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PROJECT: ZIMMER SLIPSTREAM MAGNESIUM  
HYDROXIDE RECOVERY DEMONSTRATION

GRANTEE: DRAVO LIME COMPANY  
ONE OLIVER PLAZA  
PITTSBURGH, PA 15222

PROJECT MANAGER: KEVIN SMITH

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## I. REPORT SUMMARY

Dravo Lime has for many years supplied magnesium containing lime in the ranges of 3-6% MgO. Several years ago Dravo Lime realized the potential operating savings its FGD customers could benefit from if magnesium could be recovered from FGD waste streams. As a result, several different proprietary processes have been developed for the recovery of magnesium hydroxide. These recovery processes include steps for magnesium hydroxide separation, purification, and crystal growth. The process implemented at The Cinninnati Gas and Electric Company's Wm. H. Zimmer Station was first piloted by Dravo Lime Company at Allegheny Power System's Mitchell Station near Monongahela, PA during the fourth quarter in 1989 and first quarter in 1990.

This pilot work was the foundation for further development of the ThioClear process at Dravo's pilot plant at CG&E's Miami Fort Station. The ThioClear process is a closed loop version of the magnesium hydroxide recovery process with the same unit operations and products but also including an absorber tower for scrubbing flue gas. Testing at Miami Fort of the ThioClear process led to improvements in separation of magnesium hydroxide from gypsum that are part of the magnesium hydroxide recovery process installed at Zimmer Station.

CG&E and Dravo Lime Company, with co-funding from Ohio Coal Development Office and Electric Power Research Institute, successfully demonstrated recovery of magnesium hydroxide, from the magnesium-enhanced lime FGD process at CG&E, W. H. Zimmer Station in Moscow, Ohio. The slipstream oxidation and magnesium recovery plant was installed for less than \$0.83/kW and operated by Dravo Lime Company from May 1994 till January 1995. Operation of the plant has since been taken over by Zimmer FGD personnel, to produce all of the magnesium hydroxide slurry required on site for acid stream neutralization purposes. These include boiler bottom ash dewatering streams, boiler discharge water, and storm drain water. Purchase of commercial magnesium hydroxide slurry is no longer necessary. In 1993, Zimmer Station purchased around \$350,000 worth of commercial grade magnesium hydroxide slurry for acid stream neutralization purposes. An economic analysis of the operation at Zimmer Station

indicates that  $\text{Mg}(\text{OH})_2$  slurry is produced for a levelized O & M cost of \$22/dry ton plus a levelized capitalization cost of \$71/dry ton, totaling \$93/dry ton. These operating costs can be alternately expressed as \$0.93/ton  $\text{SO}_2$  removed or \$0.05/coal consumed. This report discusses the results of testing that has occurred over nine months of operating the magnesium hydroxide recovery plant.

## II. EXECUTIVE SUMMARY

### A. Project Results

The presence of highly soluble alkaline magnesium species in magnesium enhanced lime FGD liquor, makes possible SO<sub>2</sub> removal efficiencies as high as 98 to 99%. At the Zimmer Station, the FGD system uses reagent lime that averages 3 to 6 weight % magnesium. The magnesium typically leaves the FGD system as a dissolved salt and is landfilled along with the waste calcium sulfite solids. It was recognized that these liquid phase salts can be oxidized and treated with lime to produce magnesium hydroxide and gypsum solids. Demonstration of this process at the Wm. H. Zimmer FGD system was particularly suited due to its strong magnesium chemistry and tight water balance. A 100 gallon per minute slipstream plant was designed and built to take FGD thickener overflow, oxidize the liquor with air, then treat with lime to form gypsum and magnesium hydroxide solids. These two products are separated with hydroclones, with the magnesium hydroxide concentrated in a conventional thickener and the gypsum sent back to the FGD system for ultimate disposal. The ultimate goal is to extract magnesium from the FGD system, reduce the loss of magnesium to the FGD waste landfill, while not significantly affecting the FGD process.

CG&E and Dravo Lime Company successfully demonstrated recovery of magnesium hydroxide, from the magnesium-enhanced lime FGD process at CG&E, W. H. Zimmer Station in Moscow, Ohio. The slipstream oxidation and magnesium recovery plant was installed for less than \$0.83/kW and operated by Dravo Lime Company from May 1994 till January 1995. This includes \$782,000 for the magnesium hydroxide plant battery limit and \$300,000 for support systems that integrated the plant with the rest of the FGD system.

Operation of the plant has since been taken over by Zimmer FGD and material handling personnel, to produce all of the magnesium hydroxide slurry required on site for acid stream

neutralization purposes. These include boiler bottom ash dewatering streams, boiler discharge water, and coal pile runoff water. Purchase of commercial magnesium hydroxide slurry is no longer necessary. 1993 purchases of commercial magnesium hydroxide slurry amounted to about \$350,000.

## **B. Commercialization Potential of This Technology**

Currently operation of the magnesium hydroxide recovery facility at the Wm. H. Zimmer Station has become seamless within the FGD system. This facility has sufficient capacity to provide for Wm. H. Zimmer's internal needs and those of CG&E's nearby power stations if desired. This project has demonstrated the slipstream magnesium hydroxide recovery process to be easily integrated within an existing magnesium enhanced lime FGD process and to produce a valuable commodity that saves a utility money.

The technology successfully demonstrated in this project, can be immediately implemented at stations utilizing magnesium enhanced lime FGD, particularly at sites where more than 800 Mwe combined are scrubbed. Larger FGD systems are more suited for this technology because the slipstream magnesium hydroxide recovery process demonstrated at Zimmer station, though relatively small compared to the FGD system, is full scale. Absolute capital expense to build this plant elsewhere would be the same, however smaller magnesium enhanced lime FGD systems could not produce the same quantity of magnesium hydroxide. Capitalization and operating costs would be spread over less product produced, obviously increasing production costs. The economics become more attractive, as this technology is utilized in FGD systems that are larger than 800 Mwe. Gavin station, where 2300 Mwe is scrubbed, would be an ideal second site for utilizing this technology, if there is an appropriate demand for magnesium hydroxide slurry.

### **C. Projected Capital and Operating Costs**

An analysis of operating costs at Zimmer station were performed by levelizing costs over 15 years at a capacity factor of 85% (2954 tpy dry magnesium hydroxide). The analysis indicates that  $Mg(OH)_2$  slurry is produced for a levelized O & M cost of \$22/dry ton plus a levelized capitalization cost of \$71/dry ton, totaling \$93/dry ton. This cost includes \$13/dry ton for fixed costs items such as maintenance materials, maintenance labor and administration and support labor. Operating labor contributes nothing to the cost of production since no new labor was necessary. Variable operating costs total \$9/dry ton for electricity to operate equipment. Reagent lime used by the process is not factored into variable operating costs because the lime used for magnesium hydroxide recovery is that much less lime used for FGD waste stabilization. Magnesium hydroxide production cost can be expressed alternatively as \$0.93/ton  $SO_2$  removed or \$0.05/coal consumed.

### **D. Waste and By-Products**

For every ton of dry magnesium hydroxide produced by this plant, about 2.25 tons of gypsum are produced. Currently gypsum produced by the plant is pumped back to Zimmer's FGD thickener center wells where the gypsum is thickened with the FGD solids waste. The gypsum is then filtered and landfilled with the other FGD waste. This gypsum is less than 0.6% of the total FGD waste produced and minimally affects the cost of FGD waste disposal.

### **E. Effects of This Project on Ohio Coal Use**

Coal fired electric power stations burning high sulfur Ohio coal are already faced with scrubbing to meet environmental constraints. Magnesium enhanced lime FGD is a proven technology to economically meet environmental regulations. The technology demonstrated in this project,

coupled with magnesium enhanced lime FGD can help utilities cope with the other effects of burning Ohio coal, i.e. coal pile runoff and bottom ash slurry neutralization. Sodium hydroxide is typically used to neutralize these acidic streams and can be purchased for the equivalent of \$280/dry ton  $Mg(OH)_2$  (Chemical Marketing Reporter; 16 February 1996). As mentioned previously, magnesium hydroxide slurry can be produced for \$93/dry ton. If used on site, little additional cost is incurred. If the product is to be used offsite, transportation costs will naturally be incurred. If large quantities of product slurry are to be transported offsite, then concentration of the slurry to 50% solids may be desirable, incurring further costs. However, the ultimate cost per dry ton of magnesium hydroxide should still be below the cost of procuring commercial grade magnesium hydroxide or sodium hydroxide.

## **F. Anticipated Next Steps**

### **1. Product Development**

Dravo Lime realized the need to produce high purity magnesium hydroxide several years ago when it performed a marketing survey for magnesium hydroxide. The higher the purity of the magnesium hydroxide the higher the product value. The \$180-200 is a conservative figure and is set to compete with the lower grade materials. Dravo Lime has patented a process using the solubility differences of magnesium hydroxide and gypsum to purify magnesium hydroxide. Magnesium hydroxide has a solubility of 9 mg/L while gypsum is around 2400 mg/l varying slightly with chloride concentrations. The magnesium hydroxide can be purified by dissolving the gypsum away with fresh water. The water and pure magnesium hydroxide can then be separated in an additional small thickener. The thickener overflow can be used as a portion of the make-up water needed by the FGD system. Pure magnesium hydroxide can be dewatered further by centrifuging or filtering. The MgO quality achieved with the dissolution procedure places the magnesium hydroxide product in the higher value category.

Work with the U.S. Dept. of Agriculture has shown gypsum to be excellent for soil amendment and conditioning. Gypsum provides much needed calcium and sulfur to plants, the sulfates also react with free aluminum in soil to reduce the aluminum toxicity of the soil. Magnesium hydroxide impurities in the gypsum help to improve the pH of the soil and provides some of the plants magnesium requirement. This fertilizer is especially applicable to Appalachian soils. The gypsum product could also be sold either to wallboard or cement manufacturers. Gypsum that has a modest amount of magnesium hydroxide contamination may also be suitable for use in producing portland cement. Currently portland cement producers are paying between \$16 to \$22/ton for natural gypsum delivered by barge or rail. In all of these applications, gypsum will need to be dewatered and agglomerated to aid in handling.

With the above in mind, a project was conceived to produce and evaluate magnesium hydroxide and gypsum byproducts that could be used in agriculture and portland cement production. Cincinnati Gas & Electric, Ohio State University School of Agriculture, and Dravo Lime Company have begun to use the magnesium hydroxide production facility at Zimmer station to produce quantities of byproducts to test. This project began in July 1995 and will proceed for two years. Approximately 600 tons of gypsum will ultimately be produced and processed for optimum use in the agriculture and portland cement industries. Up to 40 tons of magnesium hydroxide slurry will be purified (gypsum washed out) and thickened to commercial grade specifications for evaluation.

## **2. Commercialization Efforts**

The work of this project has been described in papers and presentations by Dravo Lime Company. Interest has been expressed in the technologies by two existing Dravo Lime customers and numerous engineering firms. Dravo Lime Company will continue to promote this technology and work toward establishing several more magnesium hydroxide recovery facilities along the Ohio River and in particular in Ohio.

## G. Magnesium Hydroxide Product Quality, Value and Use

In 1989, 1,144,000 metric tons of MgO was used in the U.S. Since 1989, magnesium hydroxide and magnesium metal demands have increased significantly. Magnesium hydroxide is replacing NaOH as the reagent of choice for acid neutralization. There are several reasons for this change. First magnesium hydroxide has twice the neutralization capacity on a molar basis as NaOH. Secondly, magnesium hydroxide is now much less expensive than NaOH or Na<sub>2</sub>CO<sub>3</sub>. Thirdly, when magnesium hydroxide is used as a neutralizing agent the natural end point or maximum solution pH possible is 9.0. This is equivalent to the NPDS discharge limit. Overshooting pH using magnesium hydroxide is not possible. Fourth, it has been found that the treatment of most waste liquids with magnesium hydroxide results in less settled sludge than the same liquids treated with NaOH or Na<sub>2</sub>CO<sub>3</sub>. The use of magnesium metal in alloys is increasing because of its strengthening properties and its light weight.

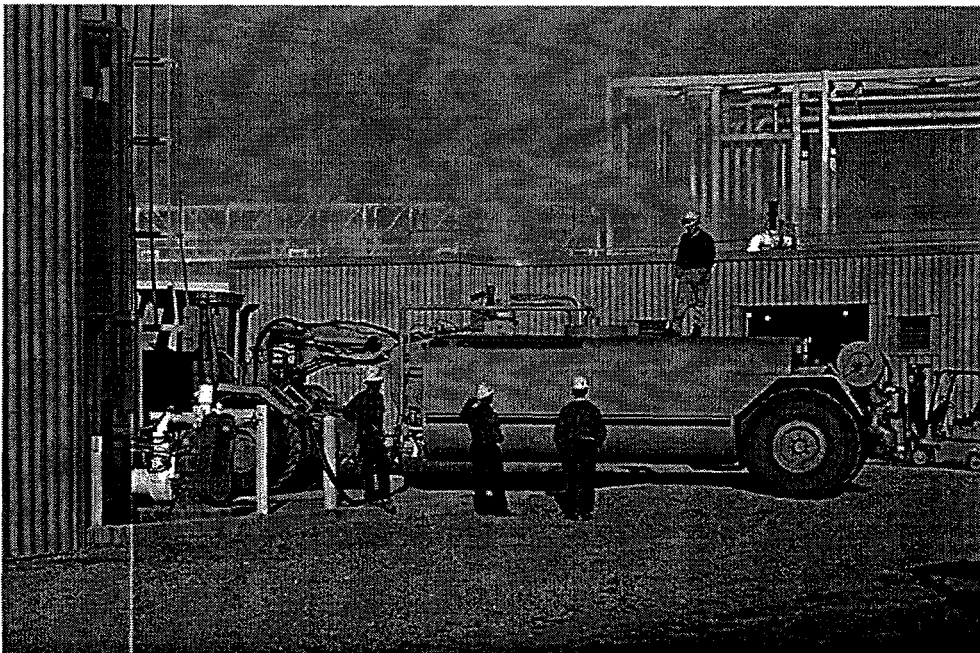


Figure 1. Loading tanker with magnesium hydroxide slurry for distribution within the Zimmer station site.

### III. INTRODUCTION

The Clean Air Act of 1990 mandates a substantial reduction in emissions of sulfur dioxides (SO<sub>2</sub>) from 261 coal-fired electric generating units in the U.S. Forty-one of these units are located in Ohio. National SO<sub>2</sub> emissions are to be reduced by 10 million tons per year in two phases beginning in 1995. Eighteen percent of those reductions are required in Ohio. In addition, a "cap" on national SO<sub>2</sub> emissions will require more stringent control of emissions for new units than is currently required.

As noted in the 1990 Ohio Coal Development Agenda, coal-fired electric utilities constitute the principal market for Ohio coal, accounting for 92% of Ohio production in 1988.<sup>1</sup> Displacement of higher sulfur Ohio coal by lower sulfur out-of-state coal to meet required SO<sub>2</sub> reductions will result in a continued decline in Ohio coal production. Accordingly, the 1990 Ohio Coal Development Agenda states that its most important objective is to develop a slate of near-term options for use on existing coal-fired utility boilers for control of sulfur dioxide emissions. The principal traits sought in such a control technology option is high SO<sub>2</sub> removal efficiency coupled with high cost-effectiveness.<sup>2</sup> Wet scrubbing is the leading proven commercial retrofit post-combustion FGD technology to effect SO<sub>2</sub> reductions required by the Clean Air Act. In some cases, wet scrubbing is the only post-combustion technology available in the near future that can meet the reduction requirements.

In addition, the Act offers incentives for use of high-efficiency wet FGD technology through provision for accumulation of excess emissions allowances if control targets are exceeded. These allowances can be used to meet reductions required at other affected units, to offset emissions from new units, or to be traded for cash. While conventional wet FGD can achieve SO<sub>2</sub> removal of 90% these provisions offer substantial additional incentive to achieve SO<sub>2</sub> removal of 98-99%.

