide concentration was spiked to 2000 ppm with a blowdown flowrate of 13.5 gpm. These changes in blowdown would help maintain the magnesium level at 3000 mg/l. The basic strategy for load following is that the absorber bleed is increased with increases in inlet sulfur dioxide concentrations which typify boiler load increases. Conversely, load following necessitates that as the sulfur content of the gas decreases, the absorber bleed should be decreased to maintain a constant magnesium ion concentration and corresponding scrubbing liquor alkalinity. The results of the load following simulation for the week are illustrated in Figure III-19.

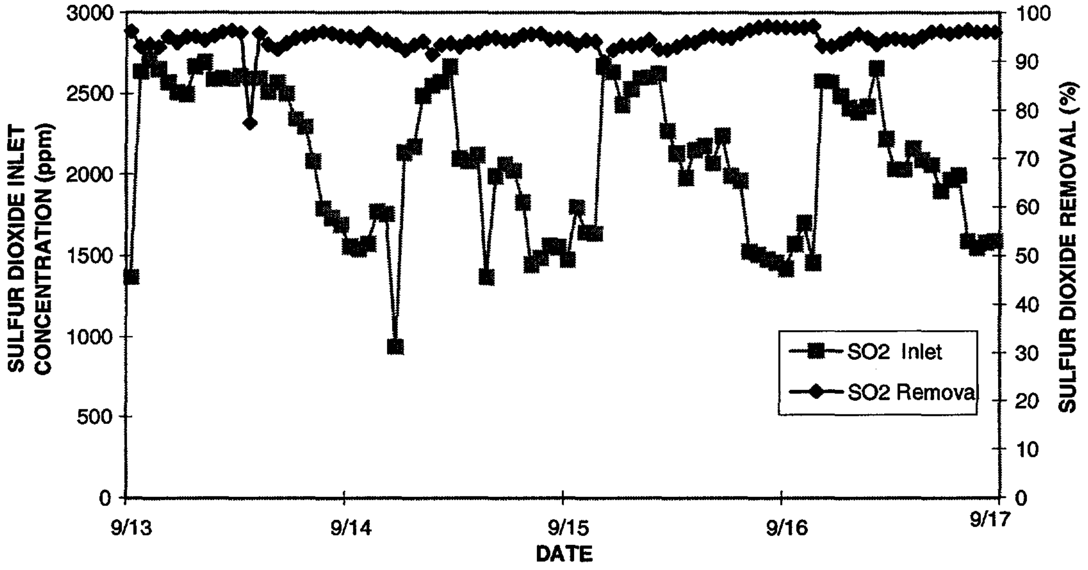


Figure III-19. Load Following

Analysis

Sulfur dioxide removal increased with increasing L/G at 10 ft/sec. Increasing the L/G increases the value of the gas film mass transfer coefficient (K_ga). The sulfur dioxide removal is dependent on K_ga as shown in the following expression:

$$SO_2\,\mathrm{Re}moval(NTU)=\frac{K_g aPZ}{G}$$

where: K_g = overall mass transfer coefficient $(\frac{lb\ moles}{hr\ ft^2\ atm})$

a = interfacial surface area $\frac{ft^2}{ft^3}$

P = total pressure in scrubber (atm)

Z = height of contact zone (ft)

G = flue gas flowrate $\frac{lb\ mole}{ft^2\ hr}$

As K_ga increases, the sulfur dioxide removal will also increase. The term K_ga is a function of the liquid flowrate and the gas velocity which influences gas-liquid contact. Therefore, within reasonable boundaries, increasing either the liquid flowrate or the gas velocity will increase the K_ga and therefore the sulfur dioxide removal. However, large increases in the gas velocity will eventually decrease sulfur dioxide removal because the removal is inversely proportional to the absorber gas velocity. At 15 ft/sec, the L/G was 45.6 with a sulfur dioxide removal of 98.1%. Maintaining the same L/G at 10 ft/sec reduced the removal to 92.5%.

Increasing the flue gas velocity also improves the absorber chemistry. By changing the flue gas velocity from 10 ft/sec to 15 ft/sec, the sulfur dioxide loading increases by 50%. This corresponds to a scrubber bleed flowrate of 15 gpm. As expected the scrubber chemistries did improve. The magnesium ion concentration increased to about 5000 mg/l and the liquid phase alkalinities approached approximately 2000 mg/l. With the stronger chemistry, 97-98% sulfur dioxide removal was achieved.

The bleed flowrate determines operating chemistry of the scrubber. Low absorber bleed flowrates ensure strong process chemistries while higher absorber bleed flows produce lean chemistries. This characteristic can be used to follow sulfur dioxide inlet changes to maintain constant alkalinity and sulfur dioxide removal in the scrubber by variation in the absorber bleed flowrate.

For the load following tests, the flowrates chosen and the level of sulfur dioxide in the gas stream actually did not produce a very strong chemistry for scrubbing. The magnesium ion concentration held constant at about 3000 mg/l and the alkalinity ranged from 400 to 800 mg/l measured as carbonate. The sulfites were less than 2000 mg/l. Even with this weak chemistry, greater than 95% sulfur dioxide capture was achieved.

6. Product Evaluation

Test Results

A five gallon sample of the product magnesium hydroxide material was sent to Premier Services Group for testing and product evaluation. Premier Services has long been a supplier of commercial grade magnesium hydroxide. Premier worked on the sample trying to purify, dewater, and find applications for it. The purity and dewatering characteristics of the sample were poor and they could not find any commercial value in the product based on their markets. As a result, the product was of no interest to Premier.

Samples were sent to Gold Bond Building Products for evaluation. They liked the crystal size and shape but the material did not meet their specifications for pH and chloride content. Their maximum acceptable pH is 8.0 and chloride content is 100 mg/kg. The respective analysis of this sample was 11.0 and 700 mg/kg. All other specifications were met by this sample.

Analysis

Magnesium hydroxide particles were evaluated using a scanning electron microscopy. Aluminum, silicon, and chloride ions were found at minor levels in the magnesium hydroxide crystal. During Phase II testing, these impurities will be removed on the belt filter before their incorporation into the magnesium hydroxide phase.

Part of the criteria of gypsum for use as wallboard is the chloride and magnesium ion concentrations and moisture content. The ions effect the calcination properties and cohesive strength of wallboard and removal of the water is energy intensive. The unwashed sample sent to Gold Bond Building Products had a chloride level of 700 mg/kg. This level is too high for the sample to have much value as wallboard. The current chloride target for FGD gypsum is 100 mg/kg. It was demonstrated that this target could be achieved with belt filter washing of the gypsum solids. Typical moisture contents of the gypsum cake were 25 - 30%. The average analysis of gypsum from Phase I of ThioClear is given in Figure III-17.

It is obvious that the magnesium ion concentration is also of concern since it is the major impurity in the gypsum and influences the wallboard set time. For Phase II studies, the low pH of the oxidizer will dissolved the magnesium hydroxide and the magnesium ions will be removed with the filtrate as it passes over the belt filter. This will lower the magnesium hydroxide impurity in the gypsum product.

F. SIGNIFICANT PROBLEMS ENCOUNTERED AND ACHIEVEMENT OF OBJECTIVES

1. Start-up

Significant Problems Encountered

This debugging period was used to train operators, conduct flow testing of the process with service water, establish control settings, and isolate and correct faulty equipment. The majority of equipment problems occurred during this period in different parts of the process.

For the absorber and recycle tank several changes were made. In the absorber, the Bete 60° MP1125 nozzles were replaced with the 90° MP1125 nozzles. This replacement was made to increase the gas phase mass transfer coefficient. This replacement was prompted by sulfur dioxide removals in the low 90's and was made in an effort to increase these removals. For the recycle tank, the diaphragm control valve for the delivery of magnesium hydroxide was oversized causing wide variations in the recycle tank pH as large slugs of magnesium hydroxide were being delivered very quickly. A smaller control valve was installed and periodically manually operated to reduce accumulation of magnesium hydroxide in the piping to the recycle tank. There was also a problem associated with the equipment connected to the absorber bleed. The magnetic flow meter showed flow measurement swings resulting from entrained air within the bleed stream. The problem was rectified by utilizing the sealed drain leg from the absorber sump to the recycle tank so as to permit deaeration of the liquor.

The oxidizer operated without any major problems. Minor problems which developed included control of the pH and the suspended solids in the oxidizer. The oxidizer pH control difficulty was resolved by replacement of the metering pumps. A process modification for controlling the suspended solids content and provide a gypsum seed crystal source for the oxidizer was made where liquor from the thickener overflow tank was pumped to the oxidizer. Prior to this modification a fraction of the primary hydroclone underflow reported to the oxidizer. The more dilute slurry did not plug the piping to the oxidizer. Another parameter affecting oxidizer performance was air flowrate. Air flowrates of 100 scfm were required to convert sulfites to sulfates to maintain exiting sulfite concentrations of less than 100 mg/l were higher than expected.

For the 8 foot diameter thickener, a process problem developed in which magnesium hydroxide permitted recirculating to the recycle tank. To improve the settling characteristics of magnesium hydroxide, polymer was added to the thickener.

During system start-up, scaling occurred at the connection point of the secondary hydroclone overflow line and recycle tank recirculation line. This resulted from incorrect plumbing where high pH/calcium liquor came in contact with high sulfite liquor. This led to the immediate formation of calcium sulfite scale. The return liquor stream injection point was changed to the center of the recycle tank. Scaling in the system was accompanied by the release of small scale particles. These particles were on the order of 1/4 inch capable of plugging the apex of a hydroclone. To prevent this from happening, an in-line filter was added just prior to the hydroclone. This removed all 1/4 inch or greater material.

Achievement of Objectives

The objectives for this task were to familiarize the operators with both the ThioClear process and the associated control system and to initiate operation of the pilot plant with the goal of achieving steady state operation. This task was comprised of two, two week segments. In the first two weeks, the system was operated on service water and the second segment consisted of establishing the FGD process chemistry.

Operation on service water enabled the technicians to operate the process without the threat of chemistry upsets. This practice enabled the liquid flow and level control systems to be evaluated while training of the technicians was being accomplished. The flexibility of the computer/PLC control system allowed rapid response to designated control problems.

Introducing flue gas to the absorber and establishing the chemistry of the ThioClear process completed the final phase of training for the operators. During this period, many additional mechanical problems were noted and generally quickly resolved. This trouble-shooting initially inhibited the smooth operation of the process. However, by the second week of operating the absorber, tuning of the control loops was being conducted and the process was operating in the automatic mode. The achievement of this milestone permitted the optimization of the process to proceed.

2. Oxidizer and Crystallizer / Regeneration Tank

Significant Problems Encountered

This period was devoted to determining the optimum parameters for the oxidizer and regeneration tank. Only a few problems developed during this period and are outlined below.

Scaling of the oxidizer increased significantly during the first week of oxidizer testing. This was the result of fluctuations in the oxidizer pH. The plant was shut down due to scale formation in the feed line to the regeneration tank. Testing did not resume until flow could be restored to the regeneration tank. During this outage, the oxidizer was cleaned of scale which had accumulated to 1/4" thickness. Methods for lowering the air stoichiometry continued to be investigated. One method included a modified air sparger and nozzles to spray recirculating oxidizer liquor. These changes were ineffective in lowering the required air flowrate to the oxidizer. Catalyst testing conducted with the oxidizer also effected the scrubber chemistry. For instance, in the third week of July, the sulfites dropped from 4000 ppm to 250 ppm over a 12 hour period. The iron and copper oxidation catalysts precipitated as hydroxides and recirculated to the recycle tank. In the recycle tank they functioned as oxidation catalysts converting sulfites to sulfates. During this period, the pH in the recycle tank climbed to 7.5 to provide the alkalinity to maintain a scrubber bleed pH of 5.8 to the oxidizer.

Scale formation in the regeneration tank slowed the response of the pH electrodes. More frequent cleaning of the pH probes was found to be effective. Diluting the measured slurry 50/50 with water reduced the relative saturation in half and allowed an accurate pH measurement and control point. Reducing the relative saturation of the solution also worked by increasing the residence time or suspended solids. Scaling in the regeneration tank also caused erroneous computer readings in the regeneration tank level because of scale formation on the pad of the regeneration tank level detector. Alternative level detectors were therefore installed.

Achievement of Objectives

The objectives of the oxidizer optimization studies were to identify optimum operating parameters to reduce costs associated with the oxidation process. This subtask successfully addressed the areas of air usage with respect to exiting sulfite concentration, agitator speed, and pH. Investigations showed trends pertaining to pH and percent suspended solids necessary for minimizing scale. Because the ThioClear process utilizes an ex-situ oxidizer from the scrubber, capital costs are not only incurred for air compressors to supply the air but also for the auxiliary equipment utilized for pH control, agitation, as well as the oxidizer vessel itself. (In the limestone forced oxidation (LSFO) FGD process, the recycle tank with its agitators and pH control equipment perform double duty for both the absorption and oxidation processes at the expense of less efficient sulfur dioxide removal when compared to magnesium-enhanced lime FGD processes.) Operating costs result from energy consumption to drive the air compressors and the agitator and from the consumption of sulfuric acid for pH control.

Because the ThioClear oxidation process pertains to oxidizing mainly liquid phase sulfites as opposed to solid phase sulfites, the process can be completed rather quickly. Figure III-7 shows that a vessel with a residence time of 1.2 hours can successfully oxidize the absorbed sulfur dioxide with an oxygen to absorbed sulfur dioxide molar ratio of 3.0. (A comparable LSFO process utilizes a lower ratio of 2.0 but has an effective residence time of 24 hours.) This evaluation was successful in providing insights into the limiting factors such as reaction rate and diffusion which impact the oxidation process.

As would be anticipated, increasing the agitator speed allows a decrease in the oxygen to absorbed sulfur dioxide ratio required to maintain the exiting sulfites below 100 mg/l. By placing some of the burden of the oxidation process on the agitator, smaller compressors can be utilized. Unfortunately, the full advantage of these evaluations could not be realized due to the limited horsepower of the exiting agitator which required higher air flowrates to stay operational.

The optimal pH with respect to residence time at similar oxygen utilizations was found to be 5.0. As the pH of the oxidizer is increased toward 5.5, a slightly longer residence time was required. This is most likely the result of solid phase calcium sulfite dissolving at a slower rate at the higher pH. Operating at lower pH, enhances the dissolution of the calcium sulfite crystal and permits a nominal decrease in residence time. However, prior proof of concept testing determined that the rate of scale formation increases below 5.0.

An unanticipated result in these studies was the ineffectiveness of metal catalysts on the oxidation process. Typically, the presence of metal ions in solution with sulfites enhances the oxidation process. However analysis of the liquid phase indicated that the metals were being precipitate at the typical operating pH of 5.0. This result necessitated the termination of catalyst usage for this process.

Parametric studies were successful in determining the relationship between the recirculated gypsum content and scale formation in the oxidizer. Operating the oxidizer with less than 1.5% suspended solids dramatically increased the scaling rate. A suspended solids concentration of 2 to 3% was sufficient to minimize the rate of scale formation.

The goal of this task was to identify optimal operating conditions of the crystallizer/regeneration tank. Such operating parameters would need to maximize the size differential between the gypsum and magnesium hydroxide crystals for effective separation, minimize scale formation for dependable equipment operation, and minimize the tankage size for economics considerations. Data generated during the regeneration tank optimization studies successfully identified relationships between residence time (tank volume), pH, and gypsum crystal size. Also, corresponding trends between increasing pH and increasing rate of scale formation were identified. Unfortunately, trends between residence time and the percent solids in the liquor in regards to scale formation could not be clearly identified in this subtask and the effectiveness of a crystal modifier was not realized.

As with oxidation, crystallization is an ex-situ operation in the ThioClear process. An external crystallizer is required because both gypsum and magnesium hydroxide, a neutralizing reagent, are co-precipitated as by-products of the process. Therefore, it is imperative to keep the magnesium hydroxide by-product external to the absorption loop. The size of this external tank needs to be minimized to maintain a low cost process. Figure III-10 details the relationships between residence time (tank volume), pH, and gypsum crystal size. These relationships represent the design and operation criteria for the regeneration tank with respect to gypsum crystal size. During these evaluations, the mean particle size of the magnesium hydroxide was unchanged at 15 microns.

Aside from minimizing tank volume and maximizing gypsum crystal size, a second consideration of the design and operating parameters of the crystallizer is to minimize scale formation. Operating in a scaling regime will reduce the reliability of the process and increase its maintenance costs. Subsequently, economic considerations for the design and operation of the regeneration vessel need to address the rate of scale formation. In fact, the aspect of reliable operation will transcend the notion of minimizing capital costs. These optimization studies detailed in Table III-3 and Table III-4 show that the lower pH operating environments lower the rate of scale formation. Fortunately, this pH regime coincides with the growth of large gypsum crystals at a reasonable residence time for the regeneration tank. Relationships between residence time and percent suspend solids within the slurry could not be established with respect to the rate of scale formation due to scatter in the data. However, additional monitoring of scale formation was conducted in Subtask 4.2, High Solids Testing.

3. High Solids Testing

Significant Problems Encountered

This subtask involved increasing the chemistry in the absorber and recycle tank by reducing the scrubber bleed from the standard of 20 gpm to 15 and 10 gpm. This period was marked by smooth operation with few problems.

One problem that occurred was the regeneration tank ultrasonic level detector periodically gave false readings which created level upsets in the regeneration tank. This prompted the installation of a bubble level detector. Hydroclone efficiency also declined as a result of the lower absorber bleed flowrate. This is most evident on examination of the magnesium hydroxide reporting to the underflow. This resulted in minimal recovery of magnesium hydroxide.

Achievement of Objectives

The ability to enrich the process chemistry by adjusting the absorber bleed (or flowrate of the by-product recovery flow loop) and control the magnesium ion/dissolved solids concentration of the scrubbing liquor is one of the major advantages of the ThioClear process. As discussed in Subtask 4.0, the accumulation of magnesium salts, which are generally soluble, permits a substantial reduction in the absorber blowdown flowrate in order to achieve desired process chemistries. Scrubbers which utilize calcium based neutralizing reagents directly in the absorber recirculation loop are limited in controlling this purge rate as a result of the suspend solids which accumulate in the recycle tank. The advantages of decreasing this flowrate in the ThioClear process include improved scrubber alkalinity which allows a reduction in the number of recycle pumps and the absorber size required for efficient sulfur dioxide removal, longer residence times in the constant volume tankage of the oxidizer and the regeneration tank which permits improved air utilization and gypsum crystallization, reduction in the number of hydroclones, smaller pumps for the by-product recovery flow loop, and a decrease in the size of the magnesium hydroxide thickener. These benefits will be realized as reductions in the capital and operating costs of the process.

As shown on Figures III-12 and III-13, operating at reduced blowdown flowrates can enhance the performance of the absorber. Maximizing the neutralization capabilities of the scrubbing liquor can permit a reduction in the number of recycle pumps required to achieve a desired sulfur dioxide removal. If the number of spray headers is reduced in accordance with the elimination of recycle pumps, the pressure drop and the overall height of the absorber tower will be reduced.

Because the ThioClear oxidation process pertains to oxidizing mainly liquid phase sulfites as opposed to solid phase sulfites, the process can be completed rather quickly. Figure III-14 shows that a vessel with a residence time of less than two hours can successful oxidize the sulfites when the molar ratio of oxygen to absorbed sulfur dioxide is two. The comparable LSFO process requires a tankage residence time of 24 hours at the same molar ratio. Therefore, this evaluation was successful in demonstrating the relationship between the required air flowrate and the vessel size and demonstrated that oxidation could be achieved in a smaller vessel when compared to LSFO.

Testing showed that the hydraulic head was an important factor as it relates to the concentration of dissolved oxygen in the solution. Increasing the liquid height improves the dissolution of oxygen and therefore the oxidation process. However, economic considerations pertaining to tank construction and agitator placement place boundary limits on this variable for design purposes.

Acid usage was determined to be a function of both the absorber and oxidizer pH's. Process changes which reduced the oxidizer pH below 5.0 create a significant increase in acid usage. Increasing the absorber downcomer pH above 5.5 also increases acid usage, but not as significantly as variations in the oxidizer pH. Optimum acid consumption was achieved at operating pH's of 5.5 and 5.0 in the scrubber downcomer and oxidizer, respectively.

Regeneration tests results from this subtask have shown improvements in both the gypsum crystal size and the deposition of scale can be made by operating with a high concentration of dissolved solids and at the minimum volume utilized in Subtask 4.1. These improvements insure good separation of the gypsum crystals from the magnesium hydroxide particles and a low maintenance system. Because of these improvements, further reductions in the size of the regeneration tank can be investigated.

4. Dewatering and By-Product Purification

Significant Problems Encountered

The Gore filter was never installed and utilized. Results from pilot scale testing at the Bruce Mansfield Station showed that crystallization occurred within the pores of the Gore filter. This resulted in blinding of the filter creating a large pressure gradient. Because of the high pH of the magnesium hydroxide slurry, application of this device to Phase I testing would result in crystallization in the pores and subsequent blockage. It was therefore deemed unsuitable for magnesium hydroxide dewatering.

Achievement of Objectives

Conditions for which the hydroclones performed at an optimum were determined. They were found to be high feed flowrate using the configuration 5/8" vortex and 1/4" apex. In addition, the higher the magnesium hydroxide / gypsum ratio in the feed material, the greater the by-product magnesium hydroxide purity.

Belt washing was found to be an effective method for decreasing the chloride ion concentration in the gypsum filter cake. The effectiveness of the gypsum dewatering was found not to be a function of the mean particle gypsum size for the range of sizes investigated (64.2 microns - 86.1 microns). The dilution wash system for increasing magnesium hydroxide purity was ineffective. The washed purity was only slightly better than the purity of magnesium hydroxide in the primary hydroclone overflow.

The analysis of centrifuge samples demonstrated that hydrocloning is more effective in gypsum / magnesium hydroxide separation. The objective was to determine which technique was better.

5. High Velocity Horizontal Scrubber Testing

Significant Problems Encountered

Construction of the horizontal scrubber was not completed before termination of the Phase I program. Completion of construction and initiation of high velocity testing of the horizontal absorber will be performed during Phase II of the program. High velocity testing of the horizontal absorber will involve sulfur dioxide removal studies with changes in gas velocity and L/G.

Achievement of Objectives

It was demonstrated that sulfur dioxide removal increases with increasing L/G at 10 ft/sec. It was also shown that at the higher gas velocity of 15 ft/sec, the sulfur dioxide removal substantially increases. Increasing the flue gas velocity while keeping the absorber bleed flowrate constant has the added benefit of improving the process chemistry.

It was shown that changing the absorber bleed flowrate in response to changes in inlet sulfur dioxide concentration kept the magnesium ion concentration constant at 3000 mg/l and the sulfur dioxide removal above 95%. This demonstrated that ThioClear had excellent load following capability.

6. By-Product Evaluation

Significant Problems Encountered

The purity of the magnesium hydroxide sample sent to Premier Services Group was judged poor based on their commercial requirements. The gypsum sample analyzed by Gold Bond Building Products had a high pH and chloride concentration.

Achievement of Objectives

Premier Services Group and Gold Bond Building Products received samples for evaluation. Neither sample was acceptable to their commercial standards. Issues raised by Gold Bond were addressed in the Phase II process modification. Limitations of the hydroclone separation process in producing a purer magnesium hydroxide by-product required Dravo to investigate markets for the magnesium hydroxide as produced by the ThioClear process.