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<sup>1</sup> Ohio Coal Development Office, 1990 Ohio Coal Development Office Agenda, January, 1990, p. 28

<sup>2</sup> Ohio Coal Development Office, 1990 Ohio Coal Development Office Agenda, January, 1990, p. 31

One of the leading wet FGD technologies for control of SO<sub>2</sub> emissions is the Thiosorbic lime process. The Thiosorbic, or magnesium-enhanced, lime process was developed by Dravo Lime Company specifically for scrubbing flue gas from high-sulfur coals like those found in the State of Ohio. The process is widely used in the electric utility industry today. Over 14,000 MW of electric generating capacity use the Thiosorbic process for scrubbing their flue gas from burning high-sulfur coal. An impediment to use of conventional wet FGD is the high cost. A study of the costs of retrofit of wet FGD to several Ohio electric utility stations found that conventional FGD cost would be expected to be over \$500 per ton of SO<sub>2</sub> removed or about \$30 per ton of coal for units at high capacity factor and burning high-sulfur coal.<sup>3</sup> Since wet FGD is the only proven near term post-combustion option to achieve strict emission reductions, determining what improvements and advancements can be made to reduce cost using wet FGD systems is important to support continued use of higher-sulfur Ohio coal.

One of the primary costs associated with magnesium enhanced lime FGD is disposal of the solids generated from the process. The proposed magnesium hydroxide recovery demonstration plant offset these costs by the following:

- Reducing the volume of by-product solids to dispose via recovery of magnesium hydroxide for resale or reuse.
- Reducing the volume of by-product solids to dispose by improving the solids content of these solids. Improved solids dewatering is foreseen to result as a consequence of improved nucleation and crystal growth of calcium sulfite solids formed in the scrubber liquor. Improved crystal growth of these solids will result from lime slaking with the gypsum saturated recycled liquor from the magnesium hydroxide recovery plant.

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<sup>3</sup> Laseke, B. A., Johnson, H. J., and Berger, D. A., Evaluation of Flue Gas Desulfurization as an Acid Rain Control Strategy for Utility Coal-Fired Boilers in the State of Ohio, Paper presented at the Tenth EPA/EPRI Joint Symposium on FGD, Atlanta, GA, November, 1986, p. 19-21

Decreased solids by-product disposal costs resulting from this demonstration project will make magnesium enhanced lime FGD a more economically attractive SO<sub>2</sub> emissions control option for Ohio utilities and other utilities burning Ohio high-sulfur coals.

The Cincinnati Gas And Electric and Dravo Lime Companies constructed and operates a 100 gpm bleed stream magnesium hydroxide recovery demonstration plant. The demonstration plant was constructed at CG&E's Zimmer Station, in Moscow, Ohio. Construction took approximately 9 months and testing lasted about 9 months. The co-sponsors for this project were the Ohio Coal Development Office (OCDO) and the Electric Power Research Institute (EPRI).

The objective of the project was to perform the final stages of process development and to demonstrate a process for magnesium hydroxide recovery from the magnesium enhanced lime FGD process. The magnesium enhanced lime scrubbing process has proven to be extremely compatible with Ohio Coals. When this process is used in conjunction with high sulfur coals, SO<sub>2</sub> removals of 98-99% are achievable. The presence of the highly soluble alkaline magnesium species makes this high SO<sub>2</sub> removal on high sulfur coals possible. At the Zimmer Station the FGD System uses an average 6% magnesium and a 92% calcium lime as the reagent. The calcium leaves the FGD system as solid calcium sulfite, and the magnesium leaves the system as a dissolved salt. If recovered, this magnesium can be a high value product. The market value of a low grade magnesium hydroxide is between \$150 to \$200/ton. Zimmer Station previously disposed of between 6 and 7 tons of dissolved magnesium salts (MgSO<sub>4</sub>, MgSO<sub>3</sub>, and MgCl<sub>2</sub>) per hour. These liquid phase salts could be treated with lime slurry to produce more calcium sulfate and magnesium hydroxide solids. The method for the recovery of magnesium hydroxide is to treat a slipstream of thickener overflow liquor from the magnesium enhanced scrubbing process with lime. (See Figure 2). The calcium salts are separated from the magnesium hydroxide by mechanical means. The magnesium extracted from the system in this fashion reduces the otherwise occurring magnesium losses with the filter cake solids and will not significantly change the nature of the current FGD scrubbing process.

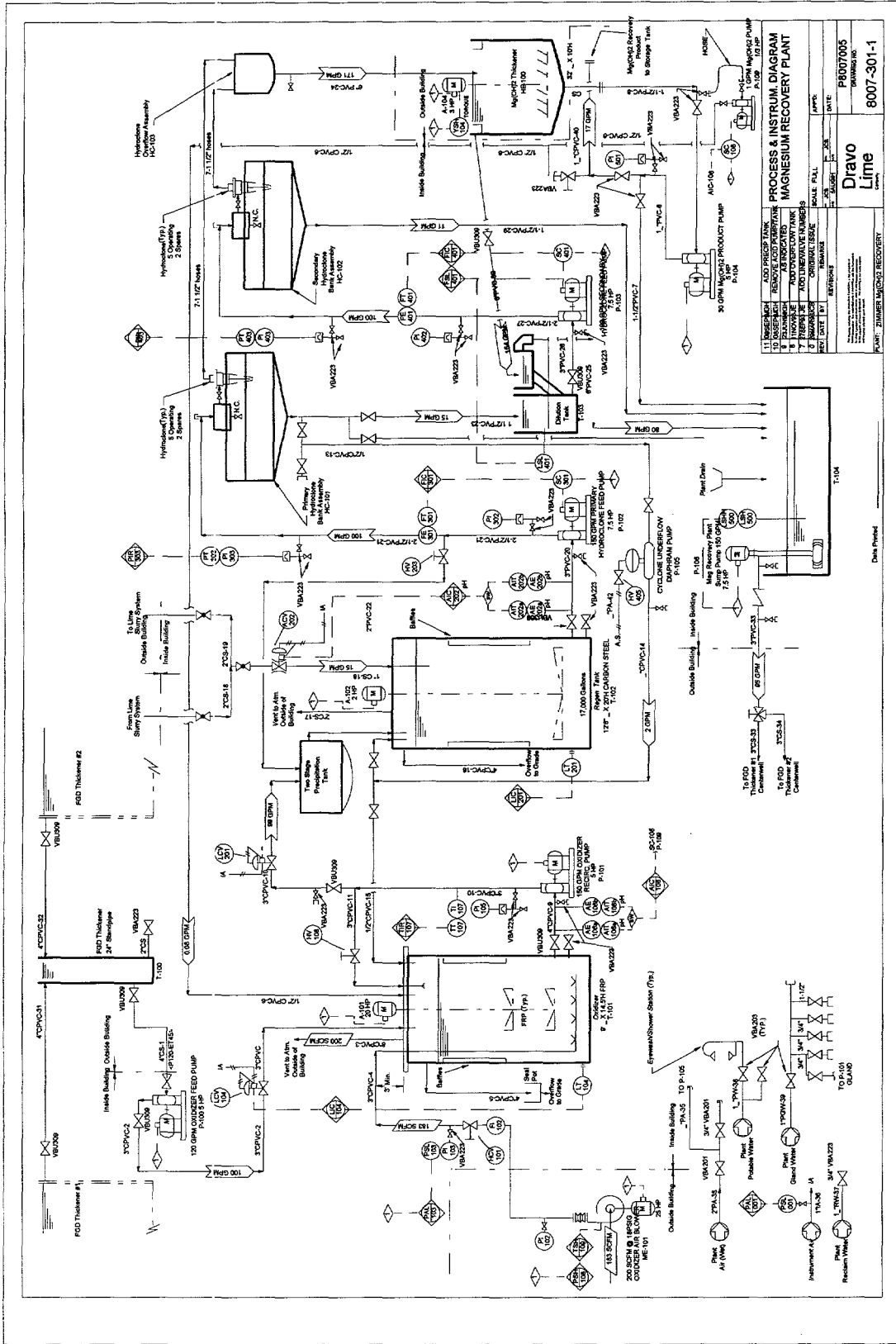


Figure 2. Process and Instrumentation Diagram

Figure 2. Process and Instrumentation Diagram

A 100 gpm slipstream from an FGD process with a strong magnesium chemistry and a tight water balance can produce up to 1000 lbs. of magnesium hydroxide per hour. The effect of this slip stream on the performance of the scrubber would be to reduce the recycle liquor alkalinity marginally. This 1/2 ton per hour magnesium hydroxide product plant will recover approximately an eighth of the magnesium leaving the system with the calcium sulfite sludge. Magnesium hydroxide has many other uses including animal feed, fertilizer, and acid neutralization.

Zimmer Station was using commercial magnesium hydroxide for water treatment to neutralize acidic waste streams. The product magnesium hydroxide from this recovery process has been substituted with no detrimental effects. The demonstration tests were necessary to improve magnesium hydroxide recovery, magnesium hydroxide crystal properties, magnesium hydroxide filtering capabilities and product purity. The supplemental income resulting from the possible sale of magnesium hydroxide will improve the overall scrubbing economics towards the use of higher sulfur coal by encouraging use of the highly efficient magnesium enhanced lime FGD scrubbing process for SO<sub>2</sub> emission control rather than fuel switching to low sulfur non-Ohio coals. Zimmer Station now has a source of magnesium hydroxide readily available for waste acid neutralization on site which will avoid the need for purchasing magnesium hydroxide for this purpose from outside sources.

#### **A. Project Objective**

Thiosorbic lime was developed to scrub flue gas resulting from the burning of high-sulfur coals. Magnesium contained in Thiosorbic lime causes the scrubbing solution to have a high dissolved scrubbing alkalinity with consequent high capacity to absorb SO<sub>2</sub>. Improvements in FGD systems designed to use Thiosorbic lime developed in pilot testing would be readily incorporated into new or retrofit FGD systems.

One of these improved process developments is the ThioClear process. (See ThioClear Process - Figure 3) The ThioClear process uses the same magnesium enhanced SO<sub>2</sub> removal chemistry as the Thiosorbic process coupled with an oxidation system for the production of gypsum (CaSO<sub>4</sub>•2H<sub>2</sub>O) from the absorbed SO<sub>2</sub>. A secondary by-product of the ThioClear process is the production of magnesium hydroxide.

Magnesium enters the process in the lime which is about 3-6% MgO. The magnesium leaving the FGD plant has to balance this. In the Thiosorbic process, the MgO typically leaves the plant as MgCl<sub>2</sub>, MgSO<sub>3</sub>, MgSO<sub>4</sub> or a combination of these in solution in the liquid portion of the filter cake. The ThioClear process allows the recovery of solid phase magnesium hydroxide. The ThioClear process was developed at Dravo's Miami Fort Pilot Plant and is ready to be demonstrated as a commercial process. An adaptation of this process allows for recovery of magnesium hydroxide and gypsum from plants already using the Thiosorbic process.

Slipstream recovery of magnesium hydroxide diverts a slipstream from the thickener overflow of an FGD plant (See Figure 5) currently using magnesium enhanced lime scrubbing. Figures 3, 4 and 5 present flow diagrams for each process. Figure 6 summarizes and contrasts these different processes.

In the magnesium hydroxide recovery process for a plant such as Zimmer that operates with a tight water balance, the magnesium can be recovered without affecting SO<sub>2</sub> removal. The quantity of gypsum recovered by this slipstream process would be very small as most of the sulfites in the Thiosorbic process are processed as calcium sulfite (CaSO<sub>3</sub>•1/2H<sub>2</sub>O) solids through the thickener underflow.