G. BY-PRODUCT DESCRIPTION

The ThioClear process is designed to be a “zero-discharge” process due to the production of the salable by-products, gypsum and magnesium hydroxide. In Phase I of this project, the production and corresponding purity of these by-products relied solely on the operation of the hydroclones. The proof of concept testing in 1990 demonstrated that a two staged hydrocloning process was more efficient at magnesium hydroxide recovery than a single stage separation system. Hence, the two stage system was incorporated into the design of the pilot plant before attempting this project. Sufficient magnesium hydroxide was recovered during Phase I operation to generate excess magnesium hydroxide beyond that which was required for controlling the pH of the scrubber and oxidizer. However, as shown in Figure III-17, nearly 4% of the gypsum and 44% of the magnesium hydroxide was composed of various contaminants.

In this phase, the final gypsum by-product was the result of filtering the secondary hydroclone via a belt filter. As the filter cake formed on the belt, a brown film was observed forming on top of the gypsum cake. This film most likely was from the contaminants (i.e.: silicates from fly ash and lime) which reported to the underflow stream. Once the filter cake was deposited on the lay down area and air dried, the gypsum took on the appearance of a snow white crystalline powder. When the counter-current cake wash was not operated, the chloride content of the filter cake was measured at 700 mg/kg. Utilizing the belt wash reduced this value below 100 mg/kg.

The gypsum filter cake’s moisture content averaged between 20-30% for Phase I testing which was greater than anticipated. As described in a pervious section, the high moisture content resulted from fine solids and plugging of the filter cloth. These factors combined to reduce the stripping velocity of the air passing through the cake from the vacuum.

Since the recovery of magnesium hydroxide is paramount to the operation of the process, the purity of this by-product suffers. The magnesium hydroxide by-product was the result of thickening the overflow stream from the primary hydroclone. In order to enhance the recovery of the magnesium hydroxide, the apex of the hydroclone was reduced in size to insure that the smaller magnesium hydroxide crystals would report to the overflow. However, fractured gypsum crystals also reported to the overflow stream and accounted for nearly 20% of the solids in this product stream. Additionally, the silica and carbonate fines continued to increase during the course of the operation due to recycling the magnesium hydroxide back to either the absorber or oxidizer.

The underflow of the thickener typically averaged 15% solids. The poor settling and thickening of the magnesium hydroxide can be explained by the shape of the crystal. The magnesium hydroxide crystal formed in the ThioClear process resembles popcorn. Because of the high surface area and multiple pores and voids, the settling velocity of the particle is greatly reduced. The hindrances of the protrusions of one crystal with the next prohibit the liquid from being displaced as the magnesium hydroxide bed forms in the thickener. Commercial magnesium hydroxide slurries are typically in the 55.58% solids range.

The appearance of the magnesium hydroxide was an off white slurry. When the material was filtered, the filter cake solids averaged only 20-25%. Obviously, the crystal shape as well as the other fine contaminants contributed to the poor dewatering. The filter cake was characteristic of a stable gelatin solid at this moisture content. When this filter cake was stored for some period of time, minimal settling and moisture release occurred.

In conducting the FGD design and economic criteria for a 300 Mw generating station, the base condition utilized are the standard conditions established by EPRI. This criteria is detailed in Table I-1. Utilizing the separation efficiencies established by the Phase I by-product purities of gypsum and magnesium hydroxide, the hourly production and composition of the by-product streams would be as detailed in Table III-11.

Table III-11

Phase I - Hourly By-Product Production and Composition (lb/hr)

By-Product Stream:	Gypsum	Magnesium Hydroxide
Composition:		
Gypsum	31781	105
Magnesium Hydroxide	557	223
Contaminants:		
Calcium Compounds	822	0
Magnesium Compounds	164	0
Inerts/Flyash	310	47
Total	336737	375

H. UTILIZATION OF BY-PRODUCTS

A benefit of the ThioClear process is the generation of salable by-products, gypsum and magnesium hydroxide. Gypsum can be utilized as a feedstock for wallboard manufacturing and magnesium hydroxide can treat various acidic stream, on and off site. However, to utilize these by-products in commercial application, either the purity has to meet or exceed current industrial standards or alternative manufacturing processes which can utilize these by-products need to be developed. As a result of the impurities shown in Figure III-17 for Phase I testing, it is unlikely either by-product will find wide acceptance in commercial markets.

Major contamination to the gypsum for wallboard manufacturing resulted from magnesium hydroxide and calcium sulfite. To a lesser extent, calcium hydroxide and calcium carbonate were found. Evaluations of the gypsum by a wallboard manufacturer found this material unsuitable for wallboard production.

If this material cannot be utilized in wallboard manufacturing, two alternatives for the final fate of this material is available. The first alternative is utilizing the gypsum in agriculture applications where the magnesium ion is considered a desirable nutrient. The second option is the landfilling of this material. Because gypsum is not a thixotropic material similar to the calcium sulfite produced in the Thiosorbic process, the cost of disposal is reduced. Fixation equipment is not required and subsequently fly ash is made available for sale. The improved dewatering of the gypsum reduces the water content of the filter cake to a third of that which would be from the Thiosorbic process. Therefore transportation costs and landfill space are reduced. Additionally, the less expensive option of stacking gypsum for disposal can be utilized as opposed to construction of a cell-styled landfill.

The purity of the magnesium hydroxide is far below that which is available on the commercial markets. Thus this material may only be restricted to treating wastewater where the contaminants can be settled or filtered from the effluent. Such wastewater streams are found on utility sites where rain or ground water from the coal piles or landfills is treated in a settling pond before leaving the site. This application is also favored due to the small amount of magnesium hydroxide generated from the ThioClear process which can be utilized internally within the utility.

I. SUMMARY OF FINDINGS

The overall objectives for Phase I were to utilize the knowledge gained in the proof of concept testing to implement modifications into the ThioClear process and to optimize the process in order for it to be a viable commercial FGD option. These objectives were successfully met. The modifications introduced into the process enabled the pilot plant to be operating in the automatic mode of the control system within the second week of absorber operation. The optimization evaluations of the oxidizer, crystallizer / regeneration tank and the hydroclones have provided sufficient data of design criteria for economic evaluations. Performance of the absorber was above expectations based on the high sulfur dioxide efficiencies achieved during high absorber gas velocities, load following simulations, and process start-up.

Efforts to improve magnesium hydroxide and gypsum by-product purity were not as successful. However, the revisions which are discussed in the Phase II Technical Discussion to improve recovery of magnesium hydroxide did remedy some of the poor purity results. Additionally, markets which may not require the commercial grade purities need to be identified. Such efforts were beyond the scope of this project, but have been successfully pursued in other OCDO/Dravo Lime Company projects.

The encouraging results of the sulfur dioxide removals in Phase I are favorable for the Phase II testing of a high velocity horizontal absorber which is designed to operate at 25 ft/sec. By decreasing the size of the commercial absorber without sacrificing the high sulfur dioxide removal efficiencies associated with magnesium-enhanced lime, the capital costs of the FGD system will be reduced. Decreasing capital costs and the production of salable by-products of the ThioClear FGD process are the keys for the commercialization of this process.

A summary of the findings for Phase I of the ThioClear project is as follows:

Start-up

1. The flexibility of the PC/PLC control system allowed rapid response to designated control problems and enabled the system to be operated in the automatic mode during the second week of operation.

2. The ThioClear process demonstrated a rapid response in scrubbing efficiency to achieve high sulfur dioxide removal within five hours of start-up on service water.

Oxidizer and Crystallizer / Regeneration Tank Optimization

1. Oxidation was accomplished within a residence time of 1.2 hours with an oxygen supply ratio of 2.5 to 3.0. (A comparable LSFO process utilizes a lower ratio of 2.0 but has an effective residence time of 24 hours.)

2. The optimal pH for a residence time of 1.2 hours was found to be 5.0.

3. The usage of catalysts for enhancing oxidation was ineffective.

4. A suspended solids concentration of 2 to 3% was sufficient to minimize the rate of scale formation.

5. The optimum crystallizer / regeneration tank operating parameters for maximizing the size of the gypsum crystal were a residence time of 1.9 hours and a pH of 10.0-10.3.

6. Utilization of the crystal modifier DBA had no effect on the shape of the gypsum crystal.

7. Scale formation within the crystallizer / regeneration tank was minimized at the lower operating pH's.

High Solids Testing

1. Reducing the absorber blowdown flowrate by 50% doubled the alkalinity of the scrubbing liquor and improved the sulfur dioxide removal efficiency from 95% to 98%.

2. Increasing the residence time of the oxidizer from 1.2 to 2.4 hours, decreased the air supply ratio from 3.0 to 1.75.

3. Optimum acid consumption for the oxidizer was achieved at an absorber downcomer pH of 5.5 and an oxidizer pH of 5.0.

4. Increases in gypsum crystal size and decreases in deposition of scale were noted from crystallizer / regeneration tank studies during high solids testing.

Dewatering and Solids Purification

1. The optimum configuration for the hydroclones utilized in this testing was determined to be a 5/8" vortex and a 1/4" apex. This configuration maximized the recovery of magnesium hydroxide to insure that an outside source was not required.

2. Washing of the gypsum filter cake with service water during secondary dewatering was successful in achieving chloride concentrations required for wallboard manufacturing.

3. Limited washing of the magnesium hydroxide from the thickener underflow was unsuccessful in achieving commercial grade purity.

4. Lower than expected dewatering results of the gypsum filter cake resulted from blinding of the filter belt fabric and the high concentration of fines.

5. Investigative testing determined that a centrifuge is not a suitable replacement for the hydroclones.

High Velocity Horizontal Scrubbing Testing

1. Although the horizontal absorber was not available for testing in this phase, increasing the velocity in the vertical tower by 50% did produce a dramatic increase in scrubber efficiency. A L/G of 70 was required to achieve a removal of 98% at 10 ft/sec. However at 15 ft/sec, this same removal was achieved with a L/G of 45.

2. The rapid response of the process chemistry by altering the absorber blowdown flowrate enables the ThioClear process to effectively maintain high sulfur dioxide removal efficiencies while inlet sulfur dioxide concentrations fluctuate as in simulated boiler load changes.

Product Evaluation

1. Samples of the gypsum and magnesium hydroxide by-products were supplied to commercial manufacturers of these products. Evaluations determined that neither by-product met commercial specifications.

III. TECHNICAL DISCUSSION (cont.) – PHASE II

A. TECHNOLOGY DESCRIPTION

A detailed description of the modified ThioClear process utilized in the second phase of this project is shown in Figure III-20. As in the conventional ThioClear process, the modified ThioClear process takes advantage of the catalytic effect of magnesium to increase the alkalinity of the scrubbing liquor. Magnesium hydroxide ($Mg(OH)_2$) is added to the recycle tank where the pH is maintained in the range of 6.0-6.5. The hydroxide reacts with dissolved SO_2 in either the recycle tank or the absorber to form the soluble alkaline salt, magnesium sulfite ($MgSO_3$). The sulfite rapidly neutralizes additional absorbed SO_2 by forming magnesium bisulfite ($Mg(HSO_3)_2$). This capability provides the scrubbing liquor additional capacity in absorbing SO_2 compared to systems where magnesium sulfite is not present.

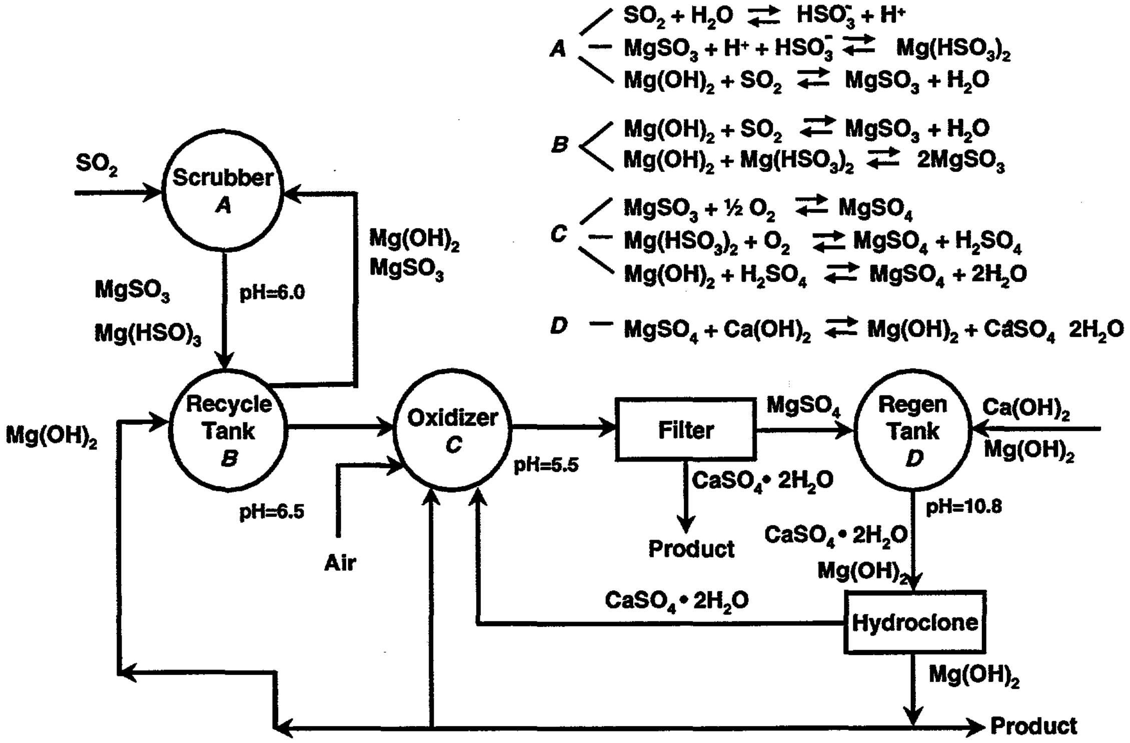


Figure III-20. Modified ThioClear Chemistry

The scrubber effluent is utilized to feed low pH liquor in the range of 5.5-6.0 to the oxidizer. Oxidation of the liquid phase magnesium sulfites and bisulfites produces magnesium sulfate ($MgSO_4$). Due to formation of sulfuric acid (H_2SO_4) from the oxidation of the bisulfites, magnesium hydroxide additions are required to maintain the pH of the oxidizer between 4.5-5.5.

Recycling the gypsum-rich hydroclone underflow with its basic contaminants (magnesium hydroxide, calcium sulfite, calcium carbonate, and calcium hydroxide) to the oxidizer satisfies a portion of the oxidizer's alkaline addition requirements. Also this recycle stream provides seed crystals that minimize the formation of gypsum scale on the walls of the oxidizer. The slurry exiting the oxidizer is continuously filtered to separate the solids from the liquid phase. Subsequently, all other solid phase contaminants, mainly silicates, are continuously removed with the gypsum by-product.

The recovered filtrate is returned to the regeneration tank. Slaked magnesium-enhanced lime that is composed of +90% calcium oxide (CaO) and 4 to 8% magnesium oxide (MgO) is added to the regeneration tank to maintain the pH between 10.0-10.8. The resulting mixture precipitates the sulfates as gypsum ($CaSO_4 \cdot 2H_2O$) and regenerates the magnesium species to magnesium hydroxide.

B. PILOT PLANT DESCRIPTION

The flow diagram of the modified ThioClear® process evaluated during the Phase II testing at the Miami Fort pilot plant is shown in Figure III-21. A slipstream from CG&E's Miami Fort Unit No. 7, downstream of the precipitator, supplies the flue gas to the pilot plant. The volume of flue gas to the absorber is controlled by a booster fan with an inlet damper capable of delivering 2000 to 15000 ACFM at 300°F. This gas flow is measured by a venturi flow meter installed immediately downstream of the fan. As a result of boiler load changes, the composition of the flue gas with respect to oxygen and sulfur dioxide will vary. An on-site SO_2 spiking system, capable of vaporizing up to 150 lb SO_2/hour, enables control of the SO_2 concentration to the inlet of the absorber. During testing, this concentration was typically maintained at 2000 ppm.

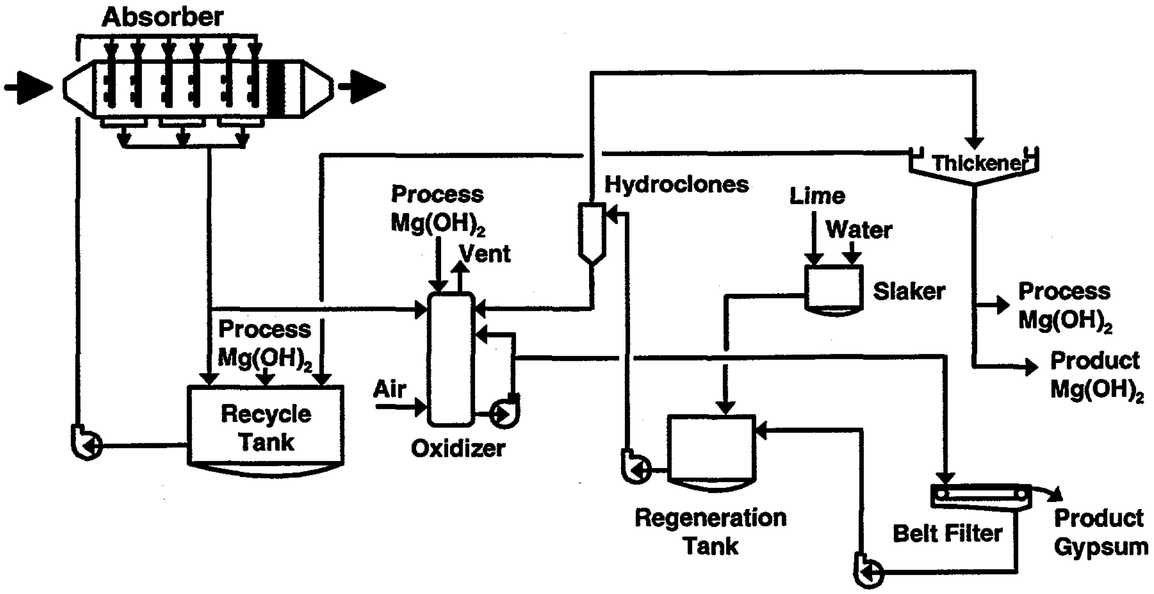


Figure III-21. Modified ThioClear Process Flow Diagram

The flexibility of the pilot plant enables absorber evaluations of either of the two 40 foot tall scrubbing towers, one 4 foot and the other 3 foot in diameter, or the recently installed horizontal absorber which has a cross sectional area of 8.7 ft^2. Aside from controlling the absorber gas velocity by the inlet damper, multiple liquid to gas ratios at a given absorber velocity can be achieved by operating any number of the three variable speed recycle pumps that are each capable of delivering a maximum flow rate of 150 gpm. Each of these pumps supply spray headers equipped with commercially available scrubber spray nozzles. Provisions within the scrubbers permit the installation of trays or packing to enhance mass transfer between the gas and the liquor. Each scrubber is capable of a two stage mist eliminator section to remove entrained liquor droplets from the exiting gas.

Both the 3 foot diameter scrubber tower and the horizontal absorber have been utilized during the second phase of ThioClear® testing. The vertical tower was evaluated in the counter-current mode of gas-liquid contact in both spray and spray/tray configurations. A 40% open area tray was installed below the lowest spray level for spray/tray tower operation. Scrubber gas velocities of 10 to 18 ft/sec have been evaluated.

The configurations of the horizontal absorber which were tested included co-current and counter-current modes of gas-liquid contact with and without packing. The packing was installed either between individual spray headers in order to enhance the mass transfer of each spray zone or in front of the mist eliminator where in addition to increasing mass transfer, it performed the additional function of a predemister. Parametric SO_2 removal evaluations were conducted at gas velocities of 10 to 25 ft/sec.

Unlike typical FGD operations, the blowdown from the absorber to the oxidizer in the ThioClear® process is a slipstream of low pH liquor from the gas/liquid contact zone. The control of this effluent flowrate and pH is important to the ThioClear® process. Modulating the blowdown flowrate provides control of the scrubber alkalinity via the liquor magnesium concentration and thereby provides excellent scrubber performance during plant start-up and boiler load changes. The lower pH associated with the blowdown improves the oxidation process. Subsequently, magnesium hydroxide additions to the recycle tank are controlled by the desired pH setting of the blowdown stream feeding to the oxidizer.

The process of oxidation is accomplished in one of two modes depending upon which absorber is in operation. When the 3 foot diameter scrubber tower was utilized, oxidation was accomplished in one vessel. This vessel is a 1600 gallon FRP tank equipped with a 5-hp variable speed agitator and an air sparging system capable of delivering 200 SCFM. The operation of the horizontal scrubber required an existing oxidizer tower to be utilized in series with the agitated tank. The additional tank volume was needed to satisfy the residence time requirements of the oxidation process. The horizontal absorber operating at 25 ft/sec treats nearly three times the amount of flue gas when compared to the vertical absorber operating at 10 ft/sec. The oxidizer tower is a nonagitated FRP vessel with a capacity of 1600 gallons. It utilizes the hydraulic head resulting from the height of the liquid in conjunction with a 200 SCFM sparging system to oxidize the magnesium sulfite liquor. Control of the oxidizer pH is accomplished by either the addition of process produced magnesium hydroxide or sulfuric acid via chemical metering pumps depending upon the desired control setpoint for parametric evaluations. Typically during steady state operation, only magnesium hydroxide additions are required in order to neutralize the acid produced from bisulfite oxidation.

A second stream entering the oxidizer is the gypsum-rich hydroclone underflow. Recycling the process gypsum to the oxidizer before final filtering accomplishes multiple tasks. The recycle stream provides sufficient crystal surface area to eliminate scaling potential which can result from calcium sulfate formation during oxidation. Additionally, the magnesium hydroxide impurities in the gypsum stream are effectively dissolved in the low pH regime. Therefore, the amount of process magnesium hydroxide required for pH control is decreased and the recovery of magnesium is maximized. Thus, minimal solid phase magnesium compounds will leave the process with the gypsum after filtering. The gypsum slurry exiting the oxidizer is fed to a continuously operating belt filter with an active area of 10 ft^2. The filter has three counter-current washes which aid in the recovery of the magnesium sulfate liquor and improve the purity of the gypsum cake. The gypsum cake is deposited on a lay down area for removal to disposal while the magnesium sulfate liquor is returned to the process.

The recovered filtrate is returned to the regeneration tank. Seed crystals extracted from a gypsum-rich process stream are also introduced into the vessel if insufficient suspend solids are present. The regeneration tank is a 7280 gallon vessel. Magnesium-enhanced lime slurry is added as required for pH control to crystallize magnesium hydroxide and gypsum. A high speed turbine agitator provides for good mixing of the lime and oxidized liquor.

Taking advantage of their size differential, separation of the magnesium hydroxide and gypsum crystals from the regeneration tank slurry is achieved by the use of two hydroclones in series. Commercially available 2 and 3 inch hydroclones were utilized. The magnesium hydroxide-rich overflow from the first hydroclone is delivered to an eight foot diameter thickener for settling and thickening. The thickened magnesium hydroxide is used for pH control in the absorber and the oxidizer. The excess production is stored in an available 5000 gallon tank. The hydroclone underflow is supplied to the thickener overflow (water management) tank and is diluted with the clear liquor leaving the thickener. The resulting slurry is fed to the second hydroclone for a second stage of physical separation. The liquor from the overflow of the second hydroclone returns to the recycle tank to maintain liquid level. The gypsum-rich underflow stream is recycled to the oxidizer for eventual filtration as described previously.