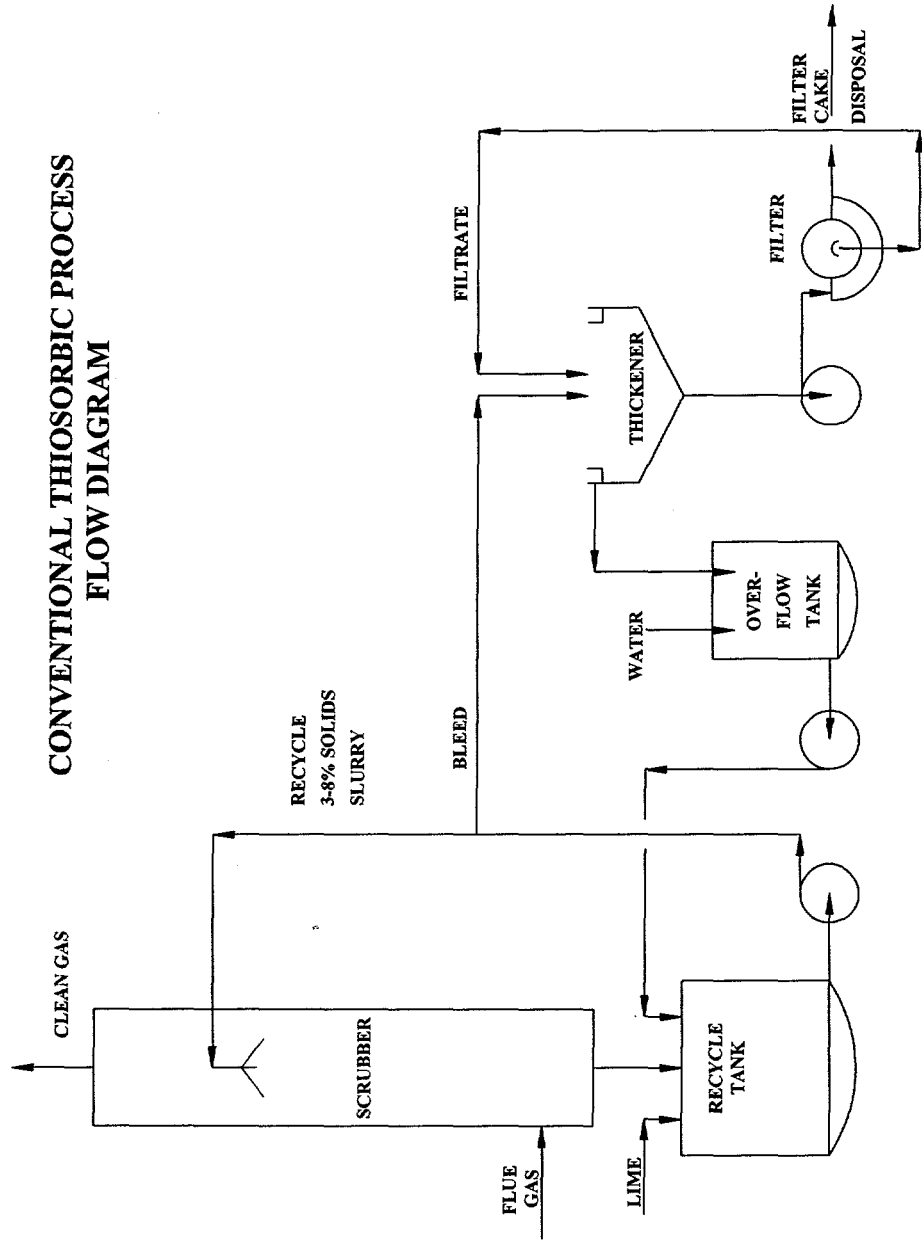


Figure 4. Conventional Thiosorbic Process Flow Diagram

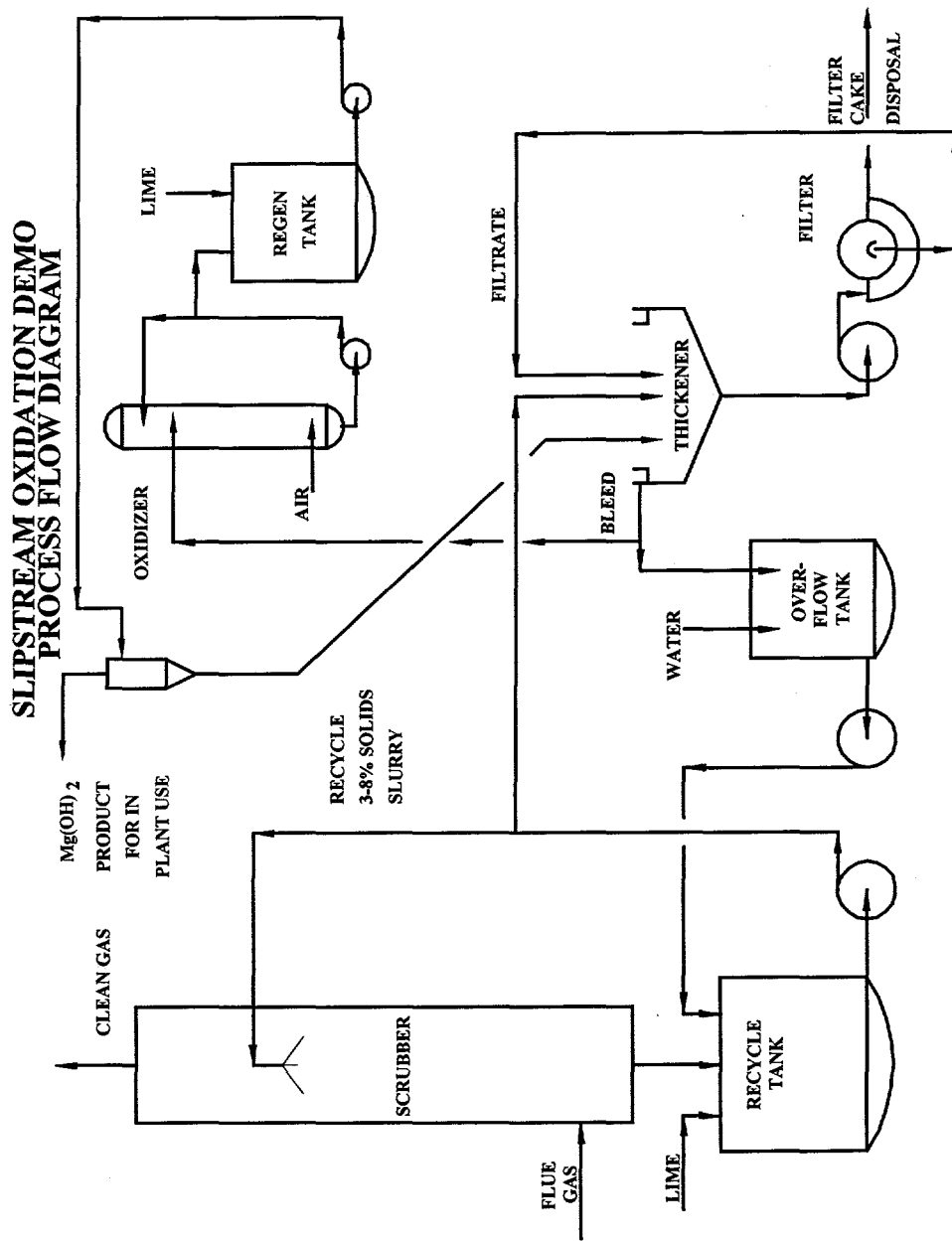


Figure 5. Process Flow Diagram

Process	Conventional Thiosorbic	ThioClear	Slipstream Oxidation	Oxidation Inhibition
Recycle Stream Solids Content	3-8 wt. %	< 1 wt. %	3-8 wt. %	3-8 wt. %
Product Solids	Primarily CaSO <sub>3</sub> , some CaSO <sub>4</sub>	Primarily Gypsum and Mg(OH) <sub>2</sub>	Primarily CaSO <sub>3</sub> and some Mg(OH) <sub>2</sub>	Primarily CaSO <sub>3</sub>
Cake Quality	About 45% Solids	Over 80% Solids Gypsum Product	About 45% Solids	About 50-55% Solids
Process Control	Simple, forgiving	Load sensitive needs additional work	Same as Thiosorbic	Need to watch Mg level with good water balance
Equipment	Basic FGD system for lime scrubbing	Oxidation system equipment additional	Oxidation system equipment additional (but smaller)	Sulfur addition system new
Current Status	Commercially accepted and well proven.	Initial pilot test very promising. Demonstration project a success.	Demonstration project a success.	Commercially demonstrated at several utilities.
Advantages	Low first cost. High removal capability. Highly reliable control	Excellent cake quality. Salable Mg(OH) <sub>2</sub> product. Clean nozzles and system.	In plant usable Mg(OH) <sub>2</sub> product. Retains advantages of Thiosorbic process.	Dewatered cake significantly higher % solids than Thiosorbic process. Easy retrofit.
Disadvantages	Poor Cake quality. Expensive landfill.	Additional equipment cost.	Poor cake quality. Minor additional equipment cost.	Cake still is not stackable without additives.
Process Patent Status	Dravo Patented	Dravo Patented	Dravo Patented	Dravo Patented

Figure 6. Comparison of Magnesium Enhanced Lime Scrubbing Processes

## B. Overall Project Objective

The objective of this project was to construct and operate a demonstration scale magnesium hydroxide recovery facility at Zimmer Station. The plant includes an oxidation tower for the conversion of magnesium sulfites to sulfates, a regeneration tank for the precipitation of calcium sulfate and magnesium hydroxide by the addition of lime slurry, mechanical separation devices for separating gypsum from magnesium hydroxide, and a thickener for magnesium hydroxide concentration. A premix tank was added for more extensive crystallization studies. Testing began after the construction of the facility was completed. The specific technical objectives included:

- Demonstrate magnesium hydroxide production from this type of commercial FGD facility.
- Reduce the solid waste from power plant scrubbers by recovering a portion as usable or salable products.
- Reduce scrubber operating cost by recovering a high value product that could be sold. Scrubber system reagent cost could be offset as much as 20% by this method of magnesium hydroxide recovery.
- Resolve operating and technical process problems such as oxidation, pH, crystallization time, liquid phase magnesium ion concentration, liquid recycle rate, hydroclone operation, lime type, mechanical separators, and dewatering equipment.
- Test a magnesium hydroxide purification system that can be incorporated into the Thiosorbic process scrubber operation that actually improves scrubber operation. A Dravo Lime Company tested method of purifying magnesium hydroxide is done by dissolution of the contaminant gypsum with water. The gypsum saturated water is then used in the slaking process of the main scrubber.  $\text{Ca(OH)}_2$  slaked in this manner and subsequently

used in scrubber operations produces better crystal growth of the  $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$  particles precipitated in the scrubber liquor. This improves solids dewatering, tightens the water balance, and decreases the total amount of solids leaving the plant. The tighter water balance makes more magnesium available for improved scrubber operations and magnesium hydroxide recovery.

- Produce a gypsum/magnesium hydroxide mixed phase as a fertilizer. This fertilizer will be tested on a long term basis. Calculations from the scrubber chemistries indicate that the precipitated gypsum and magnesium hydroxide as a combined product have the exact composition necessary for a fertilizer that is currently being sold commercially.
- Utilize product magnesium hydroxide as a substitute for NaOH or purchased magnesium hydroxide in the power plant's acid treatment system.
- Produce a high purity magnesium hydroxide that can be used for higher valued purposes and sold for greater than \$200/ton.

The magnesium hydroxide recovery facility is capable of producing a high purity magnesium hydroxide, an intermediate purity magnesium hydroxide and a combined magnesium hydroxide/gypsum product for use as fertilizer. The high purity and intermediate products will be available for water purification or animal husbandry. The dewatering properties of the products have been maximized on a laboratory scale to reduce shipping costs.

## IV. TECHNICAL DISCUSSION

### A. Magnesium Hydroxide Recovery Process Description

The Thiosorbic Magnesium-Enhanced lime wet FGD process was developed during the early 1970's specifically to remove sulfur dioxide from stack gases resulting from the combustion of high-sulfur coal. This process requires use of lime containing 3 to 6 weight percent magnesium oxide (MgO) for SO<sub>2</sub> capture in a wet flue gas desulfurization (FGD) system. Magnesium acts as a catalyst to improve SO<sub>2</sub> removal and to eliminate scaling which can occur in wet scrubbing systems. The key to the process is the generation of a scrubbing slurry with a high capacity to absorb SO<sub>2</sub>. Calcium oxide comprises the bulk of the lime and when added to the scrubber, reacts with SO<sub>2</sub> to form an insoluble compound, calcium sulfite (CaSO<sub>3</sub>). The MgO, contained in Thiosorbic lime, reacts with SO<sub>2</sub> to form a soluble salt, magnesium sulfite (MgSO<sub>3</sub>). Being highly soluble, magnesium sulfite accumulates in solution and is brought into contact with the flue gas to absorb SO<sub>2</sub>. Dissolved MgSO<sub>3</sub> in the scrubber liquor rapidly neutralizes absorbed SO<sub>2</sub> while increasing SO<sub>2</sub> removal capacity (alkalinity) compared to when MgSO<sub>3</sub> is absent (ex: lime/limestone without Mg being present).

The magnesium hydroxide recovery process begins by taking a small slipstream from the FGD thickener overflow (TOF). The magnesium rich TOF stream is normally recycled back to the scrubber to maintain liquid level. Magnesium in solution leaves the FGD system as part of the thickener underflow stream. Since magnesium is routinely lost in this way, the magnesium level of the scrubber can be decreased via the TOF slipstream bleed without significantly affecting the SO<sub>2</sub> removal. The clear TOF is fed to the top of an oxidation tower that is designed to maximize liquid/air contact for the oxidation of the sulfites to sulfates.

The oxidized liquor is bled to a precipitation or regeneration tank. Lime slurry is added to this tank to maintain pH between 10.5 and 10.8. Magnesium hydroxide and gypsum simultaneously precipitate.

The double precipitation is followed by mechanical separation of the two compounds. Hydroclones are used to separate relatively small magnesium hydroxide crystals (<10m) from the larger gypsum crystals (>50m). The overflow from the hydroclones, rich in magnesium hydroxide, is thickened and stored in an agitated tank where it can be delivered for acid neutralization via an on-site tanker.

The gypsum by-product, underflow from the separation process, is sent back to the FGD thickener. In the thickener it settles and exits the scrubbing system via the dewatering equipment.

### **B. Magnesium hydroxide Recovery Process Chemistry**

The magnesium hydroxide recovery facility uses TOF liquor as feed. This thickener overflow contains dissolved magnesium. This magnesium is in the form of  $MgSO_3$ ,  $Mg(HSO_3)_2$ ,  $MgCl_2$  and  $MgSO_4$ .

In the oxidizer the sulfites are oxidized to sulfates by the following reactions:

- 1)  $MgSO_3 + \frac{1}{2} O_2 \rightarrow MgSO_4$
- 2)  $Mg(HSO_3)_2 + O_2 \rightarrow MgSO_4 + H_2SO_4$

The oxidized solution is pumped to the crystallization tank where it is reacted with lime slurry. The following reactions occur in the crystallization tank:

- 3)  $MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow Mg(OH)_2 + CaSO_4 \cdot 2H_2O$
- 4)  $MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$
- 5)  $H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O$

Excess gypsum and liquor (containing  $CaCl_2$ ) are added back to the FGD thickener centerwell.

### C. Plant Equipment

The magnesium hydroxide recovery plant process flow diagram (Figure 2) and material balances (Appendix I) for both Black River (3 % MgO content) lime and Maysville (6 % MgO content) lime have been included. The feed material for this plant is a 100 gpm TOF bleed stream from the FGD process. The TOF is fed to a 7,000 gallon agitated oxidizer column. In the oxidizer, the sulfite is converted to sulfate. The required air is produced by an air blower (25 Hp) capable of providing an air flowrate of 220 SCFM. This tank is equipped with an agitator to increase the amount of surface area of the air bubbles. Air is entered into the bottom of the tank through a single open pipe located beneath the blade of the Chemineer CD-6 agitator (20Hp). This arrangement is shown below (Figure 7). The blade essentially breaks the large air bubbles up into smaller ones giving the air bubbles more surface area and a better ability to dissolve oxygen.

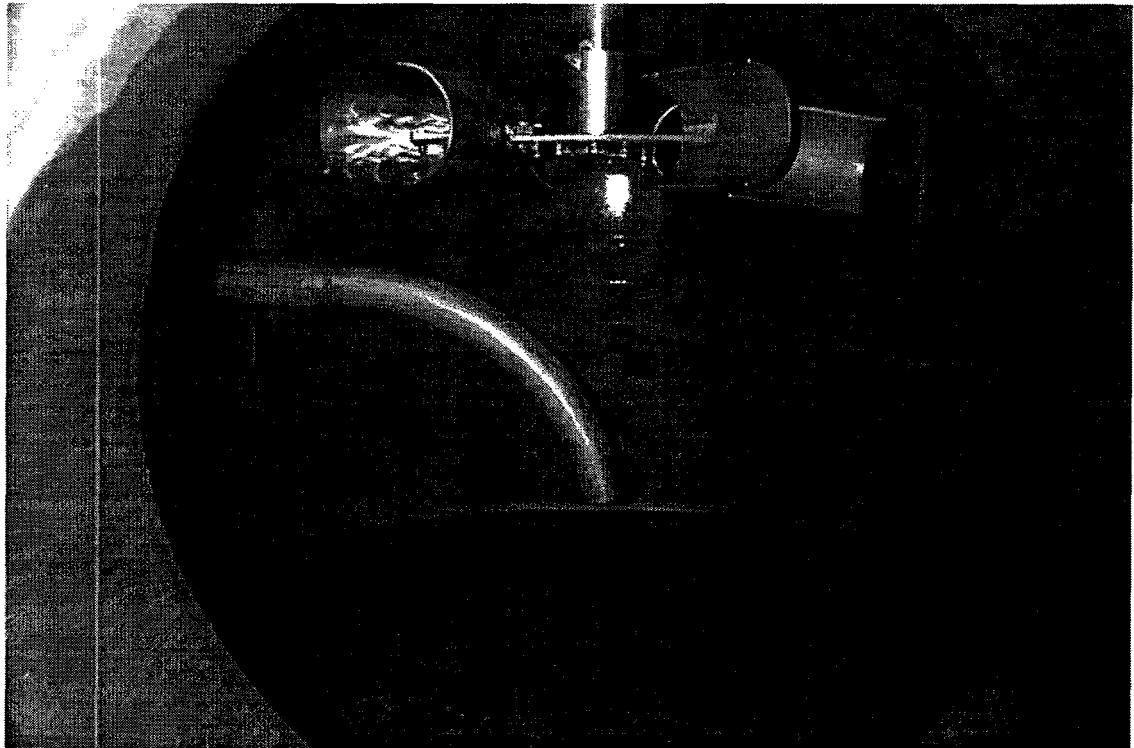


Figure 7. Chemineer CD-6 Agitator blade and single open pipe through which air is entered into the oxidizer.

Sulfuric acid and magnesium hydroxide (from magnesium hydroxide thickener underflow) were originally designed to be alternately used to maintain oxidizer pH at around 5.5. However, the sulfuric acid system was abandoned due to the acid producing chemical reaction (2). The acid metering pump was converted to add polymer to the magnesium hydroxide thickener for testing of polymer addition to magnesium hydroxide for improved settling characteristics. Gypsum from the cyclone underflow can also be added to the oxidizer as a crystal seed.

The oxidized liquor stream is fed into a 18,000 gallon agitated crystallization tank. Slurry pH is automatically controlled in the tank with lime slurry addition. Magnesium hydroxide and gypsum crystals precipitate in this crystallization tank.

Magnesium hydroxide and gypsum are separated with two sets of hydroclones. Slurry from the crystallizer tank is pumped to the first set of six hydroclones, five operating and one spare. Magnesium hydroxide rich overflow reports to a collection tank where it is sent to the centerwell of the magnesium hydroxide thickener. The underflow is rich in gypsum yet still has some magnesium hydroxide contamination.

This is delivered to a dilution tank which takes magnesium hydroxide thickener overflow to dilute the 25 wt. % solids underflow to 5 wt. % solids. This diluted underflow is sent to another bank of six hydroclones, 5 operating and one spare, to increase magnesium hydroxide production and gypsum purity. The overflow of these hydroclones is also sent to the collection tank to be sent to the centerwell of the magnesium hydroxide thickener. The underflow of these hydroclones is sent to the sump along with the excess magnesium hydroxide thickener overflow where the combined stream will be delivered to the FGD thickener centerwell. The settled magnesium hydroxide thickener underflow is pumped to an agitated storage tank where it can be delivered for acid neutralization.

#### **D. General Arrangement of the Pilot Plant**

The layout of the magnesium hydroxide recovery plant is shown in Figure 8. All equipment, except for the magnesium hydroxide thickener and storage facility, is located inside a 30' x 41' x 35' high prefabricated building which is situated close to the existing thickener. Other equipment was placed as necessary during testing. The concrete floor slab was constructed at existing grade level. Piling was not needed.

All equipment is controlled by a P.L.C. mounted inside the motor control center. Operator interface for start/stop, monitoring and data collection was through a graphics software package. Manual override of electrical motors is located at the motor control center. Refer to the attached Equipment List (Table 1) and Single Line Electrical Diagram (Figure 9) for details.