C. OBJECTIVES

The focus of Phase II was to initiate pilot plant operation in the modified ThioClear process mode, evaluate SO_2 removal performance at absorber gas velocities above conventional design standards, and investigate gypsum stacking for facilities where production for a wallboard market is not feasible. Optimized parameters determined during the Phase I evaluations were utilized in this phase. The methods of operating the pilot plant facility and analyzing the data were consistent with those methods established in Phase I.

1. Modified ThioClear Operation

The initial period of operating the modified ThioClear process was devoted to developing process chemistry, evaluating equipment performance, and collecting baseline data for comparison to Phase I operation. In this configuration, the only other process change from gypsum recycle and continuous filtering included operating the two site oxidizers in series so as to have sufficient residence time when operating at the higher throughputs of the horizontal absorber. When the process chemistry achieved steady state and sufficient data was collected pertaining to process operation and SO_2 removal in the 3 foot vertical spray and tray scrubber configuration, operation of the facility was secured for installation of the horizontal absorber. Since no impediments were observed when operating the ThioClear process in conjunction with the horizontal absorber, operation for the remainder of this phase was conducted with the horizontal absorber.

2. High Velocity Scrubbing

The purpose of this testing was to demonstrate that the ThioClear process can efficiently remove SO_2 similar to the Thiosorbic process at absorber gas velocities greater than the current industry design standard of 10 ft/sec. Higher design gas velocities would allow a reduction in the absorber size or reduce the number of absorbers to treat the same volume of gas. Prior testing at the Miami Fort pilot plant has demonstrated the effectiveness of the Thiosorbic process in removing SO_2 at high absorber gas velocities in the 3 foot diameter tower in both the spray and tray tower configurations. These tests were repeated with the ThioClear process to verify that similar results are achievable.

Due to the limitation of re-entrainment of accumulated liquor from vertical flow mist eliminators while operating at velocities above 18 ft/sec, a horizontal absorber was installed and evaluated. A horizontal absorber utilizes horizontal flow demisters which can effectively function at higher gas velocities than the vertical style. Sulfur dioxide removal efficiencies were determined from parametric studies of gas velocity, recycle flowrate, and packing configurations.

3. Gypsum Stacking

Gypsum is a high volume low value commodity which will not find a market if a wallboard manufacturer or other user of this material is not nearby. The difficult problems of overproduction of gypsum for local markets coupled with the transportation costs for this relatively low value commodity make disposal of gypsum an alternative option. There are still advantages to be gained by producing gypsum rather than calcium sulfite. Gypsum production lowers the capital and operating costs of dewatering and disposal. Thickeners, belt filter requirements, and fixation equipment can be substantially reduced and/or eliminated. The reduction in the moisture of the filter cake reduces both the volume and weight of the material to be transported and landfilled.

To further reduce the disposal costs, the gypsum can be stacked in an impoundment which eliminates the need for all dewatering equipment. In commercial applications, gypsum slurry is pumped to the impoundment area. Trenches are maintained in the impoundment which permit the liquor to return to a collection area for eventual return to the process. The gypsum settles in the impoundment area and periodically is excavated to insure sufficient area for the solids to settle. The excavated gypsum is stacked on the perimeter. This procedure of excavating the gypsum is continually repeated until a mound of gypsum cake is formed. To verify this option as a viable solution for landfilling ThioClear gypsum, gypsum slurry was impounded and measurements of its dewatering capabilities made.

D. PILOT PLANT OPERATING DESCRIPTION

1. Modified ThioClear Operation

As in the first phase, service water was utilized to verify the process flow loop and the control logic. The evaluation of the start-up focused on the flow and control of the dual oxidizers and the gypsum recycle loop. The process and instrumentation diagram for Phase II is shown in Figure III-22. Since the bulk of the equipment and piping was unchanged from the Phase I operation, the shakedown on service water proceeded rather rapidly.

After the operators became familiar with the new system, operation of the revised ThioClear process was initiated the week of March 8th. The configuration and operation of the 3 foot diameter vertical scrubber tower were similar to those utilized in Phase I. The absorber tower was operated in the counter-current mode with a 40% open area tray installed. Bete MP 1125 90° spray nozzles were installed on each of the three recycle headers. Operating targets included the utilization of two pumps at 125 gpm each to achieve a L/G of ~70 at a scrubber gas velocity of 10 ft/sec. The liquid flow in the by-product recovery loop was controlled at 10 gpm which would provide a liquid phase magnesium ion concentration of 4000 mg/l. The levels in the oxidizer and the oxidizer tower were maintained at 90% and the level in the regeneration tank at 40%. Both oxidizers were not required for the start-up with the vertical absorber operating at a gas velocity of 10 ft/sec. However, planned high velocity testing in both the vertical tower scrubber and the horizontal absorber would require both. Therefore, this configuration was utilized from the beginning to verify its operation and performance.

After operating the pilot plant in the modified ThioClear mode for 3 weeks, the configuration of the facility was changed so as to remove the vertical scrubber tower from the process and incorporate the horizontal absorber. Parametric SO_2 removal studies were conducted with the new absorber. In these studies the gas velocity was varied from 10 to 25 ft/sec, the L/G was adjusted by utilizing one, two, or all three

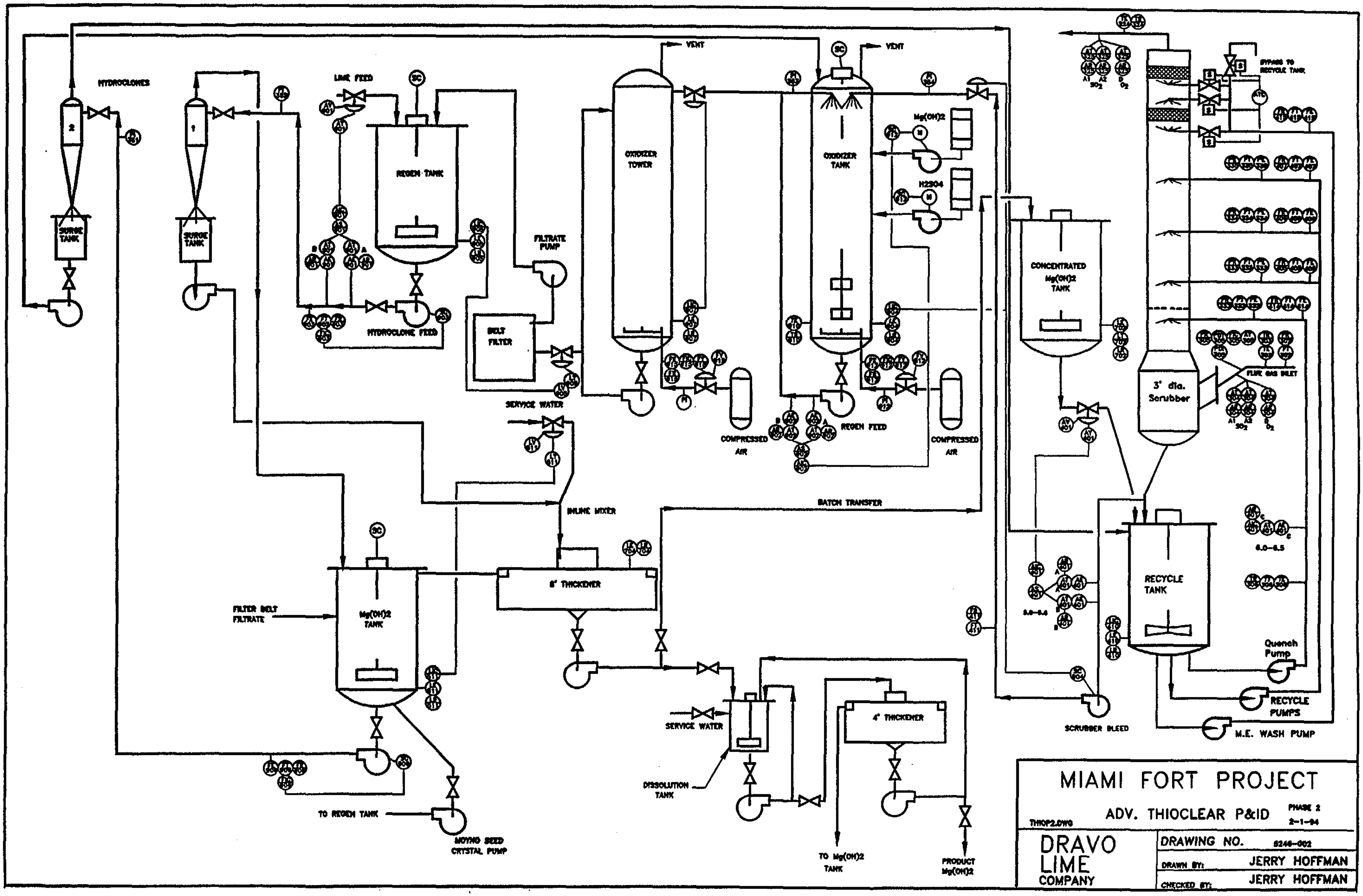


Figure III-22. Modified ThioClear P&ID

recycle pumps, and a mesh packing was installed in multiple locations and thicknesses in order to identify the optimum SO_2 removal configuration. Initially three recycle headers equipped with two Bete TF56 nozzles were installed, one for each pump. However, testing proved that the installation of two headers, each equipped with two Bete TF40 nozzles per pump, provided improved removals. During these studies, the absorber chemistry was controlled at an alkalinity of 2250 mg/l of comparable carbonate by adjusting the absorber bleed. The oxidizers and the regeneration tank levels were maintained at a safe residence time to minimize scale formation during the constant flowrate changes while attention was devoted to the absorber performance.

After the parametric SO_2 removal studies were completed on the horizontal absorber, a period of steady state operation was maintained. This operation focussed on the long term SO_2 removal of the horizontal absorber and verification of by-product purity resulting from the modifications to the by-product flow loop to support the operation of the horizontal absorber. Other than these changes, the operation of the ThioClear® process with the horizontal absorber was virtually the same as that with the vertical scrubber operation at the beginning of this phase.

The internals of the horizontal absorber were maintained in the configuration which maximized the SO_2 removal at a gas velocity of 25 ft/sec. Each of the three recycle pumps supplied two headers within the absorber. Two Bete TF40 nozzles were installed on each header which were oriented to provide a counter-current spray to the gas flow. The recycle pumps were operated to provide a L/G of 37. The mesh packing was installed after the spray zone. The liquid flow in the by-product recovery loop was controlled at 30-35 gpm.

As a result of the increased flowrate in the by-product recovery loop, two hydroclones were installed at both the primary and secondary separation stations. Limitations of the existing belt filter required the installation of a desliming hydroclone over the belt. This hydroclone thickened the slurry deposited on the belt so that the available filter area was sufficient to handle the high flowrates. The overflow from the hydroclone was fed to the

12 foot diameter thickener where the fine solids were permitted to settle. The clarified liquor exiting the thickener and the filtrate from the belt filter were utilized to maintain level in the regeneration tank.

2. High Velocity Scrubbing

In order to fully understand the benefits of operating scrubbers at higher gas velocities, parametric SO_2 removal studies in both the vertical and horizontal absorbers were conducted during Phase II. Many of these benefits were outlined in Phase I. In the vertical scrubber tower, parametric studies conducted in both spray and tray tower configurations included gas velocity and L/G. The horizontal absorber parametric studies pertained to gas velocity, L/G, and internal configuration changes with nozzles and mesh packing.

In Phase I, a preliminary study on the impact of velocity on SO_2 removal efficiency was conducted. By operating at 15 ft/sec, the L/G could be reduced by 37% to achieve the same SO_2 removal obtained at the 10 ft/sec velocity. Encouraged by these results and their potential impact on existing scrubbers, the in-depth parameter study of the vertical scrubber SO_2 removal capabilities was undertaken.

Due to the limitations of vertical flow mist eliminators in effectively removing droplets from the gas stream at high velocities, the horizontal absorber was constructed and installed at the Miami Fort pilot plant. Currently, commercial horizontal absorbers are operated in a spray scrubber configuration which contribute to its inefficiencies. By placing the nozzles within the gas flow, some of the inefficiencies can be minimized. Because the ThioClear liquor is nearly void of solids, advanced mass transfer devices such as mesh packing can be installed to enhance the SO_2 removal efficiency. FGD systems which operate with a high percentage of solids in the recycle liquor would plug these mass transfer enhancements. The parametric SO_2 removal studies of the horizontal absorber involved changes in gas velocity, L/G and multiple internal absorber configurations. The three recycle pumps supplied either one or two recycle headers.

When utilizing one header per pump, Bete TF56 nozzles were installed. Operation of two headers per pump required the utilization of Bete TF40 nozzles. The headers were oriented either co-current or counter-current to the gas flow. The gas flowrate was controlled by the damper on the fan and enabled testing of gas velocities between 10 to 25 ft/sec. A variety of packed absorber configurations were evaluated in which the placement and the number of mesh packing layers were changed. To insure the highest efficiency of droplet removal, different styles of horizontal flow demisters were also evaluated.

One must be cautioned concerning the direct interpretation of pilot scale scrubber performance to commercial size facilities. In general, the SO_2 removal achieved at the pilot plant is lower than that of a utility FGD scrubber at similar operating conditions. The droplets exiting the spray nozzles in the scrubbers utilized for these studies contact the walls of the scrubbers to have minimal beneficial impact on SO_2 removal. This is not the case in the utility scrubbers where greater utilization of the liquor is achieved due to minimal spray contacting the walls. Prior testing at the Miami Fort pilot plant has shown that up to 50% of the liquor entering the scrubber does not contribute to SO_2 removal when duplicating operating conditions of commercial facilities.

3. Gypsum Stacking

To simulate an impoundment area, a dike was installed within the existing filter cake laydown area. The dike was fabricated of wood and provided the space to deposit slurry as well as act as a separator of the slurry from the gypsum being deposited on the laydown area from the belt filter. The dike was perforated to permit the liquid from the slurry to drain. Geotextile membrane was installed within the impoundment to maintain the solids within the confines of the dike and to allow drainage of the slurry. As with the belt filter, a desliming hydroclone was initially utilized to thicken the 5% solids slurry to 20-25% solids before being deposited in the impoundment. Measurements of the percent moisture in gypsum samples taken from the impoundment were made at different depths during this evaluation period to determine the drainage characteristics of the gypsum.

E. RESULTS AND ANALYSIS

1. Modified ThioClear® Operation

Test Results

As a result of the inactivity at the pilot plant between Phase I and Phase II, the shakedown of the pilot plant on service water enabled the calibration of the flow measuring devices and familiarized the operators with the control of the modified ThioClear® process. Because of the minor alterations in implementing the modified ThioClear® process with the gypsum recycle, this effort was able to be completed within one week.

As in the start-up of Phase I, Phase II operation was initiated in a cascading fashion of the individual unit operations. Due to the operating experience gained in the prior operation of the pilot plant, overall plant operation proceeded smoothly.

The impetus for evaluating the modified ThioClear® process is the improved recovery of magnesium hydroxide. Thus the purity of the gypsum by-product should show improvement when compared to Phase I data. Verifying these two enhancements was the focus of the first two weeks of operation. In the first week, the process instrumentation was tuned and the operators became familiar with the revised process. The scrubber SO_2 removal efficiency exceeded 95% at the baseline operating conditions. In the second week of operation where steady state conditions were maintained, the SO_2 removal averaged 97% as illustrated in Figure III-23. Coinciding with this excellent removal efficiency was the expected improvement in the gypsum purity. Figure III-24 details the gypsum and magnesium hydroxide purity during the second week. The corresponding percent moisture content of the gypsum by-product was 23.8.

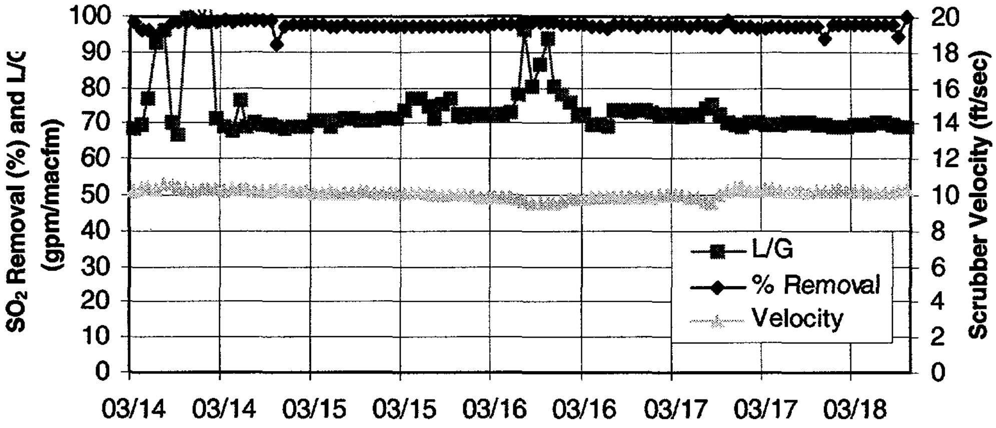


Figure III-23. Tray Tower Sulfur Dioxide Removal

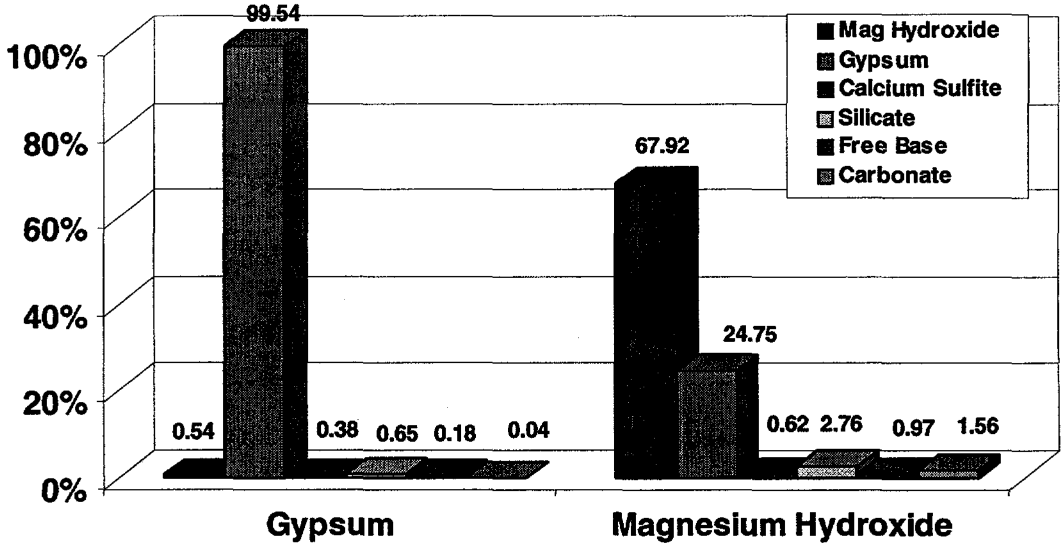


Figure III-24. Tray Tower By-Product Purity

After establishing the steady state chemistries in the second week and verifying the expected improvements, efforts at the pilot plant focused on the parametric SO_2 removal studies in the vertical scrubbing tower. The results of these evaluations are detailed in the High Velocity Scrubbing section. Upon completing the operation of the pilot plant with the vertical tower scrubber, the horizontal absorber was integrated into the ThioClear® process in preparation of its high velocity SO_2 removal characterization.

The start-up of the ThioClear® process in conjunction with the horizontal absorber was initiated at a gas velocity of 10 ft/sec. Although this was the same gas velocity as that utilized in the vertical absorber, the larger cross section of the horizontal scrubber required 30% more flue gas to be treated at this velocity when compared to the vertical tower. Subsequently, new flowrates of the by-product recovery loop needed to be established and the configuration of the hydroclones' vortex and apex were changed. Tuning of the controllers was required. During this week, the SO_2 removal achieved 97% at a L/G of 95.

Over the next two weeks the gas velocity of the absorber was increased from 10 ft/sec to 25 ft/sec. This effort was conducted in increments of 5 ft/sec to enable small adjustments to the control logic of the product recovery loop. By controlling the blowdown from the absorber to the oxidizer, the alkalinity was maintained between 2000-3000 mg/l measured as carbonate. In all cases, the SO_2 removal efficiency typically averaged above 95%. Absorber operating parameters and SO_2 removal efficiency for the 10-20 ft/sec velocities are shown in Figure III-25. Once the operation of the scrubber was verified at 25 ft/sec, the parametric studies for SO_2 removal efficiency were initiated as described in the High Velocity Scrubbing section.

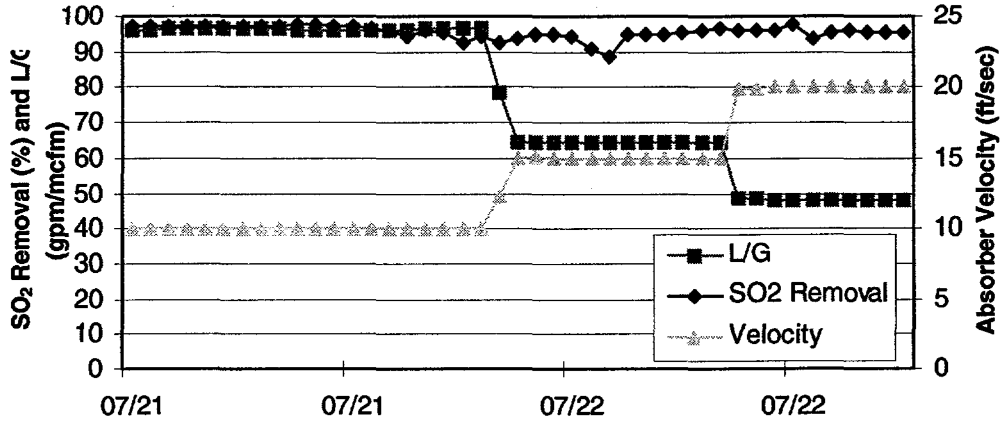


Figure III-25. Horizontal Absorber Sulfur Dioxide Removal

After completing the SO_2 removal studies, the horizontal absorber was configured into the optimum mode for operation at a gas velocity of 25 ft/sec. In this configuration, the pilot plant was operated at steady state conditions to observe the operation of the facility and analyze the by-products. During this period, the gypsum by-product was dewatered via the filter belt and a simulated gypsum stacking method. The latter method of dewatering is described in detail in the Gypsum Stacking section. The SO_2 removal efficiency averaged above 95% during steady state operation with an average scrubbing liquor alkalinity of 3000 mg/l measured as carbonate. A representative sampling of the absorber performance is illustrated in Figure III-26 for the week of August 22nd. The corresponding by-product purities are detailed in Figure III-27.