#### **E. Approach to Meet Project Objectives**

A set of test matrices, containing various operating conditions, were developed for the independent testing of the oxidizer, crystallizer, and hydroclones. Procedures for the testing campaigns appear in Appendix II and titled Test Set-Up Sheets. These sheets were used by the operators to setup operating parameters for each test period. Analysis of all liquor samples was performed on-site via a chemical laboratory located in the operators station. The results of these analysis are located in Appendix III. Solids' Analysis were performed at Dravo Research Center and are listed in Appendix IV. Scanning Electron Microscope (SEM) pictures and typical microtrac analysis of the sampled slurry streams sampled are in Appendix V.

The overall focus was on the production of high purity magnesium hydroxide. Parameters that may effect purity that were tested during the project were:

- The pH of the oxidizer tank.
- Residence time in the oxidizer tank.
- The concentration of magnesium ion in solution in the feed liquor.
- The pH of the crystallization tank.
- Residence time in the Crystallization tank.

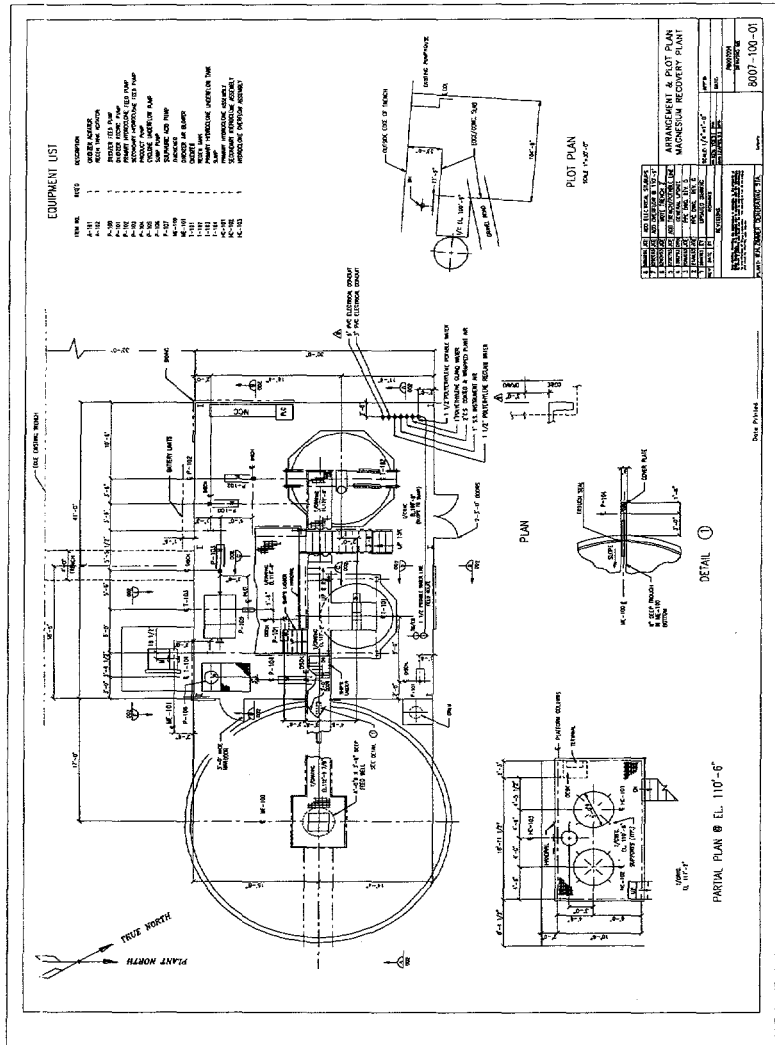


Figure 8. Plot Plan

Figure 8. Plot Plan

**Table 1. Equipment List**

**DRAVO LIME COMPANY**

**EQUIPMENT LIST**

**PROJECT: MAGNESIUM HYDROXIDE RECOVERY PILOT PLANT - 100 GPM**

Equip. No.	Qty.	Title	Description
<u>Pumps:</u>			
P-100	1	Oxidizer Feed	100 GPM @ 100 TDH
P-101	1	Oxidizer Recirculation	150 GPM @ 100 TDH
P-102	1	Primary Hydroclone Feed	115 GPM @ 100 TDH
P-103	1	Secondary Hydroclone Feed	115 GPM @ 100 TDH
P-104	1	Mg(OH) <sub>2</sub> Product Pump	30 GPM @ 100 TDH
P-105	1	Hydroclone Underflow	Diaphragm Pump
P-106	1	Recovery Plant Sump	150 GPM @ 100 TDH
P-108	1	Polymer	7 GPM
P-109	1	Magnesium Hydroxide Metering	Chemical Metering Pump
<u>Tanks:</u>			
T-100	1	FGD TOF Standpipe	
T-101	1	Oxidizer Column	
T-102	1	Crystallizer	
T-103	1	Dilution	
T-104	1	Mg(OH) <sub>2</sub> Product Storage	
T-105	1	Precipitation	
HC-101	1	Primary Hydroclone Underflow Collection	
HC-102	1	Secondary Hydroclone Underflow Collection	
HC-103	1	Hydroclone Overflow Collection	
<u>Others:</u>			
A-101	1	Oxidizer Agitator	
A-102	1	Crystallizer Agitator	
HE-100	1	Thickener	
ME-101	1	Oxidizer Air Blower	
	12	Hydroclones	



- The effect of liquid recycle from the magnesium hydroxide thickener overflow for dilution and crystallization purposes, and the effect of a two stage magnesium hydroxide precipitation step.
- The hydroclone operation for separation of magnesium hydroxide and gypsum will be evaluated for each change in the system.

The magnesium hydroxide recovery process has three major areas: oxidation, crystallization, and solids separation. Oxidation is the process of injecting air into an agitated tank filled with process liquor to convert liquid phase sulfite ions to sulfate ions. Crystallization is the process of adding magnesium enhanced lime into the oxidized process liquor to form magnesium hydroxide and gypsum. Solids separation is the separation of magnesium hydroxide and gypsum by taking advantage of the difference in particle size of the two compounds.

## 1. Oxidation Analysis

Oxidation is influence by many factors. Some of these factors are pH, residence time, sulfite concentration, air flowrate, and agitation speed. All of these factors have been tested and will be discussed in detail. Values of  $k_L a$ , the liquid phase mass transfer coefficient, will be compared to literature values and previous test from Miami Fort. The assumption was made that all independent parameters other than the test variables were held constant.

### a) Oxidizer pH

pH has been shown in FGD processes to have a large effect on oxidation. Normally decreasing the pH can increase oxidation. The oxidizer tank was operated at a pH range of 5.0 to 6.0. This range was chosen due to the safety hazard of off-gassing  $\text{SO}_2$  with a pH of 4 or less. Also, a pH over 6.0 could decrease oxidation and increase the amount of magnesium hydroxide used for neutralization.

In Table 2 the mean pH values for the tests were normally close to their setpoints; however, the standard deviations were high. Thus, the pH controller was unable to test small pH intervals accurately. With high standard deviations, pH units overlapped in the test ranges. For example, some of the low pH values found in a 6.0 pH test would be the same as high pH values found in a 5.5 pH test. Even with differences in pH, the mean outlet sulfite concentration was statistically established to have no dependence on a change in pH. The mean value for outlet sulfite concentration was 85 ppm with a standard deviation of 45 ppm. Since there was no linear or logarithmic function of the data and little variance from the mean for outlet sulfite concentration, it is concluded that pH had no effect on the outlet sulfite concentration.

Table 2. Oxidizer Inlet-Outlet Sulfite Concentration Statistical Data

Date	Oxidizer pH			Outlet SO <sub>3</sub>	
	Setpoint	Mean	Standard Dev	Mean	Standard Dev
6/15/94	5	5.4	0.51	54	29
6/17/94	5.5	5.6	0.17	34	18
6/16/94	6	5.8	0.95	104	48
6/27/94	5	5.0	0.36	149	65
			Total	85	45
				mean + stddev	130
				mean - stddev	41

**b) Inlet Sulfite Concentration**

Since the outlet sulfite concentration seemed to be constant over the period of the tests above, a larger period was implemented to see if the inlet sulfite concentration had any effect on the outlet concentration. In Table 3 various sets of data were taken. Most had other operating conditions downstream of the oxidizer being changed. The inlet sulfite concentration changed for the testing periods. However, the outlet sulfite concentration values did not vary over the set of inlet concentration values. It is concluded that sulfite oxidation does not show any relationship with inlet concentration.

Table 3. Oxidizer Inlet-Outlet Sulfite Concentration Statistical Data

Date	Feed SO <sub>3</sub>		Outlet SO <sub>3</sub>	
	Mean	Standard Dev	Mean	Standard Dev
6/8/94 - 6/9/94	6511	128	93	44
6/15/94 - 6/17/94	5777	359	66	46
6/27/94 - 7/1/94	5647	894	152	64
7/5/94 - 7/7/94	3266	121	144	38
Total	5300	1220	114	36
	mean + stddev	6520	mean + stddev	149
	mean - stddev	4080	mean - stddev	78

Since inlet sulfite concentration and pH did not have an effect on sulfite oxidation, outlet sulfite concentration appears to be independent of reaction kinetics. Therefore, an analysis of the absorption of oxygen into the liquid phase was performed. Mechanically agitated gas liquid contactors can be evaluated for their effectiveness in terms of the mass transfer coefficient,  $k_L a$ , by using the following rate equation<sup>1</sup>

$$R = k_L a A^*$$

where  $R$  = the rate of absorption per unit volume,  $k_L$  = liquid-phase mass transfer coefficient, cm/s,  $a$  = interfacial area per unit volume of solution, and  $A^*$  = concentration of the gas at saturated conditions. It is normally accepted that the gas-side resistance is negligible. For an air-water system at 120 °F, the saturation concentration of oxygen is 5.7 ppm. (Perry's 5th Ed.) Other assumptions with the rate equation are as follows: negligible effects of the gas concentration in the bulk liquid phase, no appreciable chemical reaction takes place in the liquid film surrounding the bubble, and dissolution of solid phase reactant does not effect absorption.

<sup>1</sup> Moran, Dave, "Analysis of Miami Fort Oxidation Data," August 26, 1993, pg. 1-2

Many researchers have tested the air-sulfite system. Calderbank has predicted values of  $k_1a$  using the following equations, which were also used at Miami Fort.

$$a = 215(hp/v)^{0.4} \frac{\gamma^{0.2}}{\sigma^{0.6}} (V_s/V_b)^{0.5}$$

$$\frac{k_1 D_B}{D_l} = 0.42(\mu_l / \rho_l D_l)^{1/2} (D_B^3 \rho_l \Delta \rho g / \mu_l^2)^{1/3}$$

Values of  $k_1a$  for the Calderbank equations were approximately  $20 \text{ hr}^{-1}$  for all testing.

Another method of quantifying  $k_1a$  was considering the rate of absorption of oxygen equal to the rate of oxygen depletion due to the chemical reaction.<sup>2</sup> The following equations show how the correlation was derived. The variables of these equations are sulfite concentration and residence time.

$$r_{SO_3^{2-}} = \frac{C_{SO_3^{2-} \text{ in}} - C_{SO_3^{2-} \text{ out}}}{\tau}$$

$$\frac{1}{2} r_{SO_3^{2-}} = r_{O_2}$$

$$\tau = \frac{V}{F}$$

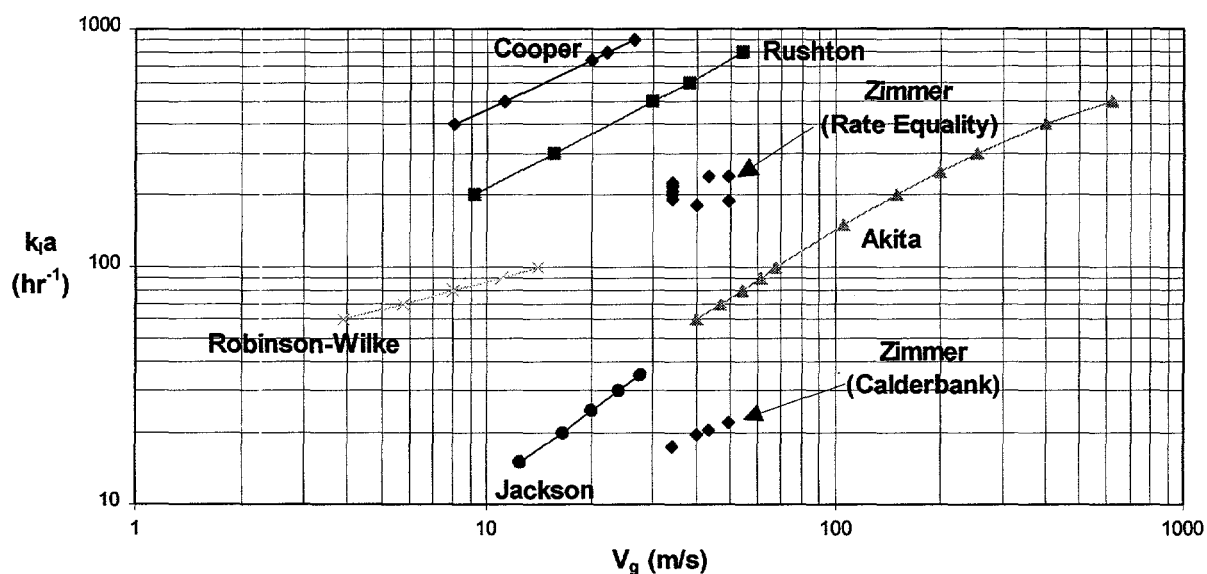
$$r_{O_2} = R = k_1 a A^*$$

<sup>2</sup> Harriot, Ph.D., Peter, September 22, 1993, page 4

c) **Oxidizer Residence Time**

The  $k_a$  values for the rate equality were approximately  $200 \text{ hr}^{-1}$ . These values are compared to literature values, Miami Fort, and Lab Scale tests. Table 4 shows the values of  $k_a$  for Zimmer, Miami Fort, Dravo Lab, and literature. When Calderbank's equations for predicting  $k_a$  were utilized on the data from Zimmer Station,  $k_a$  was very low compared to literature. Figure 10 shows the comparisons of both Calderbank's equations and the rate equality equations to literature. Rate equality agreed with the literature data quite well. Changing the residence time did not have a drastic effect on  $k_a$ .

Figure 10. Correlation of  $k_a$  to Superficial Gas Velocity



Due to the relatively good agreement of rate equality data and literature values, rate equality values will be used instead of Calderbank data for comparisons with other data. In Figure 11, Zimmer's data was found to be superior to that of the small scale testing performed to show the effects of mixer speed on  $k_a$ . The mixer in the oxidizer was more efficient than those used in the small scale tests. Also in Figure 12 the rate equality values correlated to the Miami Fort oxidizer values using the prediction methods of both Calderbank and Fuch's. Figure 13 shows that the rate equality values for  $k_a$  were very

close to those of Fuch's scaling effects. The rate equality data from the Zimmer Station was found to be in accordance with both literature and other plants in existence.

Figure 11. Effect of Mixer Speed on  $k_a$

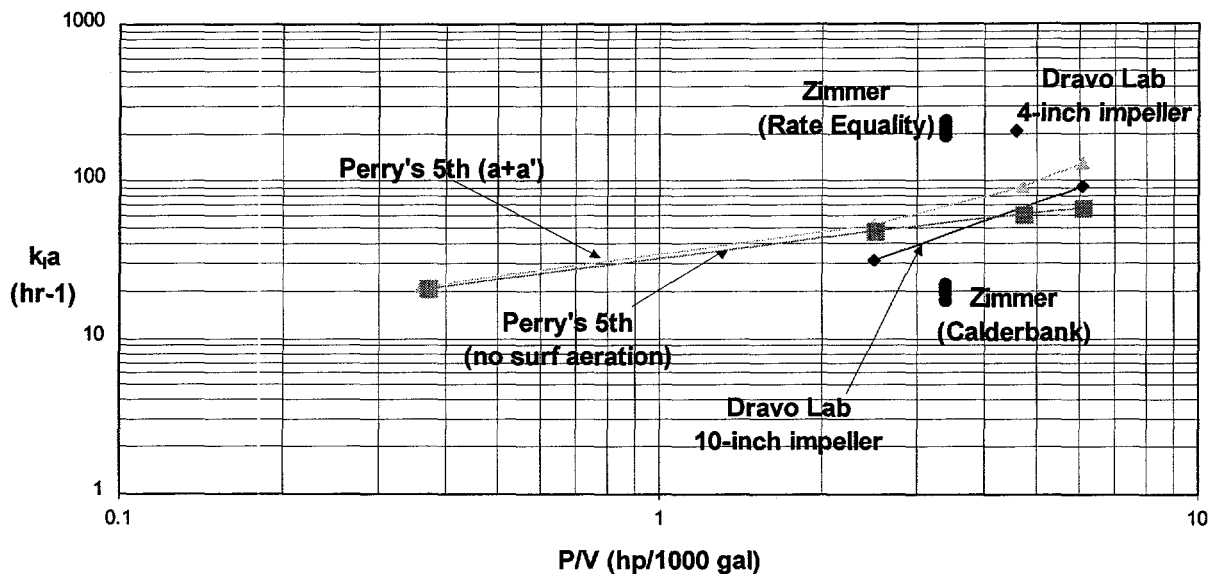
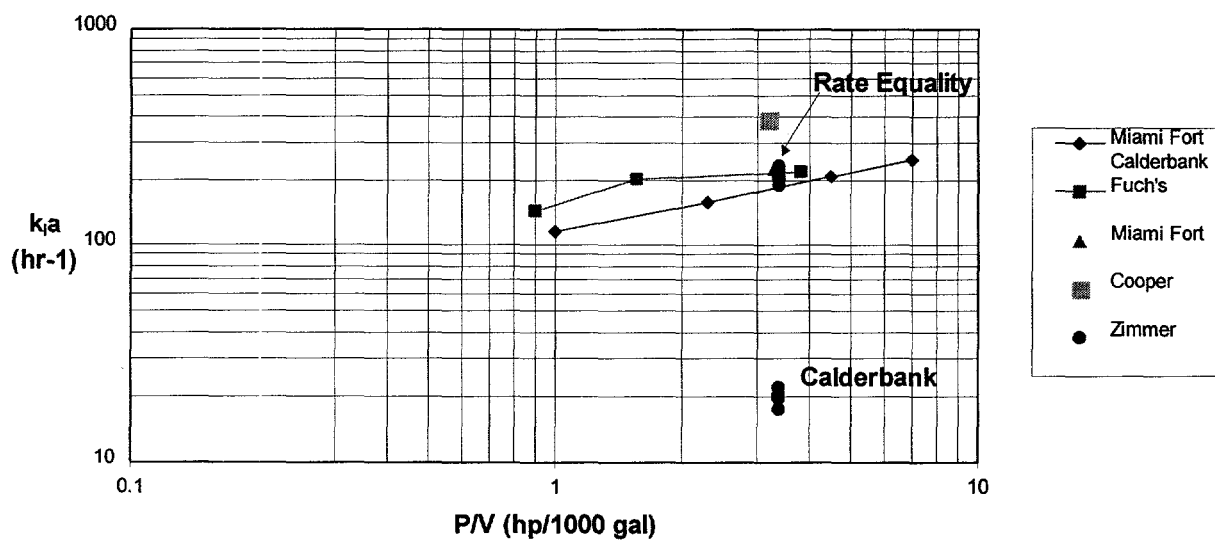


Figure 12. Comparison of Zimmer, Miami Fort, and Literature Values of  $k_a$



Summary of Zimmer Calculation				Conditions at Wm. H. Zimmer Station					
Calderbank		Rate Equality		Residence Time		Air Velocity		Flowrate	
$k_a$ ( $hr^{-1}$ )	$k_a$ ( $hr^{-1}$ )	$k_a$ ( $hr^{-1}$ )	$k_a$ ( $hr^{-1}$ )	(hr)	(fps)	(SCFM)			
18	203	183	183	1	0.0307	240			
20	183	183	183	1.22	0.0367	168			
20	183	183	183	1.22	0.0360	165	P/V		
20	183	183	183	1.22	0.0369	170	(hp/1000 gal)		
22	239	239	239	0.98	0.0452	216	3.39		
21	240	240	240	0.98	0.0397	184			
22	189	189	189	1.22	0.0458	223			
22	189	189	189	1.22	0.0452	220			
22	189	189	189	1.22	0.0454	221			

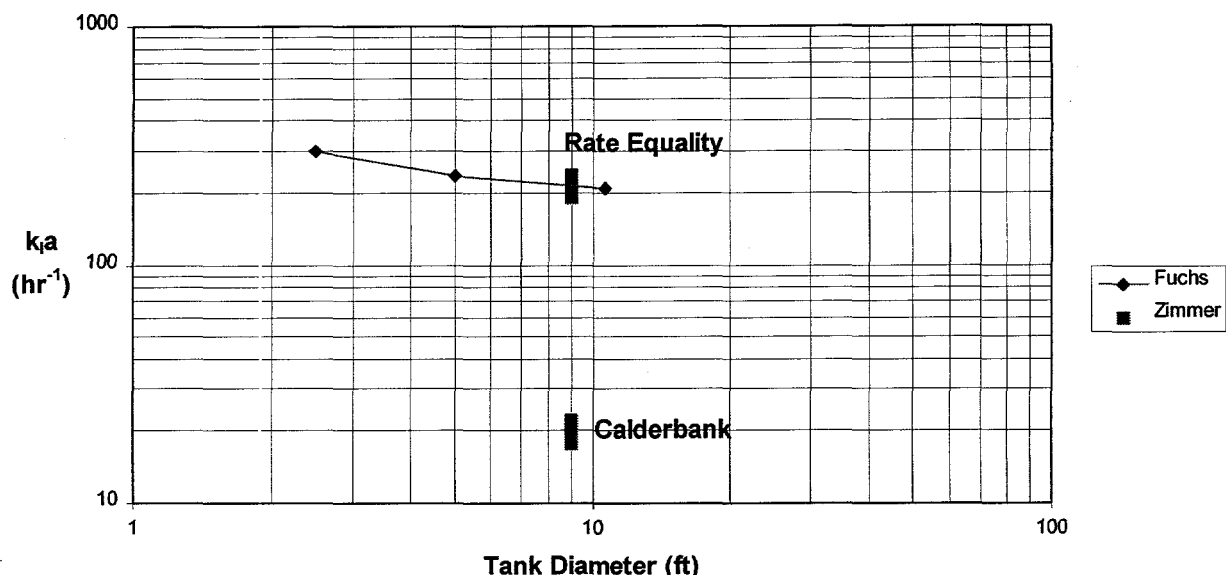
Literature Values									
Cooper		Rushton		Robinson-Wilke		Akita		Jackson	
$V_g$ (m/hr)	$k_a$ ( $hr^{-1}$ )	$V_g$ (m/hr)	$k_a$ ( $hr^{-1}$ )	$V_g$ (m/hr)	$k_a$ ( $hr^{-1}$ )	$V_g$ (m/hr)	$k_a$ ( $hr^{-1}$ )	$V_g$ (m/hr)	$k_a$ ( $hr^{-1}$ )
8.05	400	9.2	200	3.9	60	40	60	12.5	15.0
11.25	500	15.5	300	5.8	70	47	70	16.5	20.0
20	740	30	500	8	80	54	80	20	25.0
22	800	38	600	11	90	61	90	24	30.0
26.5	900	54	800	14	100	68	100	27.5	35.0
						105	150		
						150	200		
						200	250		
						255	300		
						400	400		
						620	500		

Dravo Lab Data					Miami Fort Data				
P/V	4" Impeller	10" Impeller	Perry's 5th ed	Perry's 5th	P/V	Calderbank	Fuch's	Miami Fort	Cooper
(hp/1000 gal)	$k_a$ ( $hr^{-1}$ )	$k_a$ ( $hr^{-1}$ )	(a+a)	(no surf. aeration)	(hp/1000 gal)	$k_a$ ( $hr^{-1}$ )	$k_a$ ( $hr^{-1}$ )	$k_a$ ( $hr^{-1}$ )	$k_a$ ( $hr^{-1}$ )
0.36			21.5		1	115			
0.37				21	2.3	160			
2.5		31.5	52.5	47.5	4.5	210			
4.6	205				7	250			
4.7			92	61				145	
6.1		93	130	67	1.55			205	
					3.8			220	
					3.3			230	
					3.2				385

Table 4.  $k_a$  Evaluation

Figure 13. Comparison of Fuch's Effect of Scale on  $k_{\text{f}}a$  and Zimmer Station  $k_{\text{f}}a$  Values



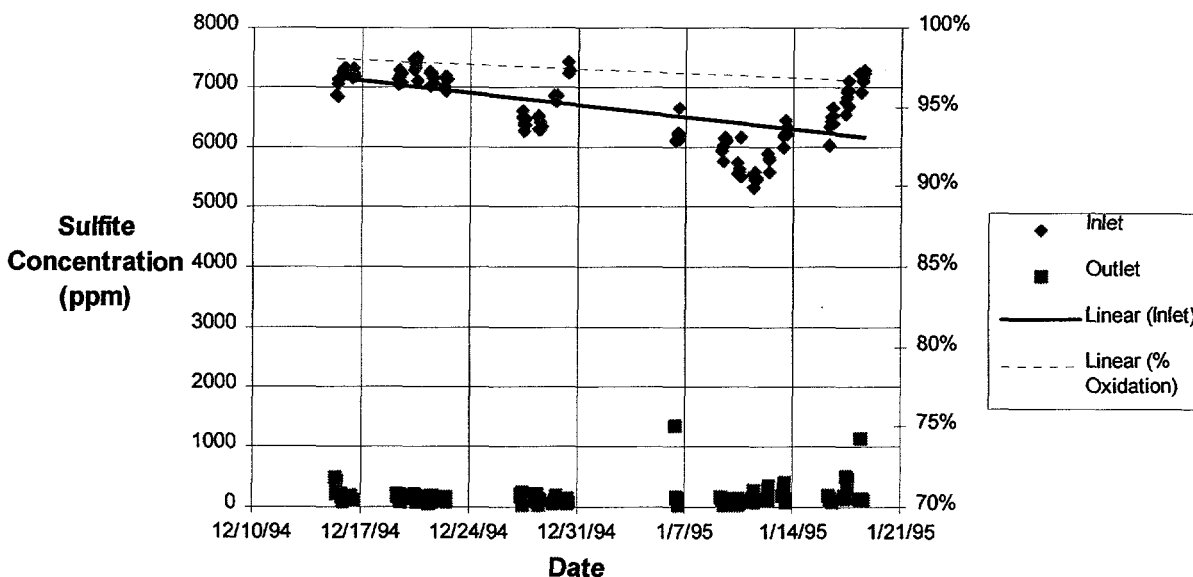
Calderbank's equations did not fit the data very well. This could be due to differences in operating conditions. Calderbank's system may have had a smaller vessel, or less agitation that could explain the differences in the values. Calderbank's equations relied on only two measured variables: the agitation ratio, which was the horsepower of the motor divided by the volume of the tank, and the superficial air velocity. The rate equality equations used more data, and it relied on the sulfite concentration as its main source of data. The comparison of rate equality  $k_{\text{f}}a$  values with literature and Miami Fort values, indicates that Zimmer data was in agreement with literature data for the air-sulfite system.

**d) Air Flowrate and Agitation Speed**

Due to design restrictions of the agitator motor, the agitator tripped when the air flow rate dropped below 160 SCFM. A variable speed drive was installed on the agitator motor so that lower air flowrates could be studied with lower mixer speeds.

The oxidizer tank was operated at a constant residence time of 0.93 hours with an inlet flowrate of 100 GPM. Inlet sulfite concentrations did vary throughout the testing period as shown in Figure 14. This will help show the relevance of inlet sulfite concentration on oxidation at low air flowrates; however, testing cannot be considered as steady state due to the inlet chemistry fluctuation. The variables to be studied were the agitator speed and the air flowrate. The agitation output range was limited to 60 to 100% (approximately 60 to 100 RPM). This range was evaluated by preliminary testing. Also the air flowrate was varied from 5-10:1 oxygen stoichiometry. When oxygen stoichiometry less than 5 was attempted, the outlet sulfite concentration was higher than the design limit of 300 mg/l. Oxygen stoichiometry is defined as the moles monatomic O per moles inlet  $\text{SO}_3^-$ .

Figure 14. Inlet-Outlet Sulfite Concentration Profile



In Table 5 the test dates and times for the testing period are shown. As Figure 15 illustrates the percent oxidation for the testing period was not considerably effected by changes in the mixer speed and oxygen stoichiometry above 6.0. Although Figure 15 contains all the testing period data, it still illustrates that most of the data meets the design criteria of less than 300 mg/l  $\text{SO}_3^-$  in the exit stream. Oxidation for the testing period remained higher than 97% for monatomic oxygen stoichiometry above 6.0. Only when

inlet sulfites were greater than 6500 ppm and monatomic oxygen stoichiometry was less than 6.0, did percent oxidation start to decrease. Therefore inlet sulfites do affect outlet sulfite concentration when monatomic oxygen stoichiometry is lower than 6.0. When monatomic oxygen stoichiometry is 6.0 or above, the inlet sulfite concentration does not effect oxidation or outlet sulfite concentrations. (Figure 16)

In Figure 17, the effect of mixer speed on  $k_a$  is shown. The values of  $k_a$  for the testing period were between 200 and 300  $\text{hr}^{-1}$ . The effect of changes in mixer speed was not apparent in the  $k_a$  values. This could be due to the high efficiency design of the mixer. The design of the bottom agitator blade is seen in Figure 18. Since the agitator blade is so efficient, running mixer speeds at higher rpm's provides little added benefit, i.e. little to no change in  $k_a$ .