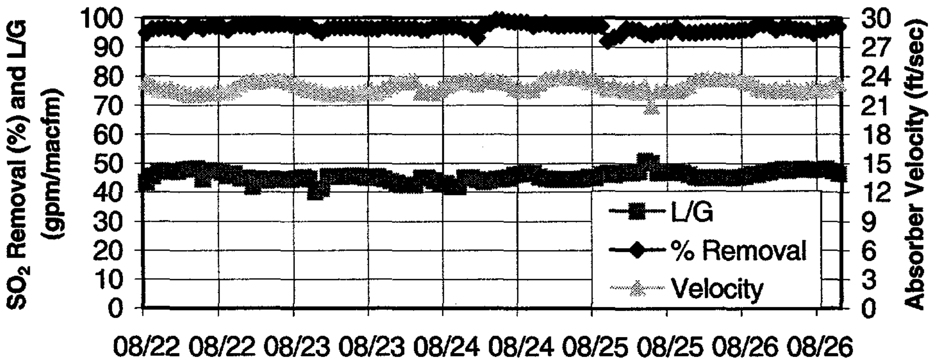


Figure III-26. Horizontal Absorber Steady State Sulfur Dioxide Removal

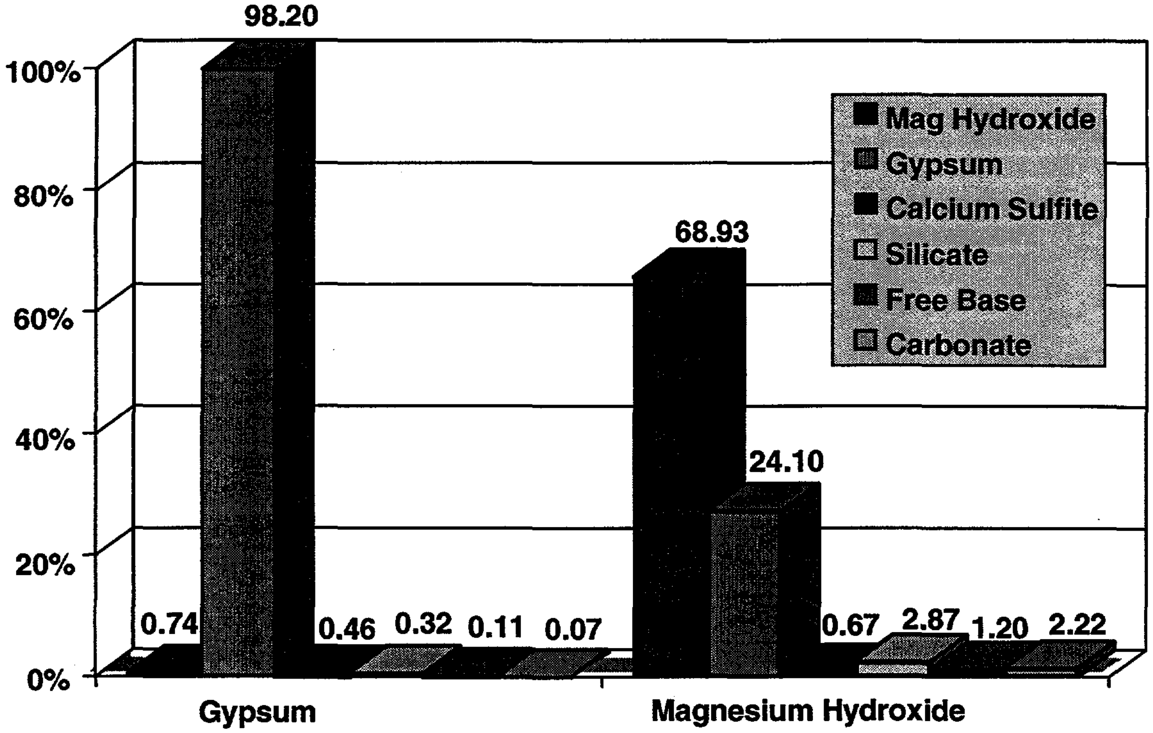


Figure III-27. Phase II By-Product Purity

Analysis

Having optimized the unit operations of the ThioClear® process in Phase I, the focus of Phase II was to verify the expectations of the modified ThioClear® process. By recycling the gypsum to the low pH regime of the oxidizer and continuously filtering, contaminating magnesium hydroxide would be dissolved from the gypsum and the continuous filtering would prohibit the build-up of silica (inert) fines. In as this modification did not change the operation of the scrubber, expectations for SO_2 removal were unchanged from that observed during Phase I. Removal of greater than 95% of the inlet SO_2 was the goal in both the vertical tray tower scrubber and the horizontal absorber configuration operations.

Figures III-23, III-25, and III-26 show that the expectations for SO_2 removal were met. In both absorber configurations, operating at vastly different velocities while controlling the chemistry of the scrubbing liquor within the absorber permitted SO_2 removals of +95% to be maintained. As has been demonstrated in prior pilot plant investigations, operation at higher velocities enable better utilization of the alkalinity of the magnesium-enhanced lime FGD process. Subsequently, the horizontal absorber was able to achieve SO_2 removals equal to the vertical tray scrubber while operating at a velocity nearly 2.5 times greater and with 1/3 less L/G.

The anticipated results of the Phase II process modifications are favorably highlighted by comparing the by-product purities illustrated in Figures III-24 and III-27 to that of Phase I. The impact of recycling the by-product gypsum to the low pH regime of the oxidizer had the desired effect of dissolving the magnesium hydroxide, free base, carbonate, and sulfite. Continuous filtration of the gypsum by-product stream minimized the accumulation of inerts reported as silicate. In comparing the vertical absorber operation of Phase I with similar operation in Phase II during the week of March 14th, the gypsum purity increased from 96.4% to 99.5%.

The success of increasing the purity of the gypsum by-product also equates to an improvement in the recovery of magnesium hydroxide. Although direct measurements as to the increase in the amount of magnesium hydroxide recovered were not feasible at the plant, the gypsum purity improvement was accepted as confirmation of achieving this goal. (Other than the magnesium hydroxide by-product stream, the gypsum by-product is the only purge of magnesium hydroxide.) Additional verification of this goal was noted in the increase in the purity of the magnesium hydroxide by-product which increased from the Phase I levels of 56.2% to 67.9% in Phase II.

Operating at the higher liquid flowrate associated with the horizontal absorber had minor impacts to the by-product purity. Both the gypsum and magnesium hydroxide purities decreased to 98.2% and 64.9% respectively when compared to the Phase II vertical scrubber operation. These results are not surprising since this testing was conducted with a mature chemistry in which inerts had sufficient time to reach equilibrium. Additionally, the higher liquid flowrates required multiple hydroclones for the separation process which increased the difficulty in optimizing the separation process at the pilot plant scale. Nevertheless, both by-products show respective 1.8% and 8.7%

improvements in the gypsum and magnesium hydroxide concentrations when compared to Phase I results.

An additional benefit of the modified ThioClear® process was a noted improvement in dewatering. Two causes can be attributed to this improvement. The first is the change in the liquor chemistry of the slurry being filtered. In Phase I, the pH of this liquor was above 10. Subsequently, air stripping of the gypsum cake on the belt filter promoted the absorption of CO_2. The adsorbed CO_2 formed calcium carbonate within the pores of the filter cloth which degraded the performance of the belt filter. Periodic acid cleaning of the cloth was required in Phase I. Thus, the percent moisture in the gypsum cake in Phase I which averaged ~30% decreased to 23.8% during the start-up period of Phase II in which the vertical tray scrubber was utilized.

Further improvements were achieved as a result of modifications required to operate at the higher flowrates necessary for the horizontal absorber. Typically when operating the horizontal absorber, the by-product flow loop was between 25 to 35 gpm. The existing belt filter could not handle this quantity of slurry. Therefore it was necessary to install a desliming hydroclone before the belt filter to concentrate the slurry from 5% solids to 25% solids in order to reduce the slurry deposited on the filter. The liquid of the hydroclone overflow was directed to a thickener where the fines were removed and the liquor returned to the regeneration tank. These fines which would blind the filter cake and limit the liquid removal by air stripping bypassed the filtering operation. The result was a further decrease in the percent moisture content of the gypsum cake to 20%. By minimizing the moisture content, the gypsum by-product become more acceptable to the commercial market because of the reduction of energy to dry the material and the lower shipping costs associated with a drier by-product.

2. High Velocity Scrubbing

Test Results

Prior testing at the Miami Fort pilot plant has demonstrated the effectiveness of the Thiosorbic process in removing SO_2 at high absorber gas velocities in the 3 foot diameter tower. To fully investigate the potential benefits of high velocity scrubbing with the ThioClear®, similar evaluations to these conducted with the Thiosorbic process were conducted with scrubber configurations being utilized at today's commercial FGD facilities. These scrubber configurations included a vertical spray tower, a vertical spray/tray tower, and a horizontal scrubber.

Figure III-28 details the results of parametric SO_2 removal studies utilizing the vertical spray scrubber. The data points were generated by establishing a set velocity within the scrubber and adjusting the flowrate among the three available spray nozzles to achieve the target removals of 86, 95, and 98% which correspond approximately to 2, 3 and 4 NTU's respectively. For these studies, the scrubber bleed was modulated to control the liquor alkalinity at an averaged 2250 ppm (measure as comparable carbonate) and the inlet flue gas SO_2 concentration was controlled at 2500 ppm by the spiking system. In order to minimize the vast differences in the surface areas produced by droplet formation at different flowrates, the flowrates to the individual nozzles were restricted between 60 to 90 gpm. Therefore, to increase or decrease the L/G to obtain the desired SO_2 removal, operation of one or two of the three recycle pumps may be initiated or terminated as required. Even though the individual nozzle flowrates were limited between 60 and 90 gpm, the corresponding Sauter mean diameters which correlate to droplet surface area varied between 2100 to 1600 microns according to the manufacturer's specifications.

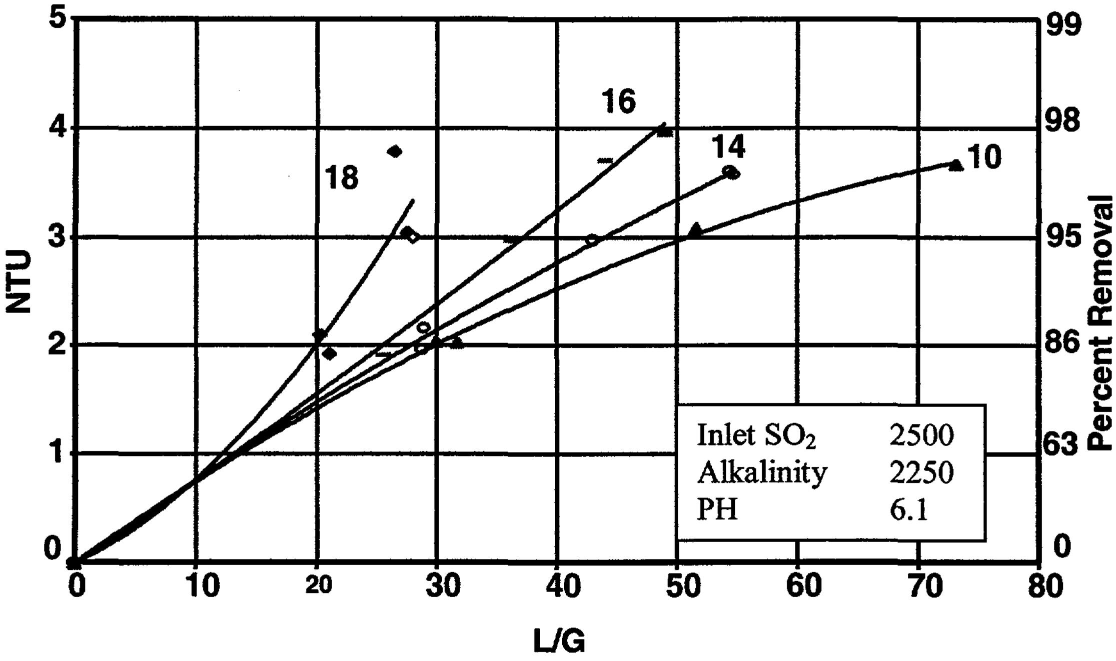


Figure III-28. Parametric Sulfur Dioxide Removal – Spray Tower

Prior testing with the Thiosorbic process provided the validity of conducting tests with this variance in the droplet size. These tests entailed operation of one nozzle at 120 gpm compared to two nozzles at 60 gpm each at the velocities of 10 ft/sec and 20 ft/sec. The removals at each velocity were virtually identical whether one or two nozzles were utilized. Two phenomena may explain these observations. The first is that within the droplet sizes observed, the overriding driving force for SO_2 removal is the difference in the relative velocities of the flue gas to the liquid as it exits the nozzle, irrespective of droplet sizes. The second explanation is that by dividing the 120 gpm between two nozzles within the pilot scale scrubber, the decrease in droplet surface area at the lower nozzle flowrates may be compensated by having two distinct mass transfer spray zones. In either case, the implication of this observation is that multiple low pressure nozzles may be as effective as fewer high pressure nozzles at the same header flowrate. The corresponding pump for such an application would have lower hydraulic head requirements and consume less energy.

Because many of the magnesium-enhanced lime FGD systems in operation today utilize a tray to enhance mass transfer, high velocity testing analogous to that of the vertical spray scrubber evaluations was conducted in the 3 foot diameter tower with a 40% open area tray installed below the spray zone. The results of these studies are shown in Figure III-29. During the prior Thiosorbic scrubber parametric evaluations, it was determined that operation above a gas velocity of 16 ft/sec was impractical. Above this velocity, the hydraulic dynamics of the tray provided an unstable operating condition. The liquid on the tray would cycle between loading and draining. Corresponding to these two events, both the SO_2 removal and scrubber pressure drop would increase while liquor accumulated on the tray and both subsequently decreased as the tray drained. Modifications which could be made to the tray to limit this phenomena were not undertaken for these evaluations. Therefore the ThioClear® tray scrubber evaluations were limited to 10, 14, and 16 ft/sec gas velocities.

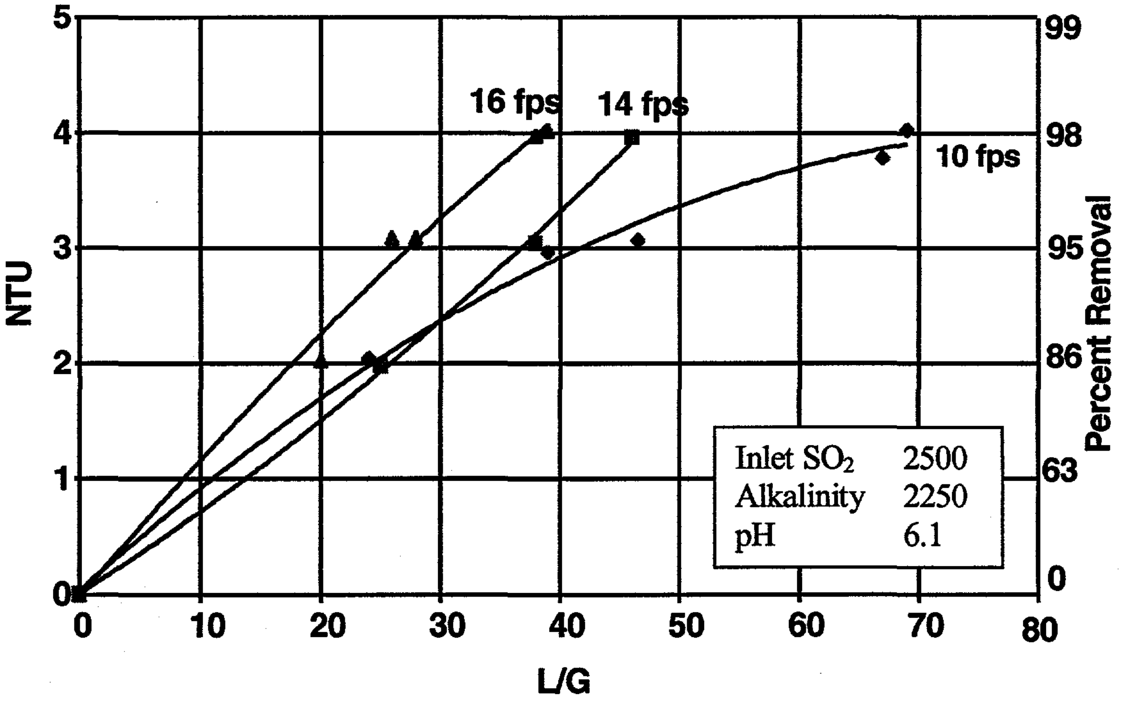


Figure III-29. Parametric Sulfur Dioxide Removal – Tray Tower

The parametric SO_2 removal studies of the horizontal absorber were quite extensive when compared to the vertical scrubber testing. Prior testing in the vertical spray and tray towers had been conducted while utilizing the Thiosorbic process. Therefore the vertical scrubber tests with the ThioClear® process were a verification that similar trends in SO_2 removal would be observed.

However the utilization of the proto-type horizontal absorber into the process introduced new variables to be investigated. As were the goals of the ThioClear® process to develop a low capital and operating cost FGD process, similar goals were established with the horizontal scrubber. In order to reduce capital costs, the scrubber was to be operated at nearly twice today's conventional design velocity standards which would reduce the size of the vessel. Operating at higher velocities as demonstrated in the vertical tower increases the mass transfer characteristics between the flue gas and the scrubbing liquor. The amount of scrubbing liquor required to scrub a unit volume of gas is reduced as the velocity increases. Therefore, lower liquid flowrates and smaller and/or fewer pumps are required to achieve similar SO_2 removals achieved at lower velocities. In order to increase the mass transfer of the absorber to insure high SO_2 removals, a packing compatible with the minimal containing solids liquor of the ThioClear® process was included in the test matrix. This packing also functions as a predemister which minimizes the overall length of the absorber vessel.

With each of the potential advantages of the above strategies comes a potential disadvantage. Operating at higher velocities increases the pressure drop of the absorber and as well as the potential of carryover from the mist eliminators. The packing as well as the various mist eliminators evaluated to control the carryover contribute to additional pressure drops requiring additional energy consumption.

Thus in conducting the parametric tests of the horizontal absorber, many of the variables changed were not pertinent to vertical scrubber tests. The following parametric changes were evaluated in the horizontal absorber:

- velocity
- liquid to gas ratio
- placement of packing
- number of layers of packing
- spray nozzle orientation to gas
- number of nozzles and spray headers

The scrubber parameters monitored during these investigations include SO_2 removal, pressure drop, and a qualitative measurement of carryover.

Table III-12 depicts the test matrix for the horizontal absorber. The results of these tests are detailed in Table III-13. Figures III-30 to III-38 illustrate the trends of SO_2 removal versus L/G and velocity for each of the absorber configurations.

Table III-12
Effectiveness of Absorber Configurations Based on Sulfur Dioxide Removal

Co-current Spray
Counter-current Spray
Co-current Packed w / 1 ply @1B, 2B, 3B
Co-current Packed w / 2 ply @1B, 2B, 3B
Co-current Packed w / 2 ply @ 3B
Co-current Packed w / 4 ply @ 3B
Counter-current (6 Headers) w / 6 ply @ 3A
Counter-current (6 Headers) Spray
Counter-current (6 Headers) w / 4 ply @ 3A

Table III – 13

Horizontal Absorber Parametric Testing

	SO2 in	SO2 out	ACFM	Q	R1	R2	R3	dPall	dP1	dP2	dP3	dPme	pH	Alk.	Vel.	L/G	NTU
Figure III-30	Mist Eliminator Floods when all pumps activated at 150 gpm																
	2076	564	5175	44.3	148	0	0	0.72	0	0	0	0.68	6.1	2060	9.9	37.2	1.3
	2133	632	5233	44.1	150	0	0	0.8	0	0	0	0.76	6.2	2331	10	37.1	1.22
	Mist Eliminator Floods when all pumps activated at 150 gpm																
	2004	398	7850	44.2	151	151	0	1.46	0	0	0	1.44	6.1	2172	15	44	1.62
	2092	328	7847	44.9	150	151	0	1.46	0	0	0	1.44	6.1	2909	15	44.1	1.85
	1944	147.2	5428	44.3	153	151	0	0.67	0	0	0	0.72	6	2230	10.4	64.1	2.58
	2079	122	5166	44.2	153	151	0	0.63	0	0	0	0.68	6.1	2581	9.9	67.4	2.84
	2066.5	407	7861	44.4	151	151	0	1.44	0	0	0	1.39	6.1	2122	15	44	1.62
	2059	427	10457	44.2	153	151	0	2.5	0	0	0	2.49	6.2	2359	20	33.2	1.57
	1958	474	10464	44.2	150	149	0	2.99	0	0	0	2.91	6	2334	20	32.9	1.42
	1923	828	7848	44.3	151	0	0	1.46	0	0	0	1.44	6.1	1964	15	24.8	0.84
	2054	812	7849	43.7	153	0	0	1.66	0	0	0	1.59	6.6	2452	15	25	0.93
	Mist Eliminator Floods when all pumps activated at 150 gpm																
	1933	888	10477	44.2	148	0	0	2.49	0	0	0	2.44	6.1	2345	20.1	18.4	0.78
	Mist Eliminator Floods when all pumps activated at 150 gpm																
	2063	612	13046	44.2	147	150	0	3.92	0	0	0	3.77	6.1	2333	24.9	26.2	1.22
	2242	720	13028	43.7	153	155	0	4.6	0	0	0	4.6	6.7	2165	24.9	26.9	1.14
	1960	973	13092	44.2	148	0	0	3.9	0	0	0	3.82	6.2	1950	25	14.7	0.7
Figure III-31	1837	108.4	5233	44.7	150	152	150	1.61	0	0	0	0.69	6	2320	10	94.8	2.83
	2009	287	5232	44.4	151	151	0	1.35	0	0	0	0.64	6.1	2256	10	66.1	1.95
	2078	670	5226	44.6	152	0	0	1.12	0	0	0	0.67	6.1	2052	10	37.6	1.13
	1986	229	7854	44.6	152	153	152	2.6	0	0	0	1.37	6.1	2458	15	63.8	2.16
	2038	422	7840	44.6	152	153	0	2.32	0	0	0	1.45	6.1	2548	15	44.6	1.57
	2162	931	7863	44.4	152	0	0	2.03	0	0	0	1.49	6.2	2073	15	25	0.84
	2048	363	10582	44.9	150	153	151	3.94	0	0	0	2.52	6.1	2638	20.3	47.1	1.73
	1978	567	10454	44.4	152	154	0	3.52	0	0	0	2.46	6.2	2091	20	33.5	1.25
	2015	949	10470	44.4	152	0	0	3.19	0	0	0	2.63	6.2	2141	20	18.8	0.75
	1993	344	13103	44.1	151	148	150	5.57	0	0	0	3.87	6.3	2474	25.1	37.7	1.76
	1960	495	13083	43.8	152	149	0	4.86	0	0	0	3.75	6.3	2170	25	26.4	1.38
	1954	883	13078	44.3	152	0	0	4.75	0	0	0	4.14	6.2	2354	24.9	15	0.79

Table III – 13 (cont.)

	SO2 in	SO2 out	ACFM	Q	R1	R2	R3	dPall	dP1	dP2	dP3	dPme	pH	Alk.	Vel.	L/G	NTU
Figure III-32	2045	130	5234	44.8	149	151	150	2.09	0.58	0.28	0.3	0.65	6	2210	9.9	94.6	2.76
	1945	170	5437	45.5	149	151	150	2.12	0.6	0.3	0.3	0.67	5.9	2054	10.4	91.1	2.44
	2035	273	5231	45.1	153	152	0	1.96	0.5	0.3	0.2	0.62	6	2348	10	67.1	2.01
	2022	627	5192	45.3	153	0	0	1.62	0.54	0.22	0	0.71	6.1	2266	9.9	38.3	1.17
	1978	260	7855	44.6	150	150	150	3.54	0.78	0.46	0.5	1.42	6	2152	15	63	2.03
	2031	294	7949	45.4	149	151	150	3.53	0.86	0.52	0.6	1.38	6	2305	15.2	62.3	1.93
	2034	380	7851	45.1	153	152	0	3.32	0.8	0.52	0.3	1.33	6	2406	15	44.7	1.68
	2111	881	7846	44.7	150	0	0	3.17	0.78	0.46	0.3	1.42	6.1	2032	15	24.9	0.87
	2133	320	10386	44.7	149	151	150	5.54	1.15	0.86	0.9	2.46	6.1	2736	19.9	47.6	1.9
	1971	359	10469	45.4	149	151	150	5.46	1.19	0.85	0.9	2.49	6	2196	20	47.3	1.7
	2132	607	10468	44.5	149	149	0	5.28	1.04	0.77	0.5	2.38	6.1	2294	20	32.8	1.26
	Outlet SO_2 concentration shows too large a range of values																
	2059	333	13032	44.6	150	150	150	8.4	1.58	1.27	1.2	4.18	6	2114	24.9	38	1.82
	1931	404	12816	45.2	149	150	150	7.88	1.55	1.26	1.3	3.81	6	2190	24.5	38.6	1.56
	2032	497	13050	44.6	151	150	0	7.62	1.49	1.25	0.9	3.65	6.1	2550	24.9	26.5	1.41
	2015	857	13039	44.6	150	0	0	7.49	1.56	0.98	1	3.74	6	2646	25	15	0.85
Figure III-33	2025	126	5241	46	152	151	151	3.63	1.15	0.9	0.8	0.61	6.1	2398	10	95.5	2.78
	2021	270	5242	46	154	151	0	3.25	1.1	0.87	0.4	0.58	6.1	2356	10	67	2.01
	2043	614	5309	45.8	154	0	0	2.5	0.5	0.11	0.1	0.62	6.1	2363	10.1	37.6	1.2
	2074	229	7845	45.9	152	151	151	5.82	1.73	1.46	1.4	1.39	6.2	2349	15	63.8	2.2
	2147	471	7884	45.8	153	151	0	5.6	1.69	1.5	0.9	1.37	6.2	2426	15	44.4	1.52
	2081	779	7836	45.8	154	0	0	4.71	0.78	0.49	0.4	1.29	6.2	2066	15	25.5	0.98
	1968	286	10463	45.7	152	151	151	8.81	2.38	2.12	2	2.36	6.1	2238	20	47.8	1.93
	2062	560	10445	45.7	154	151	0	8.51	2.32	2.12	1.7	2.36	6.2	1805	20	33.6	1.3
	1991.5	892	10519	45.7	154	0	0	8.1	1.13	0.98	1.3	2.47	6.2	2262	20.2	18.98	0.8
	2035	274	12760	45.5	149	150	151	12.6	3.14	2.9	2.6	3.82	6.1	2922	24.4	38.9	2
	2185	518	13027	45.5	153	151	0	12.31	3.26	3.1	2.2	3.69	6.2	2672	24.9	26.8	1.44
	1982	796	12920	45.6	154	0	0	12.31	3.14	2.98	2.2	3.58	6.2	2406	24.7	15.4	0.91

Table III – 13 (cont.)

	SO2 in	SO2 out	ACFM	Q	R1	R2	R3	dPall	dP1	dP2	dP3	dPme	pH	Alk.	Vel.	L/G	NTU
Figure III-34	2103	92	5172	45.7	151	150	152	1.44	0	0	0.8	0.58	6	2053	9.9	96.4	3.13
	1958	191	7846	45.7	151	150	151	2.74	0	0	1.3	1.31	6	2248	14.9	63.4	2.33
	1884	274	10668	45.6	151	150	150	4.7	0	0	2.1	2.57	6	2561	20.4	46.5	1.93
Figure III-35	2024	64.5	5218	43.9	149	152	151	2.56	0	0	1.8	0.75	6.09	2474	10	95	3.45
	2006	44	5226	46.2	150	151	153	2.68	0	0	2.2	0.62	6.04	2070	10	95.6	3.82
	2079	127	5225	43.9	151	151	154	2.65	0	0	2	0.71	6.1		9.9	95.9	2.8
	1963	122	5212	46.2	150	151	0	1.88	0	0	1.3	0.7	5.96	2054	10	66.6	2.78
	1935	182	5236	43.7	150	150	0	2	0	0	1.2	0.75	6.1	1994	10	65.7	2.36
	2111	153	7845	46.2	150	151	152	4.38	0	0	3.2	1.3	6.03	1902	15	63.6	2.62
	1967	267	7855	46.3	150	151	0	3.67	0	0	2.4	1.36	6.06	2587	15	44.2	2
	1882	380	7857	43.9	149	150	0	3.6	0	0	2	1.6	6.1	2285	15	43.7	1.6
	1991	341	7850	43.9	151	152	0	3.68	0	0	2.1	1.6	6.1	2277	14.9	44.1	1.76
	1928	694	7854	45.9	150	0	0	3.1	0	0	1.7	1.36	6.08	1991	15	24.9	1.02
	2085	167	10463	46.1	150	151	152	6.84	0	0	4.5	2.4	6.11	2549	20	47.6	2.52
	1820	427	10464	46	150	151	0	5.92	0	0	3.7	2.29	6.12	2206	20	33.1	1.45
	2180	504	10460	43.8	151	151	0	6.2	0	0	3.5	2.84	6.2		20	33.1	1.46
	2029	914	10456	45.8	150	0	0	5.71	0	0	3.4	2.31	6.19	2146	20	18.7	0.8
	2082	890	10455	43.4	151	0	0	6.4	0	0	3.4	2.91	6.2	2207	19.9	18.5	0.85
	2058	246.3	12951	45.8	150	151	152	10.3	0	0	6.1	4.14	6.17	2405	24.8	38.4	2.12
	1979	460	12802	46	150	151	0	8.34	0	0	5	3.44	6.13	2654	25	27.1	1.46
	2061	911	13236	45.7	150	0	0	8.9	0	0	5.3	3.78	6.22	2352	25.2	14.8	0.82
Figure III-36	1916	70.8	10478	55.9	152	152	151	8.7	0	0	0	2.48	6.2	2400	20	48.8	3.3
	1988	259	10553	56	151	150	0	7.99	0	0	0	2.59	6.2	2216	20	33.8	2.04
	2020	621	10348	55.8	151	0	0	6.94	0	0	0	2.55	6.3	2317	19.8	20	1.18
	2029	197	12228	56	151	150	150	11.2	0	0	0	3.44	6.2	2134	23.4	41.5	2.33
	2096	289	12497	55.6	151	150	0	10.6	0	0	0	3.68	6.3	2394	23.9	28.5	1.98
	1990	625	12890	55.6	152	0	0	10.2	0	0	0	3.9	6.3	2366	24.6	16.1	1.16

Table III – 13 (cont.)

	SO2 in	SO2 out	ACFM	Q	R1	R2	R3	dPall	dP1	dP2	dP3	dPme	pH	Alk.	Vel.	L/G	NTU
Figure III-37	2073	86.6	10485	53.8	151	153	152	4.75	0	0	0	2.9	6.1	2116	20.1	48.6	3.18
	2025	217	10462	54.3	151	152	0	4.12	0	0	0	2.81	6.2	2409	20	34.2	2.23
	1895	555	10472	54.2	153	0	0	3.68	0	0	0	2.93	6.2	2469	20	19.7	1.23
	2104	735	10497	53.6	153	0	0	3.68	0	0	0	2.94	6.4		20	19.6	1.05
	2013	109	13098	54	153	153	151	6.68	0	0	0	4.58	6.2	2167	25.1	39	2.91
	2084	274	13100	54.2	151	156	0	6.07	0	0	0	4.56	6.3	2332	25.1	27.6	2.03
	2044	567	13051	54.1	151	0	0	5.38	0	0	0	4.5	6.3	2511	24.9	15.7	1.28
Figure III-38	2066	49.7	10463	52.2	151	148	150	7.5	0	0	0	2.77	6.2	2436	20	47.9	3.73
	1885	191	10435	50.1	149	152	0	6.63	0	0	0	2.64	6.3	2105	20	33.6	2.29
	1958	615	10649	51.7	150	0	0	6.25	0	0	0	2.92	6.5	2264	20.3	18.9	1.16
	1892	61.7	13119	51.5	150	151	152	11.04	0	0	0	4.54	6.3	2315	25.1	38.5	3.42
	1955	196	13105	49.9	149	151	0	9.78	0	0	0	4.3	6.4	2452	25.1	26.7	2.3
	1977.5	669	13066	52.6	151	0	0	8.79	0	0	0	4.33	6.3	2248	25	15.6	1.08
	1970	706	13112	52.8	152	0	0	9.15	0	0	4.2	4.38	6.1	2252	25	15.6	1.03
	2020	608	13100	52.8	152	0	0	9.48	0	0	0	4.61	6.5	3185	25	15.6	1.2

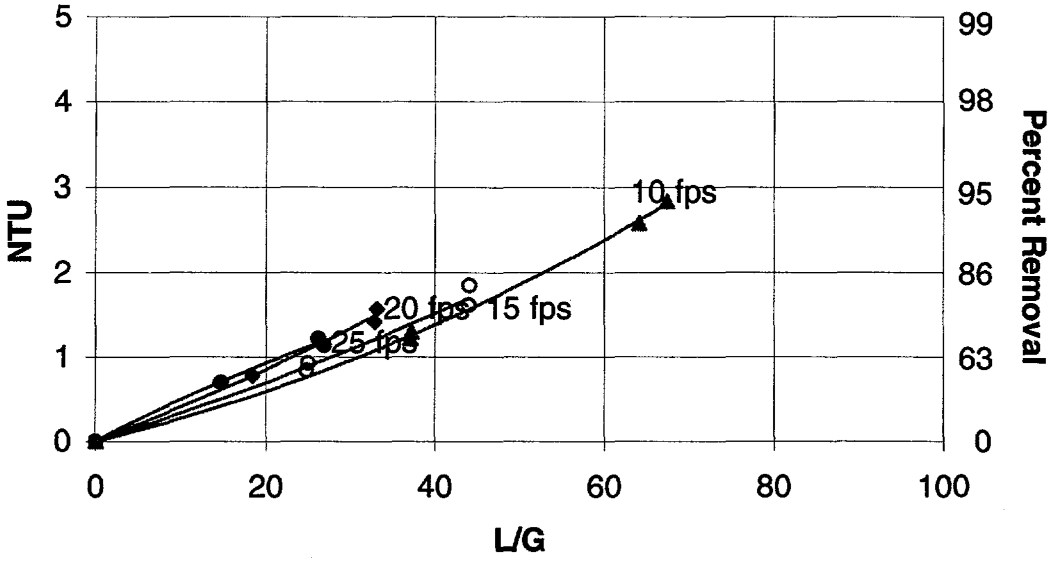


Figure III-30. Parametric Sulfur Dioxide Removal – Co-current Spray

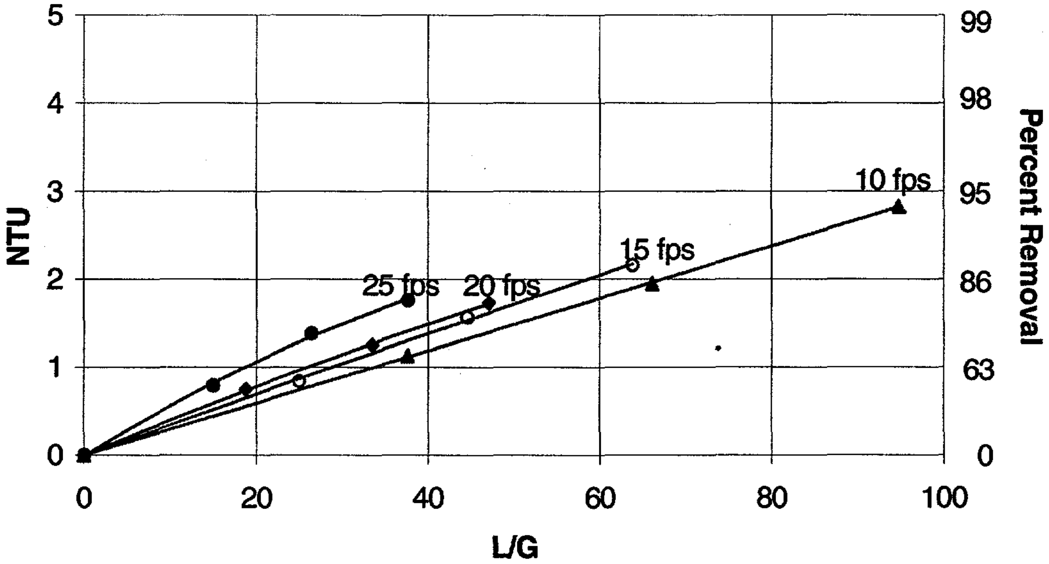


Figure III-31. Parametric Sulfur Dioxide Removal – Counter-current Spray

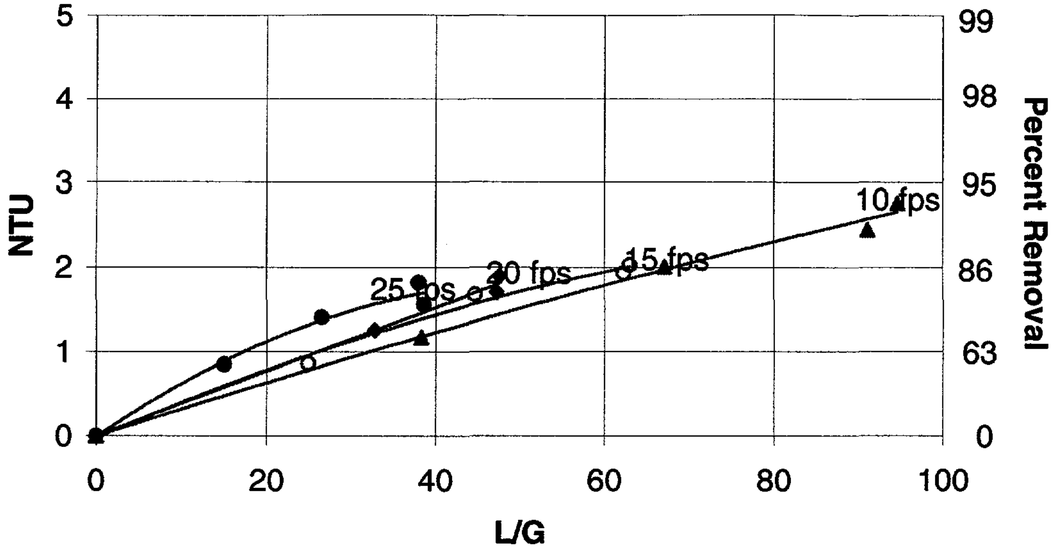


Figure III–32. Parametric Sulfur Dioxide Removal – Co-current Packed with 1 Ply after Individual Spray Zones

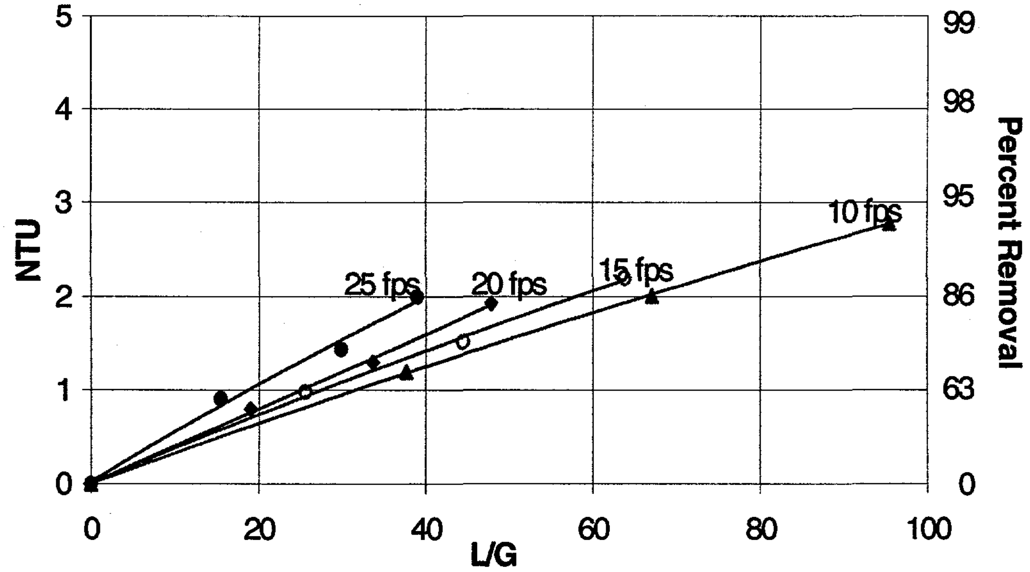


Figure III-33. Parametric Sulfur Dioxide Removal – Co-current Packed with 2 Ply after Individual Spray Zones

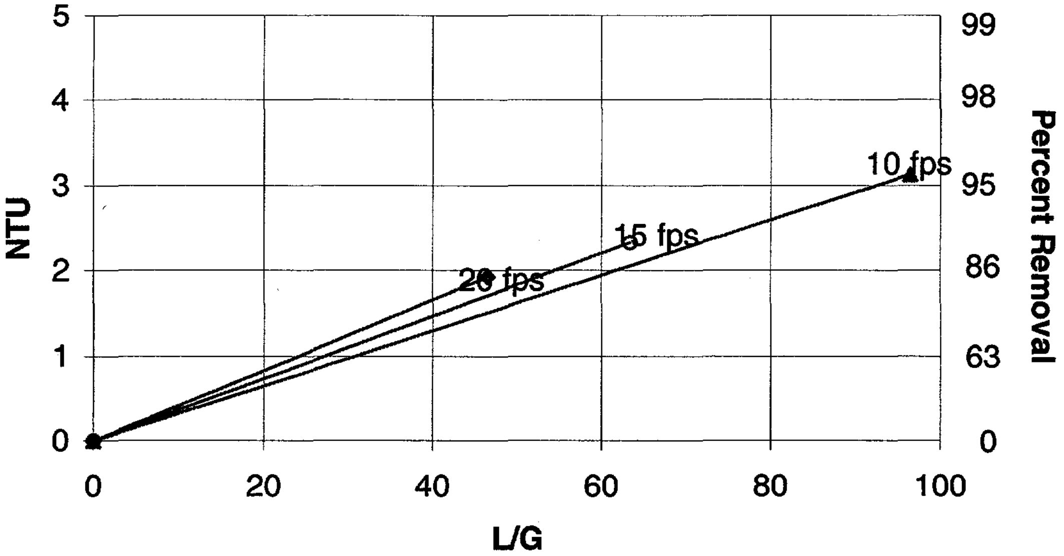


Figure III-34. Parametric Sulfur Dioxide Removal – Co-current Packed with 2 Ply after Entire Spray Zone

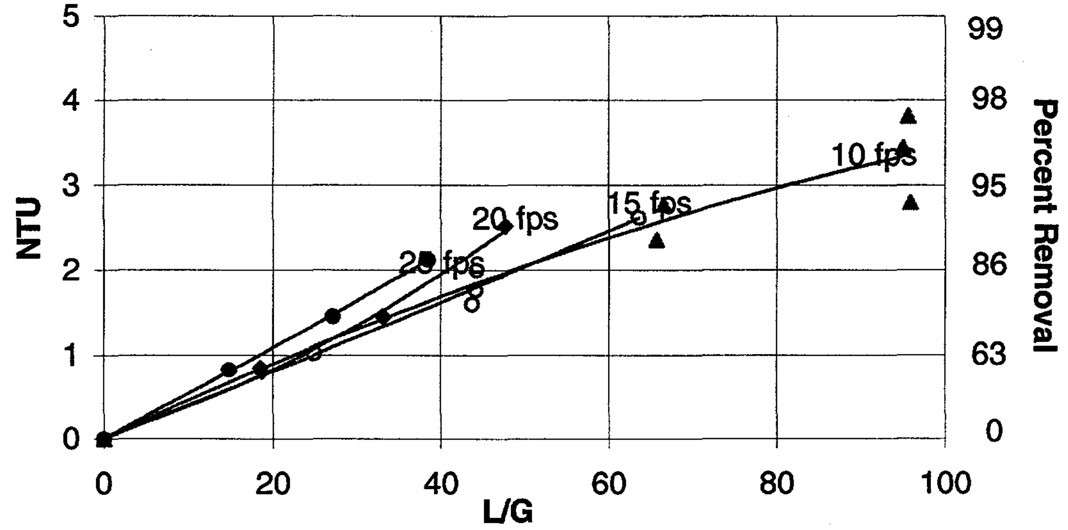


Figure III-35. Parametric Sulfur Dioxide Removal – Co-current Packed with 4 Ply after Entire Spray Zone

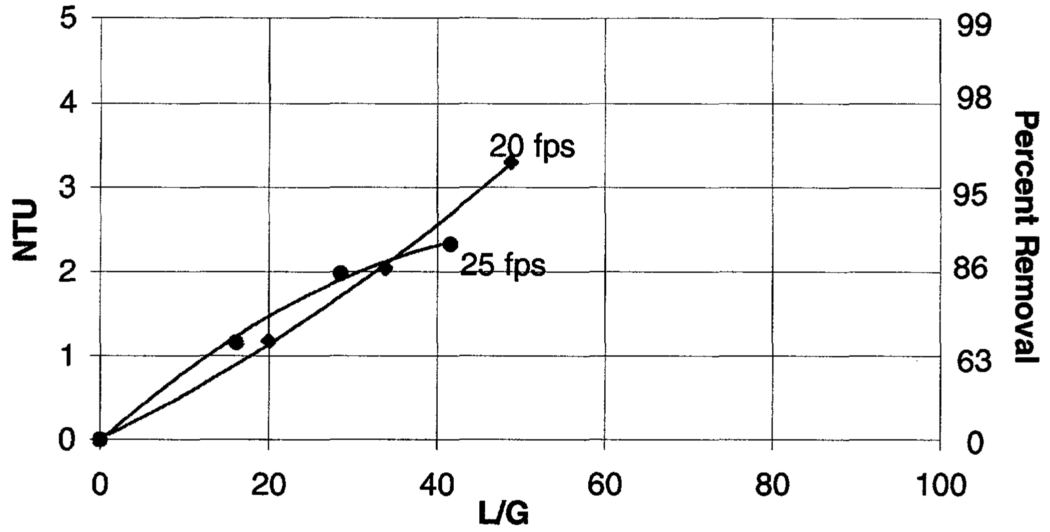


Figure III-36. Parametric Sulfur Dioxide Removal – Six Headers Counter-current Packed with 6 Ply after Entire Spray Zone

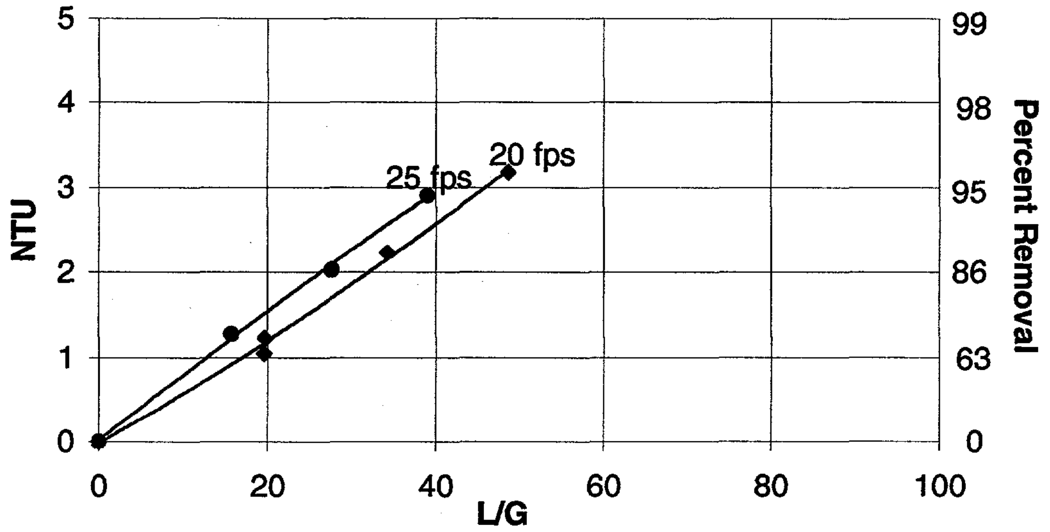


Figure III-37. Parametric Sulfur Dioxide Removal – Six Headers Counter-current Spray

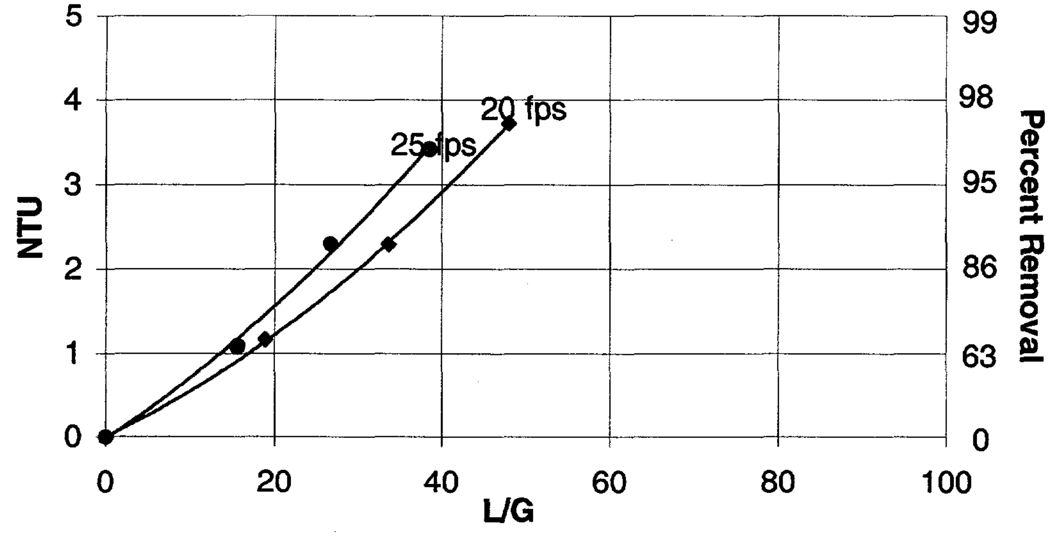


Figure III-38. Parametric Sulfur Dioxide Removal – Six Headers Counter-current Packed with 4 Ply after Entire Spray Zone

The order of increasing effectiveness for each of the configurations is detailed in Table III-12. This order was established based on the SO_2 removals at comparable L/G's as well as the effectiveness of the configuration to achieve 95% SO_2 removal at velocities of 20 and 25 ft/sec. As can be expected the spray configurations were the least effective when utilizing the same number of spray headers. The 1 ply packing installed after each of the individual spray zones showed no improvement when compared to the countercurrent spray absorber.