Figure 15. Effect of Inlet Sulfite Concentration

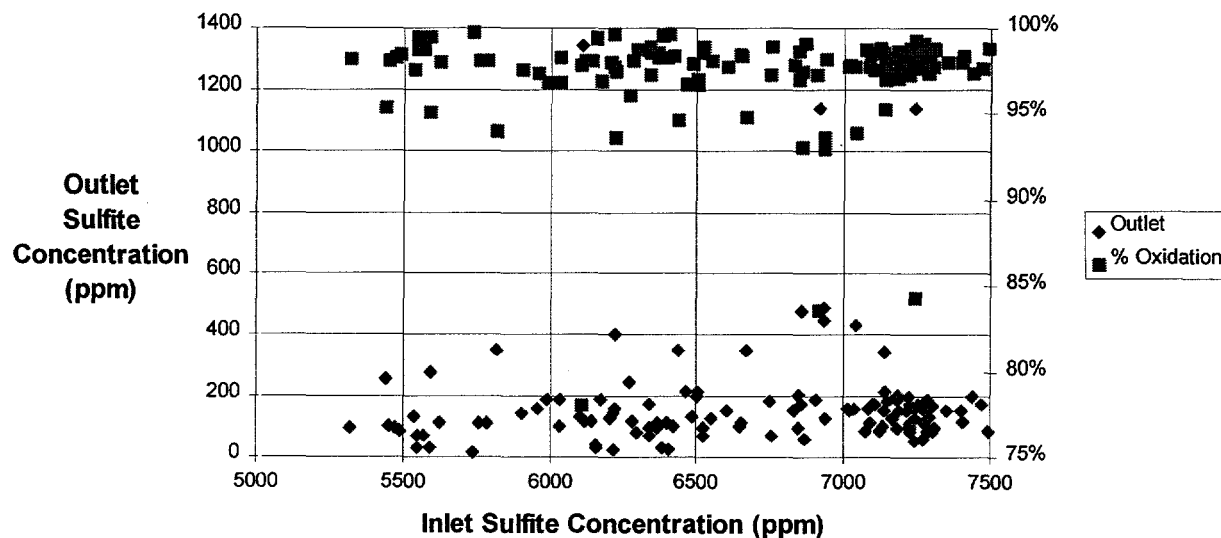


Figure 16. Oxidation Analysis

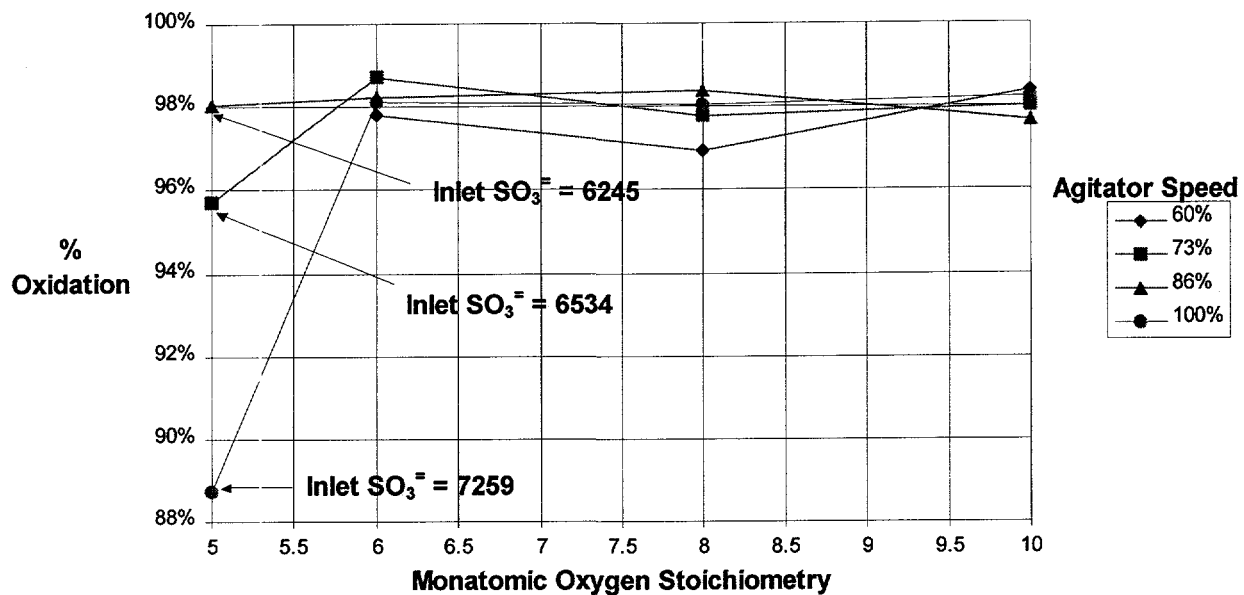
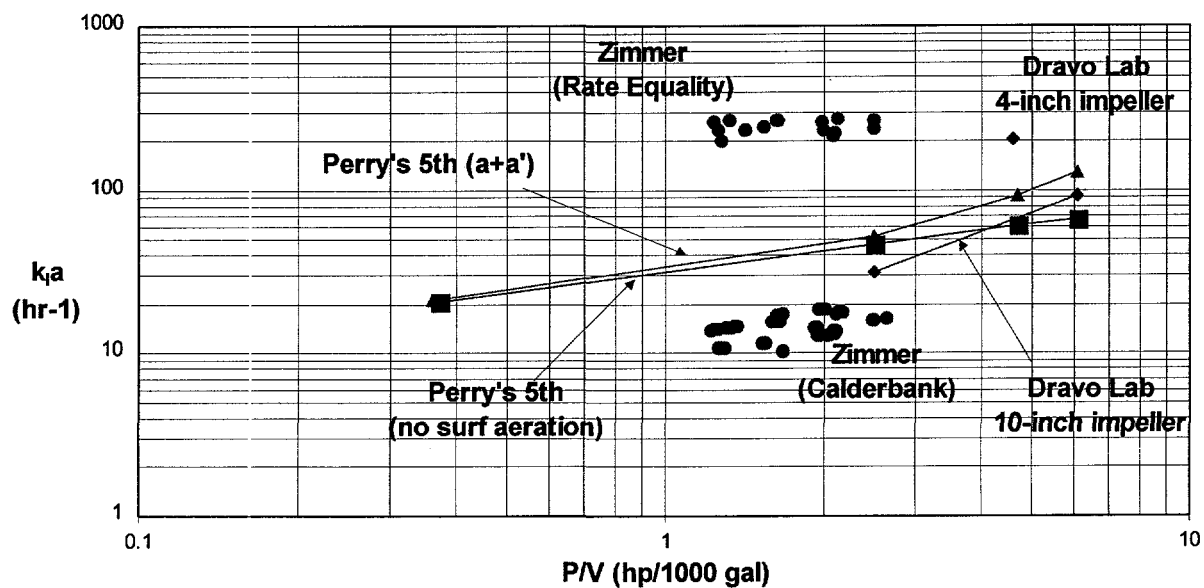


Figure 17. Effect of Mixer Speed on  $k_a$



**Table 5. Test Setpoint Dates and Times Conducted**

<b>Oxidizer Parametric Testing</b>				
Stoichiometry O/SO <sub>3</sub> <sup>=</sup>	Oxidizer Agitator VFD Output (%)			
	100	86	73	60
10	12/22/94 1000-1400	12/19/94 1000-1400	12/27/94 1000-1400	12/28/94 1000-1400
8	12/20/94 1000-1400	12/16/94 0900-1300	12/15/94 1800-2200	12/15/94 1400-1800
6	12/21/94 1000-1400	1/9/95 1000-1400	1/10/95 1000-1400	1/11/95 1000-1400
5	1/18/95 0900-1100	1/16/95 1000-1400	1/17/95 1000-1400	N/A

**Notes:**

- 1) Stoichiometry is with respect to inlet SO<sub>3</sub><sup>=</sup> concentration. Air flowrate was adjusted with each measurement of inlet SO<sub>3</sub><sup>=</sup> to maintain the desired stoichiometry.
- 2) With each change of setting in the oxidizer agitator VFD and air flow, the amperage pulled by both the oxidizer agitator and the air blower were measured and recorded.
- 3) The oxidizer outlet SO<sub>3</sub><sup>=</sup> level should never exceed 300 mg/l. If this occurs, check if desired stoichiometry has been maintained. If stoichiometry has been maintained but outlet SO<sub>3</sub><sup>=</sup> remains unacceptably high, then terminate the set point.

Comparing the values of  $k_a$  to previous testing, there was no decrease in  $k_a$  due to lower air flowrates and mixer speeds. As seen in Figure 19, the data points were labeled "old" and "new." For the same air flowrates,  $k_a$  values for different mixer speeds remained about the same.

Figure 18. Oxidizer Agitator Blade

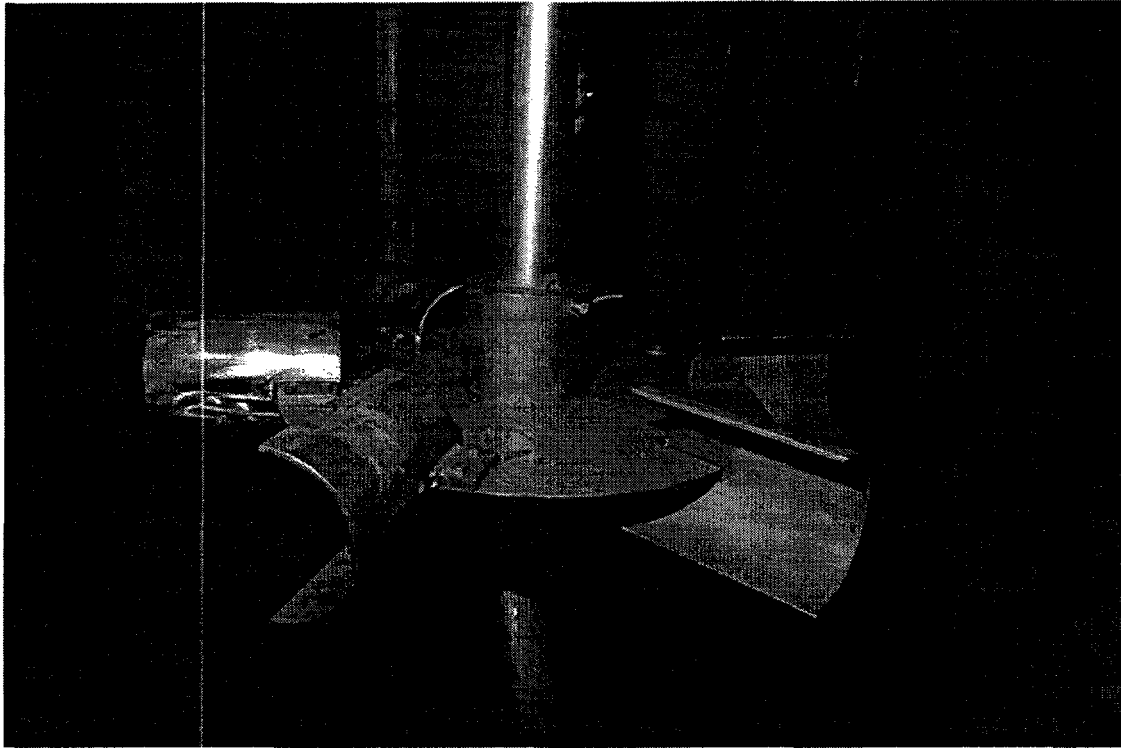
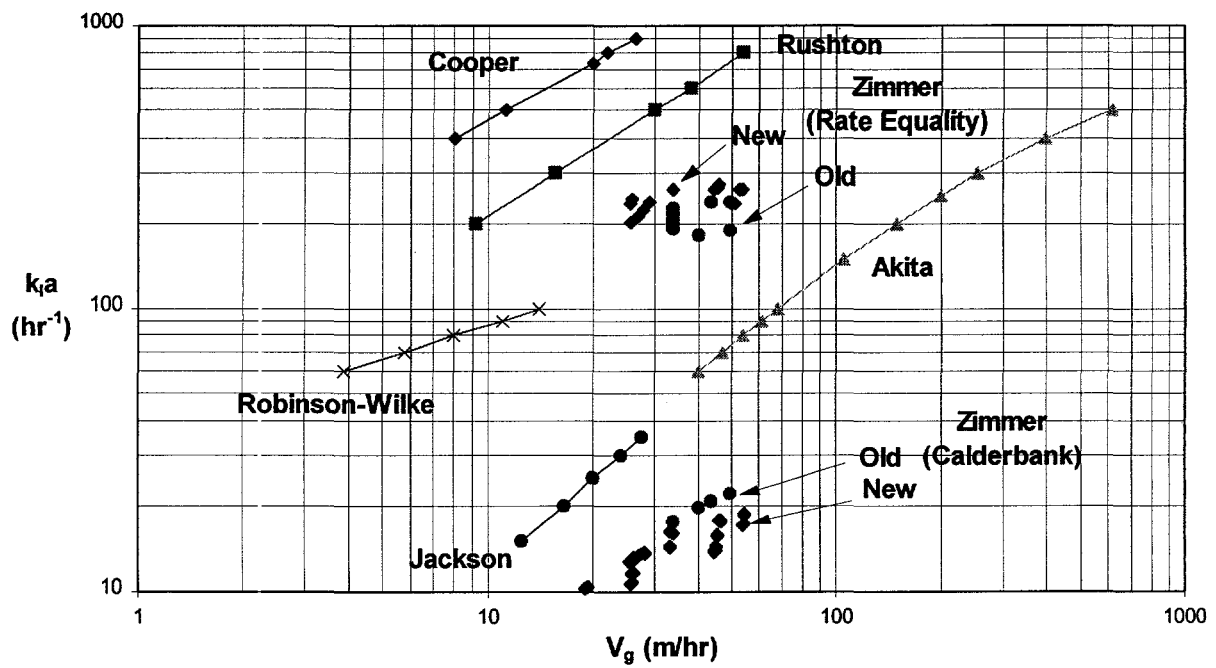


Figure 19. Correlation of  $k_a$  to Superficial Gas Velocity



e) **Conclusions from Oxidizer Testing**

For the oxidizer, pH, and residence time did not have a significant effect on outlet sulfite concentration. Therefore, outlet sulfite concentration was limited by mass transfer and not by chemical reaction. With monatomic oxygen stoichiometry running around 8 to 10, the changes in air flow and residence time did not drastically change  $k_a$ . The  $k_a$  values from rate equality equations were 200 (1/hr). Airflow and mixer speeds are the two main factors in oxidation. For the Zimmer oxidizer, optimal operating conditions are to maintain monatomic oxygen stoichiometry at 6.0 or above and to keep mixer speeds at least 75% of the maximum rpm. The minimum air flowrate to the oxidizer should be 150 SCFM. This provides a stoichiometry of 6.0 for an inlet sulfite concentration of 7500 ppm. The  $k_a$  values from rate equality equations were between 200 to 300 (1/hr). Oxidation was still >97% complete when monatomic oxygen stoichiometry was 6.0 or above.

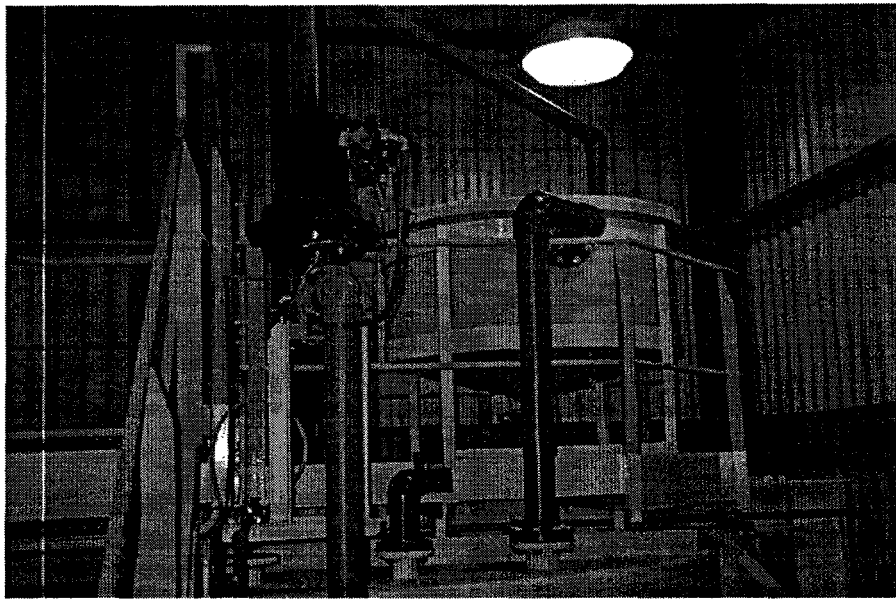
2. **Crystallizer Analysis**

Crystallization of magnesium hydroxide and gypsum is accomplished by adding magnesium-enhanced lime to a liquid stream rich in magnesium sulfate. There are two methods of crystallizing magnesium hydroxide and gypsum at this facility: single and double stage crystallization. Single stage crystallization is precipitating both compounds at a pH of 10 - 11. Two stage crystallization consists of stepping the pH up from 5.5 to 11 using a separate vessel to give an intermediate pH that allows gypsum to precipitate before magnesium hydroxide. Two stage crystallization was accomplished by inserting a 300 gallon tank between the oxidizer and crystallizer tanks. This tank, seen in Figure 20, was located on top of the crystallizer tank. Coming into the tank are the oxidizer outlet and either crystallizer recycle or magnesium hydroxide slurry streams. These streams mix and then drain to the crystallizer.

Tests performed in single stage crystallization mode consisted of changes in pH, residence time, and gypsum recycle to the oxidizer and crystallizer tanks. Samples analyzed for particle size,

gypsum, and magnesium hydroxide purity were evaluated. Crystallization of magnesium hydroxide and gypsum was tested similarly in the 2 stage crystallization mode for the effects of pH, residence time, and crystallizer or magnesium hydroxide recycling to the precipitation tank. Samples were analyzed for particle size, gypsum, and magnesium hydroxide purity and evaluated. The performances of the hydroclones were also evaluated at this time. The results of the 2-stage precipitation will be compared to the results of the single stage crystallization study.

Figure 20. Precipitation Tank



a) Single stage crystallization

Three operating parameters were investigated. Gypsum slurry from the primary hydroclone underflow stream was capable of recycling to both the oxidizer and the crystallizer tanks. Testing included recycling gypsum to the crystallizer tank, to both oxidizer and crystallizer tanks, and no recycling to either tank. pH setpoints of 10, 10.5, and 10.8 were evaluated for pH's effect on crystallization. The effect of crystallizer residence time was assessed for residence times of 2.17, 2.6, and 3.25 hours. Crystallizer tank slurry density was maintained between 5 and 6 wt. % solids.