The SO_2 removal was increased by and average of 1 NTU by increasing the number of packing layers from 1 ply to 2 ply. Installation of a 2 ply packing at the end of the absorber before the mist eliminator section duplicated the results of the 2 ply after each spray zone. The utilization of 4 ply in this configuration improved removals by 0.2 and 0.3 NTU's when compared to the 2 ply. However, the 6 header configurations were the only tests which were able to exceed 95% SO_2 removal at flue gas velocities of 20 and

25 ft/sec. As would be expected, the 4 ply configuration exceeded the results of the countercurrent spray absorber. However, installation of 6 ply was a hindrance to removals. This configuration was comparable to the 6 header spray absorber without the packing.

In reviewing the data in Table III-13, the general trend that increasing the absorber pressure drop coincides with an increase in the SO_2 removal. Two exceptions to this rule were configurations which utilized the three sections of 2 ply packing and one section of 6 ply packing. In these two cases, the SO_2 removal did not appreciatively increase with the added mass transfer pressure drop resulting from increasing the layers of packing. In the latter case, the SO_2 removal actually decreased from that which was observed with 4 ply when operating at similar conditions.

Throughout the parametric SO_2 removal studies, the horizontal flow two stage mist eliminator configuration was unchanged. Visual observations were made to determine if the mist eliminator was in a failure mode in which collected liquor droplets were being stripped from the collection surface and reintrained in the gas stream. Once the SO_2 removal efficiency of the absorber exceeded 95%, efforts were devoted to minimizing the pressure drop of the scrubber without negatively impacting the SO_2 removal capabilities nor the collection efficiency of the demisters. These investigations are detailed in Figure III-39.

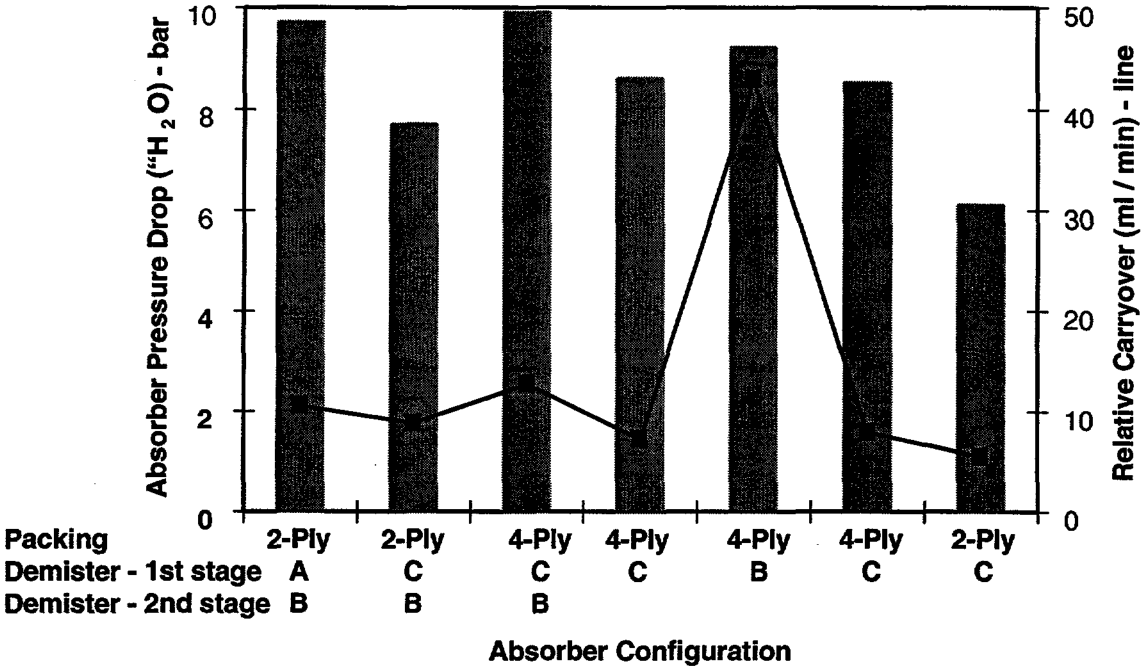


Figure III-39. Pressure Drop Reduction

The pressure reduction investigations required reducing the number of layers of packing, evaluating different styles of demisters, and reducing the number of mist eliminator stages. The scrubber configuration nomenclature of Figure III-39 details the number of packing layers in the 3A position and the B, C, and D letters represent the different styles of demisters installed. When only one letter is present, the mist eliminator was operated as a single stage demister.

Because there was no downstream droplet collector for carryover analysis, a relative measurement of the mist eliminator efficiency was made by monitoring the condensate stream at the outlet of the absorber in addition to the visual observations. These measurements are shown in conjunction with the scrubber pressure drop for the various configurations. As illustrated in Figure III-39, the pressure drop of the absorber was able to be reduced from 10 to 6 inches of water while maintaining the same relative carryover and greater than 95% SO_2 removal efficiency at a gas velocity of 25 ft/sec.

Analysis

As detailed earlier, the scrubbing liquor of a magnesium-enhanced lime FGD system is highly alkaline due to the presence of magnesium sulfite. It rapidly neutralizes the captured SO_2 making the absorption process controlled by the rate at which the SO_2 transfers from the gas phase to the liquid phase. To take advantage of the alkalinity of a magnesium-enhanced lime FGD system, a mass transfer enhancement device such as a sieve tray is typically installed in the scrubber to improve gas/liquid contact. Because the tray provides additional mass transfer capability within the scrubber, the reliance on the mass transfer characteristics of spray droplets alone is diminished. Thus the amount of liquor required to be sprayed can be reduced.

An alternative (or supplement) to a mass transfer device such as a tray can be the operation of the scrubber at velocities greater than today's standards. Operating at higher gas velocities can provide the following benefits in the spray zone with regards to mass transfer improvements:

1) Higher gas velocities will increase the turbulence and interaction between the flue gas and the spray droplets which decreases the gas-film resistance.

2) Increasing the gas velocity increases the shear force between the up-flowing gas and the counter-current spray droplets which enhances the movement of fluid within the droplet. This fluid movement renews the liquid boundary film layer and decreases its corresponding resistance.

3) The increase in the gas velocity will decrease the rate at which droplets fall through the scrubber and will increase the percentage of droplets which will be suspended within the scrubber. Both of these factors contribute to an increase in the mass transfer surface area per unit volume of the scrubber.

Similar phenomena resulting from high velocity operation can also enhance mass transfer of the gas and liquid on the sieve tray or with a packing.

The relationship between the mass transfer coefficient and SO_2 removal is defined by the following equation:

$$SO_2 \mathrm{Re}\, moval(NTU) = \frac{K_g aPZ}{G}$$

where: NTU - SO_2 removal expressed as number of transfer units
H - Height of scrubber (ft)
k_g - overall mass transfer coefficient (lb-mole / ft^2-hr-atm)
a - mass transfer surface area per unit volume (ft^2 / ft^3)
G - flue gas flowrate (lb-mole / ft^2-hr)
P - total system pressure (atm)

Therefore, the benefits in mass transfer outlined above will have a positive impact on SO_2 removal provided the product of the enhancements to the mass transfer coefficient (minimizing film resistance) and the surface area (increasing droplet surface area per scrubber volume) are greater than the detrimental offset due to the increased gas velocity.

In examining the vertical spray tower data presented in Figure III-28, one trend is evident. Significant reductions in L/G to achieve the same removal can be realized by increasing the gas velocity within the scrubber. This trend indicates that the product of the mass transfer coefficient and the mass transfer surface area is positively influenced by one or more of the potential benefits of enhancing mass transfer at higher velocities described earlier. Furthermore, the proportional increase in this product more than compensates for the proportional decrease of SO_2 removal which would be expected with the reduced residence time resulting from the increased gas throughput within the scrubber.

For example from Figure III-28, 98% SO_2 removal is achieved at a L/G of 90 for 10 ft/sec. If the corresponding liquid flowrate was held constant and the flowrate of flue gas to the scrubber was increased by 60% to obtain a scrubber velocity of 16 ft/sec, the resulting L/G would be 56. However, the pilot plant data shows that the L/G required for 98% removal at 16 ft/sec is only 48 L/G, 15% below that which is theoretically available. These findings suggest that existing magnesium-enhanced lime FGD facilities constructed with multiple scrubber modules designed for 10 ft/sec and a fixed liquor flowrate can maintain or even exceed the design SO_2 removal efficiencies. This can be accomplished by reducing the number of operating modules in order to increase the flue gas velocity within the remaining units. Obviously, sufficient fan capacity and adequate mist eliminator performance at the higher velocities are prerequisites.

A second trend identified during the analysis of the parametric studies involved the curvature of the trend lines. The SO_2 removal trend lines for scrubber velocities of 10, 14 and 16 ft/sec have a slight curve to the right. The remaining trend line at 18 ft/sec has a slight curve to the left. Prior visual observations, as well as carryover determinations, have identified that accumulation of scrubbing liquor occurs on the mist eliminators at gas velocities in excess of 18 ft/sec. This phenomena has the demisters effectively functioning as a packing. Therefore substantial increases of SO_2 removal occur as a result of the increase in the mass transfer surface area from the demister as opposed to the removals at the lower velocities which are dependent solely on the surface area of the spray zones. In commercial applications, the resulting carryover emissions and increased pressure drop due to the accumulation would make operating at velocities of 18 ft/sec or greater with this style of mist eliminators impractical.

Figure III-29 details the results of the vertical tray scrubber parametric SO_2 removal studies. As was expected, utilization of a tray enhances the mass transfer for SO_2 removal above that which was observed for the spray tower. Removals of 98% SO_2 at velocities of 10, 14, and 16 ft/sec required a L/G of 72, 45, and 38 respectively. Whereas the spray tower operating at the same velocities required a L/G of 90, 62, and 48, respectively. However with the utilization of the tray, the incremental increase of the

SO_2 removal resulting from increasing the scrubber velocity was not as great as that of the spray scrubber. For example from Figure III-29, 98% removal is achieved at a L/G of 72 for 10 ft/sec. If the flue gas flowrate was increased by 60% to achieve a scrubber gas velocity of 16 ft/sec while maintaining a constant liquid flowrate, the L/G would be reduced to 45. However, the data on Figure III-29 indicates that and L/G of 38 would be sufficient. This value is 10% below that which is theoretically available whereas the spray scrubber achieved a 15% decrease. Because of the enhancement of mass transfer on the tray, the percentage of this theoretical reduction was not as great as that of the spray tower. However, these reductions are significant and the overall L/G required when utilizing a tray is substantially below that necessary in a spray tower to achieve comparable SO_2 removals.

In comparing the SO_2 removal performance of the horizontal absorber to that of the vertical scrubber tower, two trends were evident. Although increasing the velocity of the flue gas permitted a decrease in the L/G to achieve the same removal, these decreases were not as substantial as observed in the vertical tower tests. At similar velocities, the vertical spray tower was more efficient at removing SO_2 than either the spray or packed horizontal absorber configurations. Three explanations can be offered for this observation. The first is the realization that the horizontal absorber with its spray nozzles oriented counter-current to the gas flow is not a true counter-current mass transfer vessel. The effect of gravity on the droplets in a horizontal scrubber tends to remove these droplets from the gas stream and therefore limit their ability to absorb SO_2. The second reason is due to the narrow walls (~2 feet apart) of the pilot plant horizontal absorber which increase the potential for wall wetting. As with the effect of gravity, this mode of removing liquor from the flue gas decreases the mass transfer surface area available from the spray droplets. A third explanation is that the mass transfer process at these higher velocities with the limited spray droplets entrained in the flue gas at the fixed alkalinity utilized in these evaluations may no longer be in the gas-film limited regime. Decreasing the availability of excess alkalinity by operating at higher velocities and "apparent" lower L/G due to wall wetting can permit liquid-film resistance to control the absorption process.

Analysis of the performance of the different horizontal absorber configuration provided insights into the advantages and disadvantages of each. The co-current spray absorber produced the lowest pressure drop of all the configurations. The overall pressure drop was approximately equal to the pressure drop attributed to the mist eliminators. This is the result of the spray nozzles imparting momentum to the gas as a result of the co-current orientation. However, co-current nozzle orientation and the lack of a mass transfer enhancement provided the lowest SO_2 removal results. Additionally, the mist eliminator section frequently flooded as a result of the scrubber liquor being carried downstream.

The counter-current spray absorber had mixed results in SO_2 performance when compared to the co-current design. At gas velocities of 20 ft/sec and below, the counter-current configuration underperformed the co-current absorber in SO_2 removals. However at 25 ft/sec, the former was superior. This can be attributed to an increase in the gas-liquid interaction at the higher velocity in the counter-current mode. Visual observation of the spray nozzle cone pattern identified a standard cone pattern at the lower velocities. However, as the velocity increased, the spray pattern began to flare out as an umbrella would do in turning inside out in a strong wind. The hindrance of the gas flow by the countercurrent nozzle orientation increased the system pressure drop by as much as 30% when compared to similar operating conditions in the co-current tests.

Unexpectedly, the introduction of mesh packing after each of the individual spray zones as a mass transfer enhancement provided minimal improvement in SO_2 removal when compared to the spray absorber configurations. As was determined in the overall parametric testing of the horizontal absorber, the mesh packing acted as a coalescer of spray droplets. Hence in this function, it may have minimized the surface area of the droplets while contributing minimal additional surface area. But as would be expected, the introduction of the three layers of packing substantially increased the absorber pressure drop by nearly 45% in some cases.

The utilization of two layers of packing after each of the three spray zones had the largest increase in SO_2 removals of the above mentioned configurations. Operation with two layers as opposed to one layer after each of the spray headers increased SO_2 removals on an average of 10%. However with a total of six layers of packing installed, the overall absorber pressure drop exceed 12 inches of water when operating at a gas velocity of 25 ft/sec. These pressure drops were 60% higher when compared to the single layer installation.

An alternative method of installing the packing was the placement of the packing after the entire spray zone. As observed with the single layer installation after each of the spray headers, the packing acts as a coaleser of droplets and therefore minimized the droplet loading on the demisters. However when installed after the spray zone, the mass transfer of the multiple layers showed beneficial results on SO_2 removal in addition to the coalesing of droplets. This absorber configuration evaluated with two layers of packing maintained or exceeded the SO_2 removals of the tests with six layers when installed as two layers after each spray zone. This feat was accomplished while substantially reducing the pressure drop to 50% of that which was recorded in the latter configuration.

Increasing the layers of packing from two to four at the end of the spray zone continued the improvement in SO_2 removals. With this configuration, SO_2 removals at a gas velocity of 20 ft/sec exceeded 90% for the first time. However, as would be expected, the absorber pressure drop increased by up to 45% due to the additional two layers. At the gas velocity of 25 ft/sec, the absorber pressure drop exceeded 10 inches of water.

All testing reviewed to this point utilized three recycle headers within the absorber. Each header contained two nozzles to evenly distribute the scrubbing liquor across the height of the cross section of the absorber. Visual observations continually revealed the loss of the scrubbing liquor to the walls of the scrubber due to the narrow width of the vessel. To resolve this deficiency, additional spray nozzle headers were installed within the absorber such that each recycle pump supplied two headers for a total of six installed headers. Because the same flowrate was maintained from the recycle pump, each header had a matched pair of Bete TF40 to replace the larger TF56 nozzles. Although these nozzles were smaller, the resulting Sauter mean diameter of the droplets was similar to that of the larger nozzles at approximately 1000 microns. The six spray headers increased the portion of liquor interacting with the gas stream. This was important in the effort to approach 98% SO_2 removal efficiency. To achieve this goal, the most efficient aspects of each of the configurations investigated were combined. The absorber internal arrangement included a spray zone with counter-current oriented nozzles followed by 4 layers of packing before the mist eliminator section. Because of the significant wall wetting observed in the prior counter-current configuration, the additional headers were required to increase the utilization of the liquor sprayed into the scrubber.

The next phase of parametric SO_2 studies was limited to absorber gas velocities of 20 and 25 ft/sec. The rational behind minimizing test conditions was to concentrate on the velocities which would have the opportunity to minimize commercial costs. Additionally, the trend of increasing velocity and reducing L/G to achieve the same SO_2 removal efficiency was a trend that was a constant throughout all the initial parametric studies. .The absorber configuration with the six spray headers oriented countercurrent and the four layers of packing before the demisters easily exceeded 95% SO_2 removal and approached 98%.

To further investigate possible improvements, two other configurations with the six headers were evaluated. The effect of six layers of packing before the demisters was tested. Unexpectedly, this configuration showed a decrease in SO_2 removals when compared to the studies conducted with four layers. As rationalized before, the packing can hinder mass transfer if it reduces the mass transfer surface area by coalesing the scrubbing liquor. The addition of multiple layers of packing may promote the rapid removal of the scrubbing liquor from the gas stream which is desirable as a predemister but not beneficial for SO_2 removal efficiencies. Additionally, the pressure drop increased by 22% as a result of the extra layers of packing. The other configuration evaluated the six headers in a spray absorber mode. This configuration was limited to 95% SO_2

removal. However, the elimination of the packing reduced the absorber pressure drop by 45% when compared to the test results with four layers of packing.

The parametric studies enable the contributions of the various internals of the absorber to be quantified in regards to SO_2 removal efficiency and pressure drop. Having achieved greater than 95% SO_2 removal, the parametric horizontal absorber investigation focused on reducing the absorber pressure drop. However, the relative carryover measured at the downstream drains was closely monitored so that this optimization did not adversely impact potential particulate emissions.

The baseline conditions for the horizontal absorber are represented by the first set of data of Figure III-39. The absorber operating at a gas velocity of 25 ft/sec and a L/G of 48 with two layers of packing generated a pressure drop of ~10 inches water and a relative carryover of 10 ml/min. Replacing the three pass first stage demister with a two pass demister reduced the pressure drop by two inches of water without impacting the carryover. The three pass design introduces more drag on the gas stream due to the longer length of the demister blades. Installing two additional layers of packing to reduce the measured carryover had no significant impact on this measurement but did increase the absorber pressure drop as was expected. Operating the mist eliminator section with its second stage removed eliminated the pressure drop associated with that stage and had no measurable impact on the carryover. These results indicate, as was observed visually, that the first stage in conjunction with the packing was efficient at removing entrained liquid droplets. Thus, a second stage was not required and approximately two inches in pressure drop were eliminated. Replacing the first stage mist eliminator with the second stage demister significantly increased the relative carryover measurement by a factor of four. This most likely resulted from the closer blade spacing of the second stage demister. The closer spacing permits additional blades to be utilized at the expense of increasing the velocity through the demister. Apparently in this case, the higher velocity prevented the capture of the entrained droplets. Reinstalling the coarse demister verified the earlier results. As a result of the four layers of packing having minimal impact on the relative carryover, the packing was reduced to two layers. Subsequently, by operating with one demister stage and two layers of packing, SO_2 removals were maintained above 95%, the relative carryover showed minimal impact from the baseline case, and the overall absorber pressure drop was reduced by four inches of water. This pressure drop compares favorably with current design standards of scrubbers which are operating at a gas velocity of 10 ft/sec. The result of these pressure reduction studies will translate into cost savings by minimizing the power consumption and capital costs as a result of reducing the fan requirements.

3. Gypsum Stacking

Test Results

The gypsum impoundment area was filled the week of November 14. The incoming slurry from the hydroclone consisted of between 20 to 25% solids. Three samples taken at different locations and depths of the resulting gypsum pile were analyzed to record the dewatering abilities of the impoundment area. One of these samples was extracted from the shallow end of the impoundment while the remaining two were from the deeper portion at depths of 6 inches and 24 inches.

The results of the gypsum stacking investigation are shown in Figure III-40. The analysis of the samples was conducted approximately two, four, and five months after the impoundment was filled. Average percent solids measurements during these intervals were 62, 66 and 74, respectively. As was expected, the sample analyzed at the two foot depth had the best dewatering measurement of 75.5% solids at the end of this investigation.

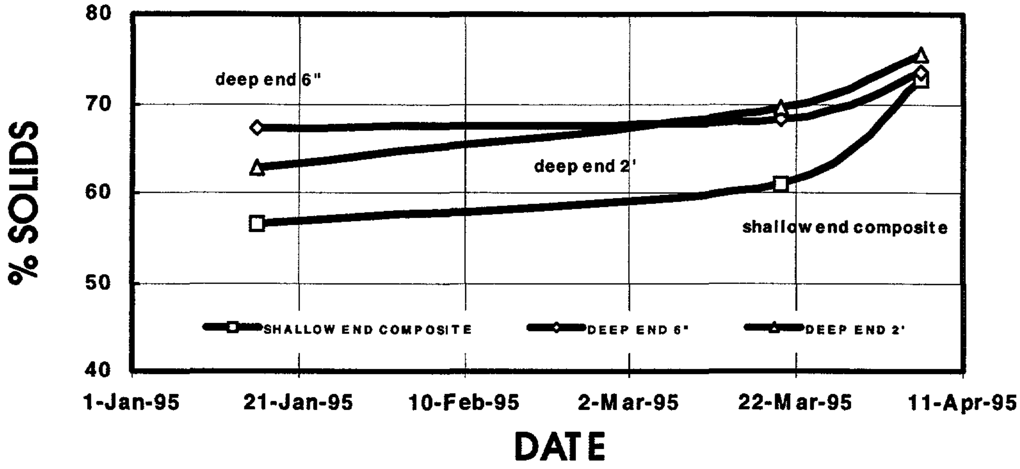


Figure III-40. Solids Analysis of Gypsum Settling Pond

Analysis

The dewatering characteristics of the simulated gypsum stack were as expected. Within the first two months the percent solids of the gypsum doubled from 25% to approximately 62%. In order to aid in the dewatering of the gypsum, a tarp was placed over the impoundment area to prevent precipitation from rewetting the gypsum. However, infrequent removal of water from the drainage collection area permitted the bottom of the stack to remain in contact with water and allowed water to travel up into the stack by "wicking." Hence the initial measurement at 24 inches in the deep end contained more moisture than the corresponding measurement at 6 inches.

As a result of the freezing temperatures associated with the on-set of winter, the entrapment of ice crystals within the gypsum stack prevented significant improvements in dewatering between January and March. Subsequently, the percent solids during this period only increased by four percentage points. However as the ambient temperatures increased during the spring months, the dewatering process resumed. The warmer weather coupled with frequent pumping of the collection pond enabled the percent solids to achieve an average of 74%. As a result of the compression effects of the overburden gypsum at the 24 inch depth sample point, this sample achieved the highest percent solids at 75.5%. This measurement, which corresponds to a settled density of approximately 79 pounds per cubic foot, meets the criteria established in other gypsum stacking investigations for successful applications of this method for disposal. In a full scale application where the height of the gypsum stack can exceed 1000 feet and improved drainage is available, the dewatering of the ThioClear® gypsum should exceed this final measurement of 75.5% solids.

F. SIGNIFICANT PROBLEMS ENCOUNTERED AND ACHIEVEMENT OF OBJECTIVES

1. Modified ThioClear® Operation

Significant Problems Encountered

As in Phase I, initial operation of the pilot plant on service water enabled the technicians to become familiar with the operation of the modified ThioClear® process and identify equipment problems before flue gas was introduced to the scrubber. In the initial two weeks of operating the modified ThioClear® process in conjunction with the vertical tray scrubbing tower, only minor problems were encountered. These were limited to plugging of the strainers and hydroclones due to dried solids on the walls of the piping and tankage from the outage. Additionally, the regeneration tank level controller was unreliable which resulted in less than ideal regeneration tank level control. As operation progressed, the dried solids responsible for the plugging problems were purged from the system and the regeneration tank level sensor was cleaned more frequently to improve its accuracy.

Incorporating the horizontal absorber into the modified ThioClear® process introduced problems which were generally related to the increase flowrate of the by-product recovery loop. These flowrates resulted from the increased capture of SO_2 due to the higher throughputs of gas in the horizontal absorber which operated at gas velocities up to 25 ft/sec. Subsequently, the recovery flow loop which operated between 10-20 gpm during Phase I, was required to handle a flowrate in excess of 30 gpm.

Maximum flow through the loop was determined to be less than 25 gpm. The problem was identified as restrictions between the oxidizer tank and oxidizer tower. These restrictions were eventually eliminated to resolve this problem.

Lack of pH control in the oxidizer tower resulted due to only one control loop being available for both vessels. Oxidation occurring in the tower caused the pH to drop below 4.9 which released the captured SO_2. Subsequently, the pH probes were relocated to the outlet effluent piping of the oxidizer tower. The magnesium hydroxide and sulfuric acid additions were retained in the oxidizer tank. Although the response of the pH control loop was delayed due to this placement, the pH of the oxidizer tower was controlled within the required limits.

The original equipment installed to transfer seed crystals from the hydroclone underflow to the regeneration tank prevented the accurate control of the percent solids in the regeneration tank. Initially, a diaphragm pump was utilized for this application. However, it was inaccurate in feed control and plugged frequently. This problem was remedied by installing a variable speed positive displacement pump to control this flowrate.

The increase in the flowrate of the by-product recovery flow loop required that two hydroclones be operated in parallel to accommodate the desired flowrates. Although care was taken to incorporate the additional hydroclone in such a manner that the flow would be distributed evenly to both, in actuality each hydroclone performed slightly different. Optimization of hydroclones was conducted in order to identify the best vortex and apex sizes for by-product purity.

Gypsum scale developed on the trailing edges of the blades from the first stage of the demister. The buildup of scale decreased the efficiency of the mist eliminator and increased it pressure drop. The formation of scale in this location resulted from poor demister washing. At velocities of 20 and 25 ft/sec, the demister wash sprays were not impacting the rear surface of the blades due to the velocity of the gas. Therefore the mist eliminator wash sprays were relocated near the blades so the spray would impact the surface.

Achievement of Objectives

The objective of the Phase II ThioClear® operation was to demonstrate that recycling the gypsum stream from the hydroclones to the oxidizer will improve the purity of the gypsum and the recovery of the magnesium hydroxide. These investigations were conducted at the optimal operating conditions established in Phase I. Both a vertical tray scrubbing tower and horizontal absorber were utilized for SO_2 capture.

As illustrated in Figure III-24, both the purity of the gypsum and the magnesium hydroxide showed significant improvements when compared to the Phase I results of Figure III-17. The improvement in gypsum quality will enable the gypsum to be accepted into wallboard manufacturing. Although the presence of magnesium hydroxide is reported in the gypsum by-product, this quantity is misleading because it results from the measurement of MgO which is typically associated with silicate inerts. In removing the magnesium hydroxide from the gypsum hydroclone underflow stream by subjecting it to the low pH regime of the oxidizer, nearly 100% of the soluble magnesium is retained within the process.

Similar results are shown in Figure III-27 which depicts the by-product purities during steady state operation with the horizontal absorber. Because of the maturing of the chemistry and the utilization of multiple hydroclones, these results show a slight decrease in purity when compared to the initial by-product purities of Phase II. However, these results still show an improvement over the Phase I results even though the hydroclone performance was less than optimal at the flowrates required for the horizontal absorber operation. As in Phase I, the modified ThioClear® process demonstrated its ability to remove 98% of the incoming SO_2 in both a vertical tray tower and a horizontal packed absorber.

2. High Velocity Scrubbing

Significant Problems Encountered

The major operational difficulty encountered in conducting the ThioClear® high velocity parametric scrubbing tests was maintaining the targeted alkalinity of 2250 mg/l measured as carbonate in the recycle tank. The mass transfer characteristics of the scrubbing process changed rapidly with velocity changes which impacted the uptake of SO_2. Because test parameters were being changed every hour, automatic control of the process was not feasible and operator intervention was required to adjust the scrubber bleed to control the alkalinity. Additionally, the recycle level was maintained at 80% level as opposed to its typical 40 to 50% level so as to serve as a storage buffer of alkalinity during the parametric studies.

The frequent changes of the absorber bleed impacted the performance of the hydroclones. The apex and vortex sizes were changed to accommodate an average flowrate. Because the hydroclones were not operating at optimal efficiency, the by-product purities were less than desirable during the parametric studies.

Operational problems pertaining to the vertical tower scrubber tests were limited to demister failure and poor tray hydraulic dynamics. During the spray tower tests, operation at a gas velocity over 18 ft/sec caused the mist eliminator to fail which produced excessive carryover. Additionally, the buildup of scrubbing liquor on the demister caused this equipment to act as a mass transfer device which skewed the SO_2 removals to higher efficiencies than would be possible with spray droplets only. The utilization of the 40% open area tray at absorber velocities greater than 16 ft/sec caused instability of the vessel pressure drop. The scrubber pressure drop fluctuated as the liquid loading on the tray increased and subsequently drained. Although modification of the tray would alleviate this problem, this was not attempted for these studies.

Operational problems pertaining to the horizontal absorber SO_2 parametric studies entailed exceeding the fan pressure capabilities, flooding of the mist eliminator section, and liquid in the analyzer sample lines. As a result of operating the horizontal absorber at gas velocities up to 25 ft/sec and with multiple layers of packing installed, the capabilities of the booster fan were exceeded. This problem resulted when the pressure drop of the absorber exceeded 12 inches of water. In these instances, the absorber gas velocity was maintained at the maximum achievable level and the parametric test conducted at this condition. While operating co-current nozzle studies, the spray droplets would carry downstream past the absorber floor drains and flood the mist eliminator section. Coinciding with this condition was excessive carryover through the demisters which was captured by the analyzer sampling system. In typical operating conditions, the small droplet collected by the analyzer sampling system would be vaporized by the heated sampling probe. However in this case, the sampling probe was overwhelmed with moisture and plugged the sampling lines. Therefore, testing was required to be suspended until the sampling lines were cleaned. Care was taken in similar tests to observe liquid flooding of the mist eliminator section. If this was observed, the test condition would be terminated.

Achievement of Objectives

The advantages of successfully operating a FGD scrubber at higher velocities than the current design standard are many. For greenfield and retrofit applications, there would be smaller and/or fewer absorber modules required to scrub the total flue gas from the facility, greatly reducing the initial capital investment. FGD facilities which are currently in operation may desire to reduce or eliminate gas bypass so as to increase the quantity of SO_2 removed in order to accumulate emission credits or offset emissions from other generating facilities. Utilities which have scrubbed and non-scrubbed generating units at the same site may opt to divert a portion of the non-scrubbed generating unit's flue gas to the existing scrubber as part of a SO_2 control strategy. Thus by evaluating the three typical designs of current absorber modules, the advantages and disadvantages of each operating at high gas velocities can be realized when utilizing a magnesium-enhanced lime. As previously explained, the effects of wall wetting in small pilot plant scrubbers reduce the effectiveness of the liquor spray in removing SO_2 when compared to full scale commercial applications.

Figure III-28 illustrates that at operating conditions of approximately 90 L/G and 10 ft/sec, the pilot plant's 3 foot diameter vertical scrubber can achieve a SO_2 removal of 98% when operating as a spray tower. When the velocity is increased by 60% to achieve a scrubber gas velocity of 16 ft/sec, the required L/G decreases to 48 to achieve the same removal. At these conditions, carryover from the mist eliminator was not observed. However at a gas velocity of 18 ft/sec, carryover was observed which would prohibit the operation of the scrubber operating at this condition. Other researchers using advanced mist eliminator designs such as a horizontal flow demister downstream of a vertical flow demister have demonstrated the effectiveness of such a design in removing entrained droplets at gas velocities up to 20 ft/sec in a vertical spray absorber.

Similarly, Figure III-29 details the impact of higher gas velocity on SO_2 removal in a tray tower. Increasing the gas velocity form 10 ft/sec to 16 ft/sec permitted a decrease of nearly 50% in L/G to achieve the same SO_2 removal of 98%. The limitation of the tray scrubber resulted from the hydraulic loading on the tray which produced unstable pressure drops.

Due to the limitations of the vertical flow demisters at high velocities, the horizontal absorber with horizontal flow mist eliminators was design, constructed, and installed at Miami Fort. This prototype absorber demonstrated the capabilities of the horizontal flow demisters to operate at velocities in excess of 20 ft/sec while effectively removing droplets from the gas stream. The achievements of this scrubber are illustrated in Figures III-30 and III-39.

The culmination of the parametric SO_2 studies demonstrated that a spray-zone composed of nozzles with countercurrent orientation to the gas flow followed by a mesh packing provided the optimal SO_2 removals. The investigation to reduce pressure drop showed that two layers of packing followed by a single stage mist eliminator was able to reduce the absorber pressure drop to 6 inches of water which operating at a gas velocity of 25 ft/sec while not adversely impacting the carryover from the scrubber. The combination of the spray nozzles inserted within the gas stream and the introduction of packing eliminated gas maldistribution common to existing horizontal scrubbers. Subsequently, the SO_2 removal improved as a result of improved gas-liquid interaction and carryover was minimized as a result of the packing acting as a predemister as well as the even gas distribution entering the mist eliminator section. Hence, the pilot plant horizontal absorber showed the capability of achieving 98% SO_2 removal at 25 ft/sec at a low L/G of 42. Due to the excessive wall wetting resulting from this pilot scale absorber, full scale commercial absorbers utilizing these design features should be able to achieve similar removals at substantially lower L/G's.

3. Gypsum Stacking

Significant Problems Encountered

The initial attempts to fill the impoundment area utilized the oxidize effluent. This stream contained only 5% solids by weight. It was determined that the percolation rate of the liquid through the geotextile membrane of the impoundment was unrealistic as a result of the small amount of solids present. Therefore, a hydroclone was installed at the impoundment area to increase the percent solids to 25% before introduction into the impoundment area.

Achievement of Objectives

The objective of this investigation was to demonstrate that in cases where there is no market for the gypsum, the method of gypsum stacking can be utilized. Because gypsum stacking eliminates primary and secondary dewatering capital and operation costs as well as costs associated with fixation, this method of disposal is relatively inexpensive when compared to disposal of the Thiosorbic FGD by-product. Also since the gypsum is not contaminated with fly ash and/or lime as would be required in a fixation process, the gypsum in the stack may be recovered at a later date if a market should develop.

The guidelines for the success of this study were established by the criteria utilized by commercial FGD gypsum stacking projects. Namely that the gypsum would need to dewater to a minimum of 75% solids. As shown in Figure III-40, this goal was met at the 24 inch depth of the impoundment area and is expected to be exceeded from the compaction effect of additional gypsum stacked on top. Additionally, the liquid recovered from this method of disposal was returned to the scrubbing process without any noted adverse effects.

G. BY-PRODUCT DESCRIPTION

For the ThioClear® process to be feasible, sufficient quantities of magnesium hydroxide need to be produced and recovered to operate the FGD process and provide a by-product stream. Thus it is important to minimize or eliminate the loss of magnesium compounds from the process. In Phase I operation in which the separation of the magnesium hydroxide and the gypsum was dependent on the effectiveness of hydroclones, nearly 4% of the gypsum by-product stream was composed of magnesium hydroxide. The loss of magnesium hydroxide in this stream limited the value of the gypsum by-product and reduced the revenue of magnesium hydroxide sales. Hence, the reconfiguration of the pilot plant for Phase II operation incorporated recycling the gypsum stream from the hydroclones to the oxidizer. The low pH regime of the oxidizer would dissolve the magnesium hydroxide as it reacts with the sulfuric acid generated in this vessel. Continuous filtration of the oxidizer effluent and washing of the gypsum filter cake removed the liquid phase magnesium compounds and minimized the build-up of inerts in the process. The composite purity of the by-products during steady state operation is shown in Figure III-27.

Aside from the improvement in gypsum purity, the modified ThioClear® process aided the dewatering of the gypsum. The combination of filtering a low pH slurry stream and continuous filtration can be credited for this improvement. The low pH slurry eliminated the formation of calcium carbonate which form during the filtering process of Phase I and hindered the dewatering process by plugging the filter cloth. The continuous filtration resulted in a lower concentration of inert fines in the slurry which reduced their impact on the filtering process. The level of fines was further reduced during the operation of the horizontal absorber as a result of a desliming hydroclone being installed at the belt filter. This hydroclone increased the percent solids in the slurry feed to the filter from 5% to 25% so that the existing belt filter could adequately filter the deposited slurry. However, the desliming hydroclone also further reduced the percentage of fines in the slurry to the filter. Operation in this manner consistently produced a filter cake with a moisture content of 20%. This average was nearly 10 percentage points less than that averaged during Phase I. As demonstrated in Phase I, the gypsum maintained its appearance of a snow white crystalline powder and the chloride content was reduced below the target value of 100 mg/kg as a result of the counter-current belt wash.

The purity of the magnesium hydroxide depends upon the efficiency of the hydroclones which separate the magnesium hydroxide crystals from the gypsum crystals in the regeneration tank's effluent stream. However, the modified ThioClear® process evaluated during Phase II of this project enabled this purity to increase because of the process modifications. The continuous filtering of the oxidizer effluent removed the fines of the process with the gypsum cake, thereby preventing the fines from accumulating in the process liquor. In Phase I, these fines typically reported to the hydroclone overflows with the magnesium hydroxide and subsequently continually recycled within the process as this neutralization reagent was used to control pH in the scrubber and oxidizer. When the desliming hydroclone was added during the horizontal absorber operation, a fines thickener was utilized to remove the fine solids from the hydroclone overflow stream before this process liquor was returned to the system. Additionally, the dessolution of the basic species (i.e.: magnesium hydroxide, calcium carbonate, and calcium hydroxide) by recycling the by-product gypsum to the low pH regime of the oxidizer enabled the resulting liquid phase contaminants to be removed in the filtering process. Hence the recovery of the magnesium ion was increased significantly over that which was achieve in Phase I and therefore the concentration of magnesium hydroxide reporting to the hydroclones increased which translated into higher magnesium hydroxide purity.

The appearance and the crystal habit of the magnesium hydroxide were unchanged from that observed during Phase I. However, by minimizing the contaminants of the magnesium hydroxide, improvements were noted in its settling and dewatering characteristics. The percent solids in the thickener underflow stream was measured at 20%. This is five percentage points above that which was observed during Phase I operation.

Improvements were also noted in the dried filter cake. Filtering of the Phase II magnesium hydroxide by-product produced a filter cake that averaged 40% solids. This measurement is nearly doubled that of the Phase I material. The improvements in both the slurry and filter cake of the Phase II magnesium hydroxide, albeit not of commercial standards, will reduce the costs of transportation and storage of this material.

Based on the by-product purities established from the Phase II operation, the hourly production and composition of the gypsum and magnesium hydroxide streams are detailed in Table III-14. These production rates are based on the EPRI FGD design and economic criteria for the 300 MW generating station.

Table III-14

Phase II - Hourly By-Product Production and Composition (lb/hr)

By-Product Stream:	Gypsum	Magnesium Hydroxide
Composition		
Gypsum	31205	229
Magnesium Hydroxide	0	617
Contaminants:		
Calcium Compounds	387	22
Magnesium Compounds	171	1
Inerts/Flyash	233	22
Total	31996	891

H. UTILIZATION OF BY-PRODUCTS

The ThioClear® process differs from the existing magnesium-enhanced lime FGD process in that usable by-products are formed with this technology. These by-products are gypsum and magnesium hydroxide which are both marketable. The marketing of these by-products can off-set some of the costs associated with this FGD process.

Gypsum has a large potential for usage in the wallboard market. However, small quantities are required for retardant in cement, stucco, stabilization of waste materials, and as a soil amendment or fertilizer. Material generated at the pilot plant was evaluated for the wallboard and fertilizer markets.

Magnesium hydroxide also is acceptable into many applications. It can be utilized for water treatment for both drinking water and wastewater. It is also used as a raw material for the manufacture of magnesium metal and refractory bricks. Magnesium hydroxide has a small market in animal feed and plant nutrients.

Two samples of gypsum from the modified ThioClear® process were submitted for analysis to Gold Bond Building Products, the same wallboard manufacturer who analyzed the Phase I generated gypsum. The average results of these two analyses are shown in Table III-15. This analysis met or exceeded the specifications of wallboard gypsum in every category except two. The two exceptions were soluble magnesium and pH which obviously resulted from magnesium hydroxide contamination. However, the total soluble salts were below industry maximums and the pH values were not significantly out of the recommended specifications of 5.0-8.0 to be of a major concern.

Table III-15

Analysis of ThioClear® Gypsum

	S1 (1)	S1 (2)	S2 (1)	S2 (2)
Silica & Insolubles (%)	0.51	0.51	0.33	0.44
Calculated Purity (%)	98.4	98.5	98.3	98.6
Soluble Cl^- (ppm)	<40	<40	<40	<40
Soluble Na^+ (ppm)	16	13	19	19
Soluble Mg^{++} (ppm)	170	167	198	165
Microtrac (u)	47.8	47.1	48.7	48.7
pH (10% solids)	9.2	9.2	9.2	9.2
As (ppm)	41	50	<40	<40
Ba (ppm)	7	43	7	9
Be (ppm)	<0.15	<0.15	<0.15	<0.15
Cd (ppm)	<2.5	<2.5	<2.5	<2.5
Co (ppm)	<2.5	<2.5	<2.5	<2.5
Cr (ppm)	11	12	11	7
Ni (ppm)	<3	<3	<3	<3
Pb (ppm)	21	33	29	24
Se (ppm)	<50	<50	<50	<50
Y (ppm)	85	103	107	75

Besides the wallboard application, gypsum is a component of various plasters. One specification which is important for this application is the whiteness of the gypsum. As a result of the purity of the lime utilized in this FGD process and the hydrocloning of the gypsum slurry before filtering to removal additional inerts, ThioClear® gypsum has a snow-like crystalline appearance which is not typically achieved in limestone FGD processes. Thus, gypsum users have expressed interest in commercial quantities of the ThioClear® gypsum for this market.

As referenced in the previous section, gains were made in improving the magnesium hydroxide by-product. However, these improvements fell short of that which would be comparable to commercial magnesium hydroxide slurry. This short coming should not detract from the fact that similar a magnesium hydroxide by-product is being utilized by Cinergy's Zimmer generating station. Preliminary evaluations have been favorable of the neutralization capabilities of this by-product on bottom ash water, coal pile rain run-off, wastewater of acid cleaning of equipment, and the plant storm collection ponds. Since there is a large need for neutralization reagents for wastewater treatment at the generating station, the quality of the by-product can be lower than that required for other commercial applications.

An investigation into improving the quality of the magnesium hydroxide was undertaken at Dravo's Research Center. In this study, the magnesium hydroxide was subjected to water washing in order to remove the gypsum contaminant. Preparation of the by-product in this manner improved the purity of magnesium hydroxide to 90% which is the low range of commercial products. However as a result of the crystal habit, the low solids content and high viscosity of the slurry will continue to be a hindrance for broad acceptance of this material. Analysis conducted by a producer of magnesium hydroxide indicated that these problems could be alleviated with the aid of a dispersant.

In order to study the acceptance of the by-products of the ThioClear® process into agricultural uses, twelve drums of gypsum containing 6% magnesium hydroxide were provided to a government agency. The effect of this soil amendment was investigated on plant growth based on the resulting dry matter on the plants. The plant species included grasses, legumes, and maize. It was determined for each of the species that an optimum application of the gypsum/magnesium hydroxide existed in which plant growth was maximized. When this optimum was exceeded, plant growth actually declined. Chemical grade gypsum and FGD gypsum improved plant growth also but a larger application was required when compared to the ThioClear® by-product mixture.