## 1) Particle Size

Microtrac analysis was performed for all samples at the end of each test. (Table 6) Typical crystallizer microtrac analysis indicates two distinct distributions of crystals. The distributions reflect the smaller magnesium hydroxide crystals and the larger gypsum crystals. Since the distributions are distinct, it is possible to estimate the average crystal size for both compounds. Since the average crystal size data for the population of the crystallizer tank as a whole did not show any relevant trends, a particle size analysis was obtained for both crystals. An average particle size for each individual distribution was determined using a population average. For the gypsum crystals, greater residence time increased gypsum particle size. In spite of this finding, there appeared to be no improved separation of magnesium hydroxide from gypsum by the hydroclones. For magnesium hydroxide crystals, the effect of residence time was not evident. There were inconsistencies in the data that led to no discernible trends for pH or gypsum recycling.

## 2) Purity of Magnesium Hydroxide and Gypsum

Quantifying the result of changing parameters, purity of both magnesium hydroxide and gypsum was calculated. (Table 7) The crystallizer, HCOF#1, HCOF#2, and product (magnesium thickener underflow) streams were evaluated. The purity is calculated by the compound's weight percentage of the solids for that stream. The amount of gypsum in the product stream was lowest for a residence time of 2.6 hours for testing with and without gypsum recycle. Also magnesium hydroxide purity (wt %) in the product was highest when there was no gypsum recycle to the crystallizer or the oxidizer. The magnesium hydroxide purity range dropped from 75-69 (wt %) to 73-58. All other streams had

conflicting data. pH testing indicates that effects of pH on crystallization were unable to be duplicated for the same setpoint.

b) **2-Stage Precipitation Analysis**

Five operating parameters were evaluated. Recycling crystallizer slurry and magnesium hydroxide separately to the precipitation tank was tested. pH setpoints for the crystallizer tank of 10, 10.5, and 10.8 were evaluated for pH's effect on crystallization. The effect of crystallizer residence time was also evaluated for residence times of 2.17, 2.6, and 3.25 hours. During these tests, the flow to the hydroclones remained at 20 GPM per hydroclone. As flowrate changed so to was the number of hydroclones changed to maintain this individual hydroclone flowrate. All hydroclones were configured with 5/8 inch vortexes for both crystallizer and hydroclone testing.

Flowrate per primary hydroclone was changed by operating either 4 or 5 hydroclones using apex sizes of 1/4 inch and 3/8 inch. All hydroclones were tested with 5/8 inch vortexes. When 4 primary hydroclones were in service, the flowrate to each hydroclone was 25 GPM. When 5 primary hydroclones were in service, the flowrate to each hydroclone was 20 GPM. Crystallizer and magnesium hydroxide recycling effected the hydroclones, gypsum, and magnesium hydroxide purity differently. Therefore, their optimal operating conditions will not be the same.



Crystallizer		Mg(OH) <sub>2</sub> Purity		Gypsum Purity	
Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time	
Gypsum Recycle to Crystallizer		Gypsum Recycle to Crystallizer		Gypsum Recycle to Crystallizer	
80 GPM & 4 Operating Hydroclones	100 GPM & 5 Operating Hydroclones	120 GPM & 6 Operating Hydroclones	80 GPM & 4 Operating Hydroclones	100 GPM & 5 Operating Hydroclones	120 GPM & 6 Operating Hydroclones
7/6/94 to 7/13/94	7/13/94	7/13/94	7/16/94 to 7/13/94	7/13/94	7/13/94
pH	3.25 Hours	2.6 Hours	pH	3.25 Hours	2.6 Hours
10	29.8	28	10	59.8	58.7
10.5	28.7	30.7	10.5	61.6	61.4
10.8	29.4	26.5	10.8	58.5	60.2
Gypsum Recycle to Ox and Crystallizer		Gypsum Recycle to Ox and Crystallizer		Gypsum Recycle to Ox and Crystallizer	
80 GPM & 4 Operating Hydroclones	100 GPM & 5 Operating Hydroclones	120 GPM & 6 Operating Hydroclones	80 GPM & 4 Operating Hydroclones	100 GPM & 5 Operating Hydroclones	120 GPM & 6 Operating Hydroclones
7/19/94 to 7/21/94	7/21/94	7/21/94	7/19/94 to 7/21/94	7/21/94	7/21/94
pH	3.25 Hours	2.6 Hours	pH	3.25 Hours	2.6 Hours
10	30.1	29.5	10	58.7	60
10.5	31.9	29.9	10.5	61.4	59
10.8	27	29.8	10.8	59	59.4
Gypsum Recycle to Crystallizer		Gypsum Recycle to Crystallizer		Gypsum Recycle to Crystallizer	
80 GPM & 4 Operating Hydroclones	100 GPM & 5 Operating Hydroclones	120 GPM & 6 Operating Hydroclones	80 GPM & 4 Operating Hydroclones	100 GPM & 5 Operating Hydroclones	120 GPM & 6 Operating Hydroclones
7/27/94 to 8/3/94	8/3/94	8/3/94	7/27/94 to 8/3/94	8/3/94	8/3/94
pH	3.25 Hours	2.6 Hours	pH	3.25 Hours	2.6 Hours
10	29.6	22.2	10	59.3	68.3
10.5	28	26.7	10.5	62.2	62.7
10.8	28.1	25.9	10.8	62	65.9
No Gypsum Recycle		No Gypsum Recycle		No Gypsum Recycle	
80 GPM & 4 Operating Hydroclones	100 GPM & 5 Operating Hydroclones	120 GPM & 6 Operating Hydroclones	80 GPM & 4 Operating Hydroclones	100 GPM & 5 Operating Hydroclones	120 GPM & 6 Operating Hydroclones
7/14/94 to 7/18/94	7/18/94	7/18/94	7/14/94 to 7/18/94	7/18/94	7/18/94
pH	3.25 Hours	2.6 Hours	pH	3.25 Hours	2.6 Hours
10	31.7	31	10	59.2	59.9
10.5	32.9	30	10.5	59	59.4
10.8	26.4	n/a	10.8	52.9	n/a

Table 7. Summary of Purity Data for Testing Period

Mg(OH) <sub>2</sub> Purity			HCOF#1		
Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time	
Gypsum Recycle to Crystallizer		Gypsum Recycle to Crystallizer		Gypsum Recycle to Crystallizer	
7/6/94 to 7/13/94	80 GPM & 4 Operating Hydrochlorones	100 GPM & 5 Operating Hydrochlorones	120 GPM & 6 Operating Hydrochlorones	80 GPM & 4 Operating Hydrochlorones	100 GPM & 5 Operating Hydrochlorones
	pH 3.25 Hours	2.6 Hours	2.17 Hours	2.6 Hours	2.17 Hours
	10	n/a	65	n/a	13.1
	10.5	68.5	67.7	14.1	14.4
	10.8	69.8	70	15.1	14.6
				12.3	13.1
	<b>Gypsum Recycle to Ox and Crystallizer</b>				
7/19/94 to 7/21/94	80 GPM & 4 Operating Hydrochlorones	100 GPM & 5 Operating Hydrochlorones	120 GPM & 6 Operating Hydrochlorones	80 GPM & 4 Operating Hydrochlorones	100 GPM & 5 Operating Hydrochlorones
	pH 3.25 Hours	2.6 Hours	2.17 Hours	2.6 Hours	2.17 Hours
	10	75.1	67	8.5	14
	10.5	73.3	71.9	11.6	n/a
	10.8	74.5	73	9.4	n/a
	<b>Gypsum Recycle to Crystallizer</b>				
7/27/94 to 8/3/94	80 GPM & 4 Operating Hydrochlorones	100 GPM & 5 Operating Hydrochlorones	120 GPM & 6 Operating Hydrochlorones	80 GPM & 4 Operating Hydrochlorones	100 GPM & 5 Operating Hydrochlorones
	pH 3.25 Hours	2.6 Hours	2.17 Hours	2.6 Hours	2.17 Hours
	10	73.2	68.8	9.7	15.4
	10.5	74.6	70.3	8.7	12.4
	10.8	74.2	72.6	9.7	11.4
	<b>No Gypsum Recycle</b>				
7/14/94 to 7/18/94	80 GPM & 4 Operating Hydrochlorones	100 GPM & 5 Operating Hydrochlorones	120 GPM & 6 Operating Hydrochlorones	80 GPM & 4 Operating Hydrochlorones	100 GPM & 5 Operating Hydrochlorones
	pH 3.25 Hours	2.6 Hours	2.17 Hours	2.6 Hours	2.17 Hours
	10	70	72.4	11.8	12.6
	10.5	73.3	74.9	12.2	10.9
	10.8	72.1	n/a	11.6	n/a

Table 7. Summary of Purity Data for Testing Period (continued)

HCOF#2

Mg(OH) <sub>2</sub> Purity		Gypsum Purity	
Decreasing Crystallizer Tank Residence Time	Decreasing Crystallizer Tank Residence Time	Decreasing Crystallizer Tank Residence Time	Decreasing Crystallizer Tank Residence Time
<b>Gypsum Recycle to Crystallizer</b>		<b>Gypsum Recycle to Crystallizer</b>	
80 GPM & 100 GPM & 120 GPM & 4 Operating Hydroclones	2.6 Hours	80 GPM & 100 GPM & 120 GPM & 4 Operating Hydroclones	2.6 Hours
7/6/94 to 7/13/94	2.17 Hours	7/6/94 to 7/13/94	2.17 Hours
pH	3.25 Hours	pH	3.25 Hours
10	n/a	10	n/a
10.5	n/a	10.5	n/a
10.8	n/a	10.8	n/a
<b>Gypsum Recycle to Ox and Crystallizer</b>		<b>Gypsum Recycle to Ox and Crystallizer</b>	
80 GPM & 100 GPM & 120 GPM & 4 Operating Hydroclones	2.6 Hours	80 GPM & 100 GPM & 120 GPM & 4 Operating Hydroclones	2.6 Hours
7/19/94 to 7/21/94	2.17 Hours	7/19/94 to 7/21/94	2.17 Hours
pH	3.25 Hours	pH	3.25 Hours
10	n/a	10	n/a
10.5	n/a	10.5	n/a
10.8	n/a	10.8	n/a
<b>Gypsum Recycle to Crystallizer</b>		<b>Gypsum Recycle to Crystallizer</b>	
80 GPM & 100 GPM & 120 GPM & 4 Operating Hydroclones	2.6 Hours	80 GPM & 100 GPM & 120 GPM & 4 Operating Hydroclones	2.6 Hours
7/27/94 to 8/3/94	2.17 Hours	7/27/94 to 8/3/94	2.17 Hours
pH	3.25 Hours	pH	3.25 Hours
10	44.2	10	41
10.5	40.9	10.5	45
10.8	n/a	10.8	n/a
<b>No Gypsum Recycle</b>		<b>No Gypsum Recycle</b>	
80 GPM & 100 GPM & 120 GPM & 4 Operating Hydroclones	2.6 Hours	80 GPM & 100 GPM & 120 GPM & 4 Operating Hydroclones	2.6 Hours
7/14/94 to 7/18/94	2.17 Hours	7/14/94 to 7/18/94	2.17 Hours
pH	3.25 Hours	pH	3.25 Hours
10	n/a	10	n/a
10.5	n/a	10.5	n/a
10.8	n/a	10.8	n/a

Table 7. Summary of Purity Data for Testing Period (continued)



## 1) Crystallizer Recycle

Crystallizer recycle was tested for its effect during the period covering 9/19/94 to 10/13/94. Crystallizer residence time of 2.6 hours resulted with HCOF#1 stream having the lowest amount of gypsum carryover (2.7 wt %) and the highest amount of magnesium hydroxide (74.9 wt %). (Table 8) A pH setpoint of 10.5 produced the highest magnesium hydroxide purity (74.9 wt %) while a pH of 10.8 produced the lowest gypsum impurity (2.7 wt %). In Table 8, there were no relevant trends for particle size.

Crystallizer recycle was tested for its effect on the hydroclones during the period covering 9/28/94 to 10/3/94. During crystallizer slurry recycle to the precipitation tank, magnesium hydroxide particle size decreased (to as low as 3.7 microns) as the number of hydroclones increased. (Table 9) The highest magnesium hydroxide purity (75.4 wt %) in HCOF#1 occurred while operating 4 primary hydroclones with 3/8 inch apexes and 5 secondary hydroclones with 1/4 inch apexes. (Table 8)

## 2) Magnesium Hydroxide Recycle

Magnesium hydroxide recycle was tested for its effect on the crystallizer during the period covering 10/4/94 to 10/7/94. Crystallizer residence time of 3.25 hours produced the lowest amount of gypsum carryover (1.8 wt %) and the highest amount of magnesium hydroxide (74.7 wt %) in the HCOF#1. (Table 8). The pH setpoint that produced both the highest magnesium hydroxide purity and lowest gypsum impurity was 10.8. Once again, no relevant trends appeared in the particle size data from the testing period. (Table 9) Problems were encountered controlling pH in the oxidizer when magnesium hydroxide was recycled to the crystallizer. The source of magnesium hydroxide slurry for pH control of the

oxidizer and recycle to the precipitation tank was the same pump that was undersized to accomplish both demands simultaneously.

Magnesium hydroxide recycle was evaluated for its effect on the hydroclone operating performance during the period from 10/10/94 to 10/12/94. During this time average magnesium hydroxide particle size decreased to 5.2 microns as the number of hydroclones increased. (Table 8) During this test series highest magnesium hydroxide purity (72.8 wt %) in HCOF#1 was achieved while operating 5 primary hydroclones with 1/4 inch apexes and 5 secondary hydroclones with 1/4 inch apexes. (Table 9) Similar to the crystallizer slurry recycle tests, magnesium hydroxide recycle caused problems in controlling crystallizer pH.

### 3) Summary of Precipitation Tank Operation

Crystallizer operation while utilizing the precipitation tank does not appear to provide any advantage when compared to standard crystallizer tank operation. The average purity of the magnesium hydroxide in the product stream was found (on a calcined basis) to be approximately 74 wt. % in both modes of operation. (Figure 21)

Considering there may be a lag time involved in the product stream, the primary hydroclone overflow, HCOF#1, was similarly evaluated. (Figure 22) The same results appeared with the average magnesium hydroxide purity for both modes of operation being 76 wt. %. The only difference between the two modes of operation indicated HCOF#2 to have an increased magnesium hydroxide purity (from 43 to 48 wt. %) during the 2-stage precipitation testing. (Figure 23) In spite of this occurrence, the product purity remained the same.