I. SUMMARY OF FINDINGS

The objectives of Phase II were to build on the optimization of Phase I and demonstrate the generation of improved by-product purity, high efficiency SO_2 removal at high scrubber gas velocities, and a low cost method of gypsum disposal. Recycling the gypsum as conducted in the modified ThioClear® process enabled gypsum to be produced which met and/or exceeded the majority of the requirements required by wallboard manufacturers. The snow-white crystalline appearance of the gypsum also interested gypsum users for other applications which would command more value. Investigations of SO_2 removal efficiencies in spray and spray/tray vertical scrubbing towers and in a proto-type packed horizontal absorber showed that 98% removal efficiencies could be achieved at gas velocities greater than current design standards. Additionally, it was demonstrated that the gypsum produced by the ThioClear® process can be disposed through current stacking methods and dewater to acceptable levels. All of the above objectives were successfully met.

A summary of the findings for the second phase of the ThioClear® project is as follows:

1. Modified ThioClear® Operation

a. The incorporation of the modifications required for the modified ThioClear® process did not have any negative impact on the overall FGD process nor on its SO_2 removal efficiencies.

b. The modified ThioClear® process demonstrated its ability to produce a high quality gypsum by-product and improved the recovery and purity of magnesium hydroxide.

c. The gypsum by-product was analyzed as acceptable to the wallboard manufacturers. The high purity of the gypsum has made it a suitable substitute for the high end markets such as plasters.

d. Although the magnesium hydroxide generated by the process was not of commercial quality, refining of this material enable commercial purity concentrations to be achieved. Additional effort will be required to achieve the desired slurry solids concentration and viscosity. A similar unrefined magnesium hydroxide by-product is being successfully substituted for commercial magnesium hydroxide for wastewater treatment at CG&E's Zimmer Station.

e. As in Phase I, the operation of this process was able to be accomplished with minimal operator intervention and relied greatly on the installed automation equipment.

2. High Velocity Scrubbing

a. High velocity scrubbing utilizing the ThioClear® process liquor successful achieved removals up to 98% in a spray and spray/tray vertical tower and in a proto-type horizontal packed absorber. The economic advantages of operating at higher gas velocities include a smaller absorber vessel, smaller and/or fewer recycle pumps, and high SO_2 removal efficiencies.

b. Testing in a vertical spray tower demonstrated that the flue gas velocity could be increased from 10 ft/sec to 16 ft/sec while the L/G is reduced by 45% and continue to remove 98% of the inlet SO_2.

c. The vertical tray tower successfully removed 98% of the SO_2 as its velocity was increased from 10 ft/sec to 16 ft/sec while the L/G was decreased from 72 to 38.

d. The incorporation of spray nozzles inserted within the flue gas stream and installation of a mesh packing enabled the horizontal absorber to achieve 98% SO_2 removals at a gas velocity of 25 ft/sec and a L/G of 50. Factors which were demonstrated to achieve these results included:

- Improved velocity distribution over current design horizontal absorbers as a results of the nozzles inserted into the gas path and the flow straightening effects of the packing.
- Enhanced mass transfer between the flue gas and the scrubbing liquor which resulted from the improved gas distribution, nozzle placement, and utilization of packing.
- Utilization of a mesh style packing due to the minimal solids and non-scaling traits of ThioClear® whereas high solids scrubbing liquors would plug this mass transfer device.
- Minimization of spray droplets on the demister due to the coalescing effects of the mesh packing,

3. Gypsum Stacking

a. The gypsum from the ThioClear® process was shown to achieve similar dewatering results as that of other gypsum generated wastes which have been successfully disposed by stacking.

b. The process liquor reclaimed by this simulation was returned to the system without any adverse effects.

IV. MARKETING / COMMERCIALIZATION DISCUSSION

A. PROCESS MARKET

The market for the ThioClear® process is worldwide. In the United States, the continuing restrictions on SO_2 emissions and corresponding environmental regulations will favor a FGD technology which is a "zero discharge" process. Coinciding with the implementation of these regulations is the deregulation of the electric utility industry. Thus, impacted generating facilities will be implementing the lowest cost methods of FGD such as ThioClear® in order to stay competitive. Overseas' markets, especially in developing countries, require low capital cost solutions to their environmental problems which ThioClear® offers. Additionally, the usable by-products, gypsum and magnesium hydroxide, would be desirable products in these economies.

Domestic markets for the ThioClear® process will be driven by clean air legislation. During Phase II of the Clean Air Act, it is expected between 9,000 to 15,000 MW of generating capacity will be scrubbed. The units to be scrubbed will more than likely be in areas inaccessible to low sulfur coal from the western United States or in areas where the existing high sulfur coal supply is reliable and inexpensive. The low cost, high efficiency of the ThioClear® process should make it a viable option in either area. Magnesium-enhanced lime FGD processes are being utilized to scrub approximately 13,500 MW. Detailed economic analysis of specific facilities have shown that the high fuel cost differentials between low and high sulfur coals are enough to justify the operation of a low cost scrubber.

Foreign markets are projected to be the most active within the next five years. Developing countries such as Korea, China, Taiwan, Indonesia, and Mexico which have rapidly expanding economies offer tremendous opportunities for FGD systems. These economies require a cheap source of electricity which is usually derived from coal combustion. The application of the ThioClear® process with a high velocity horizontal absorber and usable by-products will be very competitive when compared to traditional limestone systems. The projected 40% reduction in capital costs should provide the incentive for developing countries to utilize this FGD process.

Two other markets which appear promising for the ThioClear® process are industrial boilers and users of the fuel, orimulsion. Industrial boilers usually have space confinements which exclude a standard FGD process. However, with the advent of the horizontal scrubber, minimal space is required. Orimulsion, which is being sold as a substitute for fuel oil, is a bitumen emulsion that has a high sulfur content. Aside from controlling the SO_2 emissions from the combustion of orimulsion, the ThioClear® process will generate magnesium hydroxide which will neutralize the impact of the high concentrations of vanadium in the orimulsion. Vanadium catalyzes the oxidation of SO_2 to SO_3 which is highly corrosive. However, injection of magnesium hydroxide into the boiler will react with vanadium to form magnesium vanadate which will not oxidize the SO_2.

B. BY-PRODUCT MARKET

1. Gypsum

a. Wallboard

Testing of gypsum produced by the magnesium-enhanced lime FGD processes at the Bruce Mansfield Station and at the Miami Fort pilot plant have demonstrated that it is of a quality acceptable to wallboard manufacturers. However, based upon market needs, this market can become restricted as a result of other FGD facilities using this option to dispose of the by-product. In order to overcome the primary obstacle of selling such a high volume, low value product, it will be necessary to keep transportation costs to a minimum. Subsequently, wall board manufacturers need to be located near the power plant or both the power plant and the wallboard facility can be on a navigable river for low cost transportation in order to benefit from this low cost source of gypsum.

There are three operating wallboard plants in Ohio. Two are in Port Clinton and the remaining one is Lorraine. The facilities in Port Clinton are located near gypsum mines. However in recent years, the purity of the gypsum has declined. Supplementing the mined material with high purity FGD gypsum is currently being conducted. Full conversion of these two plants to FGD gypsum is possible, provided the specifications of wallboard quality gypsum is maintained. The Lorraine plant currently receives mined gypsum rock from Michigan which is shipped via barges on the Great Lakes. Thus, a ThioClear® installation accessible to this form of transportation can easily supply this facility's needs.

b. Plasters

ThioClear® gypsum has a crystalline snow-white appearance. This appearance results from the minimization of impurities in the gypsum because of the purity of the lime neutralization reagent utilized for the FGD process and the series of hydroclones which remove additional impurities. This high purity and brightness of the gypsum are traits which are desirable for the formulation of plasters. Because plasters are utilized as finishes to construction, premiums are paid for the raw materials which can provide the required texture and whiteness. Although, this is not as large of a market as the wallboard market, the acceptance of FGD gypsum other than the ThioClear® gypsum should be minimal due to the strict specifications.

c. Cements

Gypsum is utilized in the cement industry as an additive which retards the set time and thereby enhances the strength of the concrete. Approximately 4% of the cement will be composed of gypsum which is added during the grinding of the cement clinker. About 100 million tons of cement is marketed in the United States yearly. Thus, the annual market for gypsum can approach 4 million tons.

Cement plants which could be accessed by gypsum generated by Ohio facilities include two plants in Ohio (LaFarge in Paulding and Southdown in Fairbourn), four plants on the Ohio River (Kosmos and Louisville Cement in Louisville, Kentucky; LaFarge in Joppa, Illinois; and Kosmos in Pittsburgh, Pennsylvania) and nine plants on or near the Great Lakes in which transportation by barge is possible (Medussa in Wampam, Pennsylvania; Essroc in Bessemer, Pennsylvania; Armstrong in Butler, Pennsylvania; Dundee in Detroit, Michigan; LaFarge in Alpena, Michigan; Medussa in Sharbelo, Michigan, and three facilities near Toronto, Ontario).

d. Fertilizers

The utilization of gypsum as a soil amendment is not new. Gypsum has been used extensively in the southeastern United States for cotton, mushroom, and peanut production. The benefit of a gypsum application is the promoting of deeper root growth which aids the plant during dry spells.

Recent tests by state and federal agencies have shown that the combination of magnesium hydroxide and gypsum, such as that which would result from the ThioClear® process, has added advantages over gypsum by itself. This amendment provides magnesium, sulfur, and calcium to the soil and also buffers the pH of the soil. Subsequently, aluminum toxicity which hinders the growth of plants is minimized.

2. Magnesium Hydroxide

a. Wastewater Treatment

The value of the magnesium hydroxide will be most realized by internal use of the generating facility in neutralizing acid wastewaters. Coal pile rain run-off, bottom ash slurry ponds, flyash landfill water run-off, and acid cleaning solutions all need to be treated. The annual usage of magnesium hydroxide by large power plants can approach 2000 tons for in-house neutralization. However, using the recovered magnesium hydroxide from the ThioClear® process can avert this expenditure on commercial magnesium hydroxide which averages $200 per ton. These uses do not require the high purity commercial grade and are therefore easily adapted to the ThioClear® magnesium hydroxide.

Aside from internal uses, shipping this material to nearby facilities which have similar wastewater treatment requirements as a utility can be a viable option. At an estimated shipping cost of $2 per mile, a truck can deliver magnesium hydroxide to within a 50 mile radius at a cost of $50 per ton and thereby provide a profit to the utility of $150 per ton based on the magnesium hydroxide content.

b. Fertilizer

As mentioned in the prior section, magnesium and pH buffering of soils are important for plant growth. Magnesium hydroxide blended with gypsum, lime kiln dust, and limestone fines will serve many areas of the fertilizer markets. These blends will serve as Ca/Mg/S fertilizers.

c. High Purity

Purifying the ThioClear® magnesium hydroxide will enable this by-product to be utilized as an intermediate for the production of magnesium metal and refractory bricks.

C. HOW PROJECT RESULTS WILL IMPACT MARKETABILITY

The results of this project have provided answers to the following commercial requirements of the ThioClear® process.

- The scrubbing efficiency of this process has been successfully demonstrated in a vertical spray tower, a vertical spray/tray tower, and a proto-type horizontal absorber. These studies achieved SO_2 removals of 98% when conducted at velocities of 10 to 18 ft/sec in the vertical scrubber tower and at 10 to 25 ft./sec in the horizontal scrubber.

- Increasing the absorber gas velocity enhances the removal capability of the scrubbing liquor. Therefore, capital and operating cost savings can be realized as a result of the smaller and/or fewer scrubbers required and due to the usage of smaller and/or fewer pumps.

- Controlling the process chemistry by regulating the flowrate of the by-product recovery flow loop enables this process to maintain high SO_2 removals during boiler start-up and during periods of boiler load fluctuations.

- The stoichiometric air requirements for oxidation are similar to those required by a limestone forced oxidation process. Subsequently, capital and operating costs in this area are essentially the same.

- The process was able to operate in an automatic mode with minimal operator intervention.

- Estimated capital and operating costs of the ThioClear® are substantially lower than for a limestone forced oxidation process due to the higher efficiency in SO_2 removal, capability of operating at higher velocities, and production of saleable by-products.

In demonstrating all these attributes of the ThioClear® process at the pilot scale, no problems have been identified which should withhold the commercialization of the process. As this report is being prepared, the first demonstration scale ThioClear® facility is being operated at Applied Energy Services, Beaver Valley Cogeneration facility. In utilizing the data and operating experience gained at the pilot plant, the next level of commercialization was able to proceed. As a result of this demonstration size facility being 140 MW compared to the pilot plants comparable capacity of 1 to 5 MW, some engineering changes have been incorporated at the Beaver Valley facility. If these modifications prove successful, the ThioClear® process will be fully commercialized and ready for installation on any size plant. These results should be known within the first quarter of 1998.

D. IMPACT ON NEAR TERM USE OF OHIO COAL

In the near future, the use of Ohio Coal by utilities will be influenced by environmental regulations, utility deregulation, and in some instances, the unique circumstances of a particular utility. Environmental regulations associated with the CAAA's will require generating stations to reduce SO_2 stack emissions either by switching to a lower sulfur fuel or by installing scrubbers. Utility deregulation will force utilities to choose the lowest cost methods to achieve environmental compliance. Facilities which have an older generation FGD system installed may find it advantageous to upgrade this system to burn a high sulfur fuel if sufficient price differential exists between high and low sulfur fuel.

In the year 2000, SO_2 emissions from power plants will need to be reduced to 1.2 lb/MMBtu. This can be accomplished by fuel switching, scrubbing, or utilization and/or purchasing of SO_2 credits. Unfortunately for Ohio coals, their sulfur content will exceed these emission's limits. The impact of these regulations can be illustrated by the Phase I CAAA's influence on Ohio coal purchased by Ohio utilities. The year before the regulations, Ohio utilities purchased 47.5% of their coal utilized from Ohio sources. In 1995, the year the regulation took effect, this percentage was reduced to 36.3%.

Because of the expansion of the railroad system into the Powder River Basin which is the source of cheap, low sulfur coal, this coal is reaching markets in Ohio at a competitive price. Provided that a utility has the option and equipment to receive this fuel, it is unlikely that such a generating station will undertake a large capital investment to install scrubbers. Hence, low sulfur fuel will be the preferred method to meet SO_2 emission regulations for Phase II.

This project has demonstrated that the ThioClear® is the lowest cost method of scrubbing when compared to conventional methods. Ohio utilities which currently have scrubbers can retrofit the ThioClear® process as has been done at the AES Beaver Valley facility. These generating stations are utilizing nearly 100% Ohio coal. Subsequently, installing a

ThioClear® system may not significantly increase the need for Ohio coal but will insure that the market share of Ohio coal does not erode when Phase II regulations become effective. Ohio coal markets will increase as a result of the ThioClear® process if a sufficient price differential with low sulfur coal exists at the generating station to warrant the installation of a new scrubber facility.

The long term use of Ohio Coal may be more promising ironically, as a result of new environmental regulations. The combination of proposed regulations for PM-2.5 and reductions of Phase II emissions by 50% by the year 2007 will require utilities to investigate the use of scrubbers even if using low sulfur fuel. ThioClear® utilized in combination with low cost Ohio coal should provide the economic incentive for utilities to chose this option of meeting the proposed regulations.

E. COST COMPARISON OF COMPETING TECHNOLOGIES

The capital and operating costs of various configurations of the ThioClear® process based on the concepts demonstrated during this project were compared with the costs of an advanced forced oxidation limestone FGD process. This economic analysis was conducted with criteria established in the Electric Power Research Institute (EPRI) publication "Economic Evaluation of Flue Gas Desulfurization Systems" (EPRI GS-7193). The basis of the analysis is a 300 MW plant utilizing 2.6% sulfur coal. In order to incorporate current trends in FGD systems, the design SO_2 removal efficiency for the processes was 95% and one scrubber module was installed. Pertinent design criteria are detailed in Table IV-1.

Table IV –1

FGD Design and Economic Criteria for 300 MW Unit with a 65% Plant Capacity Factor

	LSFO	ThioClear®	ThioClear® Horizontal Wallboard	ThioClear® Horizontal Stacking
SO_2 Removal	95%	95%	95%	95%
Scrubber Modules	1	1	1	1
Scrubber Type	Spray Tower	Tray Tower	Horizontal Absorber	Horizontal Absorber
L/G Ratio	120	27	35	35
Absorber Velocity	10 fps	10 fps	25 fps	25 fps
Absorber Pressure Drop	5 in H_2O	1.9 in H_2O	6 in H_2O	6 in H_2O

Plant Life Depreciation	30 years
Capital Recovery Factor	16.5%
Inflation Rate	5.0%
Real Annual Escalation Rate	0.3%
Discount Rate	11.5%
Capital Cost Retrofit Factor	1.3
Operating Labor	$20.00/man-hour
Electricity	$50.00/MW-hr

In computing the economics, it was assumed that the gypsum production for all scenarios was the same and of wallboard quality which provided a credit of \$2/ton. The magnesium hydroxide produced by the ThioClear® process provided a credit of \$200/ton. As a result of all FGD by-products being salable commodities, no cost was associated with disposal. Additionally, no credit was taken with regards to SO_2 credits for over-scrubbing.

Annual gypsum production for the economic analysis was 89,735 tons and the magnesium hydroxide production for the ThioClear® process was 2465 tons based on the utilization of magnesium-enhanced lime containing 6% MgO. In the ThioClear® process, the utilization of magnesium-enhanced lime as the FGD reagent substantially reduces the capital costs of the SO_2 removal and reagent handling systems. This high SO_2 removal efficiency associated with the ThioClear® process liquor allows a significant reduction in the L/G required for similar removals when compared to limestone based systems. Subsequently fewer recycle pumps and spray levels are necessary which reduce the absorber height and pressure drop. Although the cost of the lime reagent, estimated at \$50/ton, is significantly higher than the estimated limestone cost at \$9.50/ton, the smaller parasitic power requirements of the ThioClear® process nullify this price differential. The results of the economic analysis are shown in Figure IV-1.

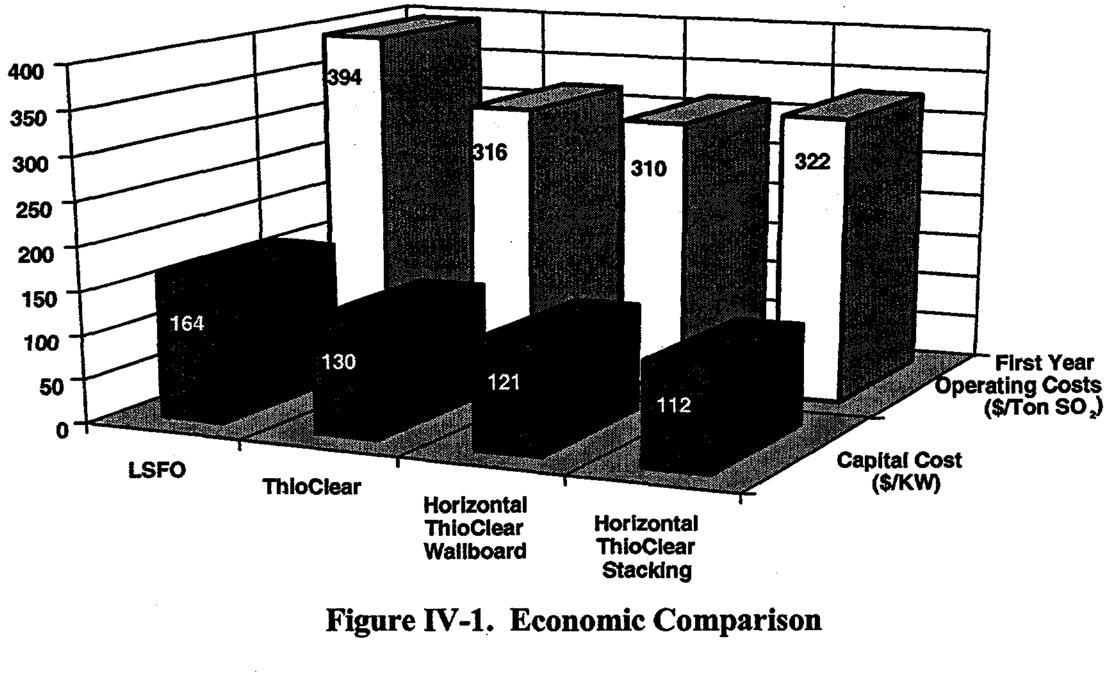


Figure IV-1. Economic Comparison

F. FUTURE EFFORTS

1. Technical

The success of this OCDO sponsored project and the resulting design criteria have enabled the ThioClear® process to move to a demonstration size operation. The installation and operation of the AES Beaver Valley Cogeneration facility in Monaca, PA will validate the pilot plant efforts and expand the design parameters beyond the limitations of the pilot plant. Pursuant to the success at this scale of operation, the ThioClear® process will be ready for full-scale commercial operation.

High velocity scrubbing whether in a vertical tower scrubber or a horizontal scrubber needs to be validated on a demonstration scale facility. As in the ThioClear® process, the installation and operating data gained at this scale will improve cost estimates and design criteria for larger scale applications. The design criteria utilized in this report's economic analysis have been conservative as a result of the wall-wetting effects of the pilot scale absorbers. Operation at the demonstration scale in which wall effects are minimized will provide a better prediction on the SO_2 removal capabilities and the cost reductions. This is important for both existing vertical scrubber towers as well as a demonstration scale packed horizontal absorber.

2. Marketing

Throughout the course of this project, Dravo Lime Company has disseminated the information gleaned from this project to potential customers. These efforts have included presentations at major conferences attended by utility representatives, meetings with existing users of the Thiosorbic FGD process and engineering companies which support the utility industry, a technology transfer open house at the Miami Fort pilot plant, and interfacing with government agencies such as OCDO to ascertain potential customers. These efforts will continue as part of Dravo's marketing strategy. Subsequently, Ohio utilities as well as out of state utilities will be made aware of the technology advancements of high velocity scrubbing and the ThioClear® process. Additionally, these advancements have been patented outside the United States as part of a plan to market these technologies abroad.

V. FINAL BUDGET SUMMATION

Table V-1

OCDO Expenditures

Budget Category	Amount Budgeted	Fund Expended
Personnel	$362,969	$366,978
Travel	$36,564	$33,109
Equipment	$110,000	$110,666
Supplies	$195,825	$195,409
Contractual	$16,500	$13,473
Indirect Charges	$346,832	$344,525
Total	$1,068,690	$1,064,160

Table V-2

Total Project Budget

Budget Category	Participant	Amount Budgeted	Fund Expended
Personnel	OCDO	$362,969	$366,978
	CG&E	$0	$0
	DLC	$151,720	$153,338
Travel	OCDO	$36,564	$33,109
	CG&E	$0	$0
	DLC	$36,564	$33,106
Equipment	OCDO	$110,000	$110,666
	CG&E	$0	$0
	DLC	$110,000	$110,665
Supplies	OCDO	$195,825	$195,409
	CG&E	$15,000	$0
	DLC	$195,825	$210,540
Contractual	OCDO	$16,500	$13,473
	CG&E	$80,000	$0
	DLC	$16,500	$93,474
Indirect Changes	OCDO	$346,832	$344,525
	CG&E	$0	$0
	DLC	$560,974	$569,616
Total	OCDO	$1,068,690	$1,064,160
	CG&E	$95,000	$0
	DLC	$1,071,583	$1,170,739