Decreasing Crystallizer Tank Residence Time		Mg(OH) <sub>2</sub> Purity		Gypsum Purity	
		Decreasing Crystallizer Tank Residence Time	Decreasing Crystallizer Tank Residence Time	Decreasing Crystallizer Tank Residence Time	Decreasing Crystallizer Tank Residence Time
<b>Crystallizer</b>					
<b>Crystallizer Recycle to Precip. Tank</b>					
9/19/94 to 10/13/94	80 GPM & 4 Operating Hydroclones 3.25 Hours	100 GPM & 5 Operating Hydroclones 2.6 Hours	120 GPM & 6 Operating Hydroclones 2.17 Hours	80 GPM & 4 Operating Hydroclones 3.25 Hours	100 GPM & 5 Operating Hydroclones 2.6 Hours
pH	10	26.6	26.4	10	63
	10.5	26.2	28.9	10.5	62.7
	10.8	28	25.7	10.8	63
<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>					
10/4/94 to 10/7/94	80 GPM & 4 Operating Hydroclones 3.25 Hours	100 GPM & 5 Operating Hydroclones 2.6 Hours	120 GPM & 6 Operating Hydroclones 2.17 Hours	80 GPM & 4 Operating Hydroclones 3.25 Hours	100 GPM & 5 Operating Hydroclones 2.6 Hours
pH	10	28.3	31	10	60.1
	10.5	31.4	n/a	10.5	55.7
	10.8	29.2	n/a	10.8	59.4
<b>Crystallizer Recycle to Precip. Tank</b>					
9/28/94 to 10/3/94	Primary 1/4" Apex Secondary 1/4" Apex	Primary 3/8" Apex Secondary 1/4" Apex	Primary Only 1/4" Apex	Primary 1/4" Apex Secondary 1/4" Apex	Primary 3/8" Apex Secondary 1/4" Apex
# of Prim. HC				# of Prim. HC	
5 Operating	28.4	26.5	27.6	5 Operating	60.4
4 Operating	28.6	27.4	27.8	4 Operating	60.7
3 Operating	n/a	n/a	n/a	3 Operating	n/a
<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>					
10/10/94 to 10/12/94	Primary 1/4" Apex Secondary 1/4" Apex	Primary 3/8" Apex Secondary 1/4" Apex	Primary Only 1/4" Apex	Primary 1/4" Apex Secondary 1/4" Apex	Primary 3/8" Apex Secondary 1/4" Apex
# of Prim. HC				# of Prim. HC	
5 Operating	29.4	30.9	30.5	5 Operating	58.8
4 Operating	27.3	30.6	31.2	4 Operating	60.3
3 Operating	n/a	n/a	n/a	3 Operating	n/a

Table 8. Summary of Purity Data for Testing Period

HCOF#1

Mg(OH) <sub>2</sub> Purity		Gypsum Purity	
Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time	
Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank	
9/19/94 to 10/13/94	80 GPM & 4 Operating Hydroclones 100 GPM & 5 Operating Hydroclones 120 GPM & 6 Operating Hydroclones	80 GPM & 4 Operating Hydroclones 100 GPM & 5 Operating Hydroclones 120 GPM & 6 Operating Hydroclones	9/19/94 to 10/13/94
pH	3.25 Hours	3.25 Hours	2.6 Hours
10	72.2	73	69.3
10.5	74.8	74.9	70.1
10.8	74.8	74.2	67.4
Mg(OH) <sub>2</sub> Recycle to Precip. Tank		Mg(OH) <sub>2</sub> Recycle to Precip. Tank	
10/4/94 to 10/7/94	80 GPM & 4 Operating Hydroclones 100 GPM & 5 Operating Hydroclones 120 GPM & 6 Operating Hydroclones	80 GPM & 4 Operating Hydroclones 100 GPM & 5 Operating Hydroclones 120 GPM & 6 Operating Hydroclones	10/4/94 to 10/7/94
pH	3.25 Hours	3.25 Hours	2.6 Hours
10	72.9	71.2	n/a
10.5	74.1	71.5	n/a
10.8	74.7	70.9	n/a
Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank	
9/28/94 to 10/3/94	Primary 1/4" Apex Secondary 3/8" Apex 1/4" Apex	Primary 1/4" Apex Secondary 3/8" Apex 1/4" Apex	9/28/94 to 10/3/94
# of Prim. HC			# of Prim. HC
5 Operating	71.4	74.6	68.6
4 Operating	68.2	75.4	74.4
3 Operating	n/a	n/a	n/a
Mg(OH) <sub>2</sub> Recycle to Precip. Tank		Mg(OH) <sub>2</sub> Recycle to Precip. Tank	
10/10/94 to 10/12/94	Primary 1/4" Apex Secondary 3/8" Apex 1/4" Apex	Primary 1/4" Apex Secondary 3/8" Apex 1/4" Apex	10/10/94 to 10/12/94
# of Prim. HC			# of Prim. HC
5 Operating	72.8	71.4	72.3
4 Operating	69.6	63.6	65.3
3 Operating	n/a	n/a	n/a
Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time	
Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank	
9/19/94 to 10/13/94		9/19/94 to 10/13/94	
pH		pH	
10		10	
10.5		10.5	
10.8		10.8	
Mg(OH) <sub>2</sub> Recycle to Precip. Tank		Mg(OH) <sub>2</sub> Recycle to Precip. Tank	
10/4/94 to 10/7/94		10/4/94 to 10/7/94	
pH		pH	
10		10	
10.5		10.5	
10.8		10.8	
Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank	
9/28/94 to 10/3/94		9/28/94 to 10/3/94	
# of Prim. HC		# of Prim. HC	
5 Operating		5 Operating	
4 Operating		4 Operating	
3 Operating		3 Operating	
Mg(OH) <sub>2</sub> Recycle to Precip. Tank		Mg(OH) <sub>2</sub> Recycle to Precip. Tank	
10/10/94 to 10/12/94		10/10/94 to 10/12/94	
# of Prim. HC		# of Prim. HC	
5 Operating		5 Operating	
4 Operating		4 Operating	
3 Operating		3 Operating	

Table 8. Summary of Purity Data for Testing Period (continued)

HCOF#2

Mg(OH) <sub>2</sub> Purity		Gypsum Purity	
Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time	
Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank	
9/19/94 to 10/13/94	80 GPM & 4 Operating Hydroclones 100 GPM & 5 Operating Hydroclones 120 GPM & 6 Operating Hydroclones 2.6 Hours 44.2 39.5 49 2.17 Hours 66.7 44.4 45.7	9/19/94 to 10/13/94	80 GPM & 4 Operating Hydroclones 100 GPM & 5 Operating Hydroclones 120 GPM & 6 Operating Hydroclones 2.6 Hours 41.2 39.1 33.6 39.3 38.8
pH	10 10.5 10.8	pH	10 10.5 10.8
<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>		<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>	
10/4/94 to 10/7/94	80 GPM & 4 Operating Hydroclones 100 GPM & 5 Operating Hydroclones 120 GPM & 6 Operating Hydroclones 2.6 Hours 44.5 47.8 n/a 43.7	10/4/94 to 10/7/94	80 GPM & 4 Operating Hydroclones 100 GPM & 5 Operating Hydroclones 120 GPM & 6 Operating Hydroclones 2.6 Hours 35.1 46.3 38.3 n/a n/a
pH	10 10.5 10.8	pH	10 10.5 10.8
<b>Crystallizer Recycle to Precip. Tank</b>		<b>Crystallizer Recycle to Precip. Tank</b>	
9/28/94 to 10/3/94	Primary 1/4" Apex Secondary 3/8" Apex 1/4" Apex 43.7 50.1 31.3 n/a	9/28/94 to 10/3/94	Primary 1/4" Apex Secondary 3/8" Apex 1/4" Apex 38.4 54.6 n/a
# of Prim. HC	5 Operating	# of Prim. HC	5 Operating
4 Operating	3 Operating	4 Operating	3 Operating
3 Operating	n/a	3 Operating	n/a
<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>		<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>	
10/10/94 to 10/12/94	Primary 1/4" Apex Secondary 3/8" Apex 1/4" Apex 63.6 48.1 34.7 n/a	10/10/94 to 10/12/94	Primary 1/4" Apex Secondary 3/8" Apex 1/4" Apex 18.4 47.4 n/a
# of Prim. HC	5 Operating	# of Prim. HC	5 Operating
4 Operating	3 Operating	4 Operating	3 Operating
3 Operating	n/a	3 Operating	n/a

Table 8. Summary of Purity Data for Testing Period (continued)

Product		Mg(OH) <sub>2</sub> Purity		Gypsum Purity	
Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time	
Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank	
9/19/94 to 10/13/94	80 GPM & 4 Operating Hydroclones 3.25 Hours	100 GPM & 5 Operating Hydroclones 2.6 Hours	120 GPM & 6 Operating Hydroclones 2.17 Hours	80 GPM & 4 Operating Hydroclones 3.25 Hours	100 GPM & 5 Operating Hydroclones 2.6 Hours
	pH 10	70.5	70.8	9.2	8.2
		70.7	70.5	8.2	10.7
		70.6	70.4	8.5	5
		70.6	69.4	8.7	7.2
					11.1
					11.7
<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>		<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>		<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>	
10/4/94 to 10/7/94	80 GPM & 4 Operating Hydroclones 3.25 Hours	100 GPM & 5 Operating Hydroclones 2.6 Hours	120 GPM & 6 Operating Hydroclones 2.17 Hours	80 GPM & 4 Operating Hydroclones 3.25 Hours	100 GPM & 5 Operating Hydroclones 2.6 Hours
	pH 10	71	n/a	7.9	18.8
		71.1	n/a	8.5	8.3
		71.2	n/a	8.3	n/a
		71.2	n/a	11.4	18.6
					n/a
<b>Crystallizer Recycle to Precip. Tank</b>		<b>Crystallizer Recycle to Precip. Tank</b>		<b>Crystallizer Recycle to Precip. Tank</b>	
9/28/94 to 10/3/94	Primary 1/4" Apex Secondary 1/4" Apex	Primary 3/8" Apex Secondary 1/4" Apex	Primary Only 1/4" Apex	Primary 1/4" Apex Secondary 1/4" Apex	Primary 3/8" Apex Secondary 1/4" Apex
# of Prim. HC	5 Operating	71.3	71	# of Prim. HC	5 Operating
	4 Operating	70.7	71		4 Operating
	3 Operating	n/a	n/a		3 Operating
<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>		<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>		<b>Mg(OH)<sub>2</sub> Recycle to Precip. Tank</b>	
10/10/94 to 10/12/94	Primary 1/4" Apex Secondary 1/4" Apex	Primary 3/8" Apex Secondary 1/4" Apex	Primary Only 1/4" Apex	Primary 1/4" Apex Secondary 1/4" Apex	Primary 3/8" Apex Secondary 1/4" Apex
# of Prim. HC	5 Operating	71.1	70.7	# of Prim. HC	5 Operating
	4 Operating	71.3	71.3		4 Operating
	3 Operating	n/a	n/a		3 Operating

Table 8. Summary of Purity Data for Testing Period (continued)

Mean Value Particle Size		Mg(OH) <sub>2</sub> Particle Size		Gypsum Particle Size	
Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time		Decreasing Crystallizer Tank Residence Time	
Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank	
9/19/94 to 10/13/94	80 GPM & 4 Operating Hydroclones 3.25 Hours 44.2 32.4 27.4	100 GPM & 5 Operating Hydroclones 2.6 Hours 32.6 36.5 30.2	120 GPM & 6 Operating Hydroclones 2.17 Hours 31.6 27.4 32.3	80 GPM & 4 Operating Hydroclones 3.25 Hours 58 52.8 59.6	100 GPM & 5 Operating Hydroclones 2.6 Hours 57 56.3 61.5
pH	10 10.5 10.8	10 10.5 10.8	10 10.5 10.8	pH	10 10.5 10.8
Mg(OH) <sub>2</sub> Recycle to Precip. Tank		Mg(OH) <sub>2</sub> Recycle to Precip. Tank		Mg(OH) <sub>2</sub> Recycle to Precip. Tank	
10/4/94 to 10/7/94	80 GPM & 4 Operating Hydroclones 3.25 Hours 28.8 30 25.2	100 GPM & 5 Operating Hydroclones 2.6 Hours 21.1 34.3 28.5	120 GPM & 6 Operating Hydroclones 2.17 Hours n/a n/a n/a	80 GPM & 4 Operating Hydroclones 3.25 Hours 54.3 60.7 51	100 GPM & 5 Operating Hydroclones 2.6 Hours 50.6 51.4 56.4
pH	10 10.5 10.8	10 10.5 10.8	10 10.5 10.8	pH	10 10.5 10.8
Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank		Crystallizer Recycle to Precip. Tank	
9/28/94 to 10/3/94	Primary 1/4" Apex Secondary 1/4" Apex	Primary 3/8" Apex Secondary 1/4" Apex	Primary Only 1/4" Apex	Primary 1/4" Apex Secondary 1/4" Apex	Primary Only 1/4" Apex
# of Prim. HC	26.7	23.9	24.5	# of Prim. HC	5 Operating
5 Operating	19.5	46.9	23.2	5 Operating	4 Operating
4 Operating	n/a	n/a	n/a	4 Operating	3 Operating
3 Operating				3 Operating	
Mg(OH) <sub>2</sub> Recycle to Precip. Tank		Mg(OH) <sub>2</sub> Recycle to Precip. Tank		Mg(OH) <sub>2</sub> Recycle to Precip. Tank	
10/10/94 to 10/12/94	Primary 1/4" Apex Secondary 1/4" Apex	Primary 3/8" Apex Secondary 1/4" Apex	Primary Only 1/4" Apex	Primary 1/4" Apex Secondary 1/4" Apex	Primary Only 1/4" Apex
# of Prim. HC	20	22.3	37.8	# of Prim. HC	5 Operating
5 Operating	23.2	27.4	27.6	5 Operating	4 Operating
4 Operating	n/a	n/a	n/a	4 Operating	3 Operating
3 Operating				3 Operating	

Table 9. Summary of Crystallizer Particle Size Data for Testing Period

Relative gypsum saturation was calculated for the 2-stage precipitation testing period and analyzed in a graphical form. (Figure 24) The relative gypsum saturation was relatively constant through the testing period at approximately 1.00. Since scaling normally occurs when relative gypsum saturation exceeds 1.2, this process appears to operate at a safe condition.

Figure 21. Comparison of Single and Two Stage Crystallizer Operation - Magnesium Hydroxide Product

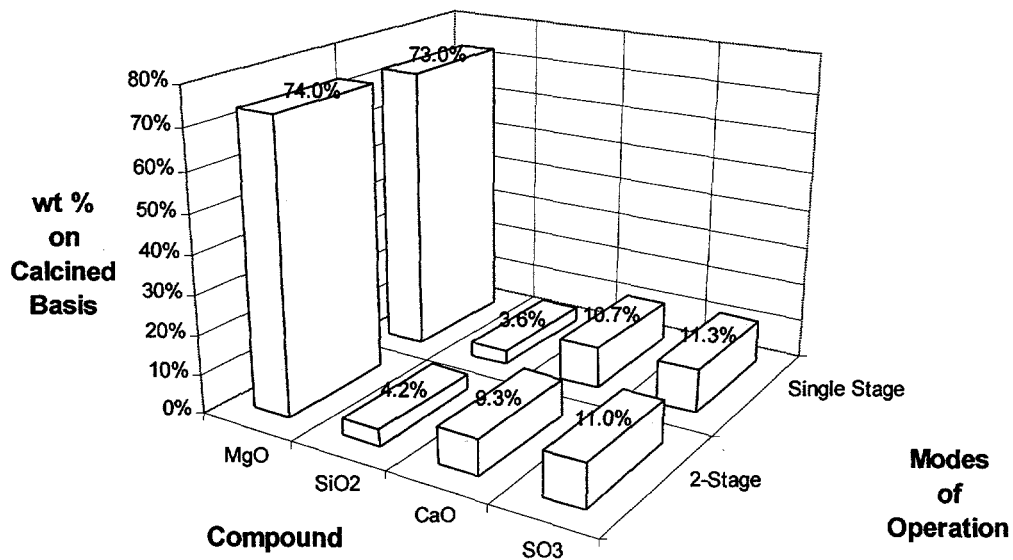


Figure 22. Comparison of Single and Two Stage Crystallizer Operation - Primary Hydroclone Overflow

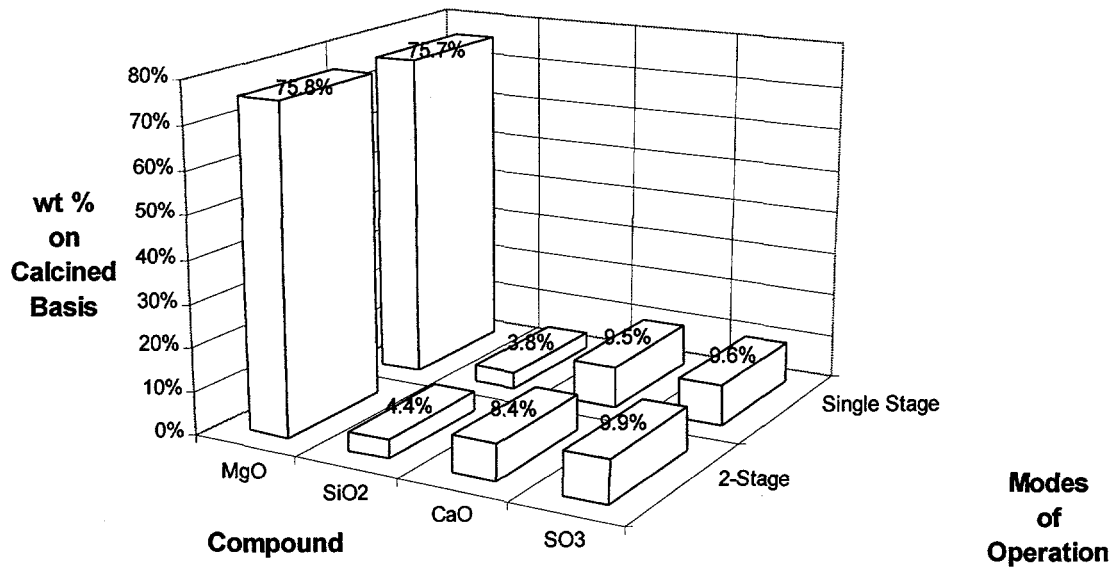
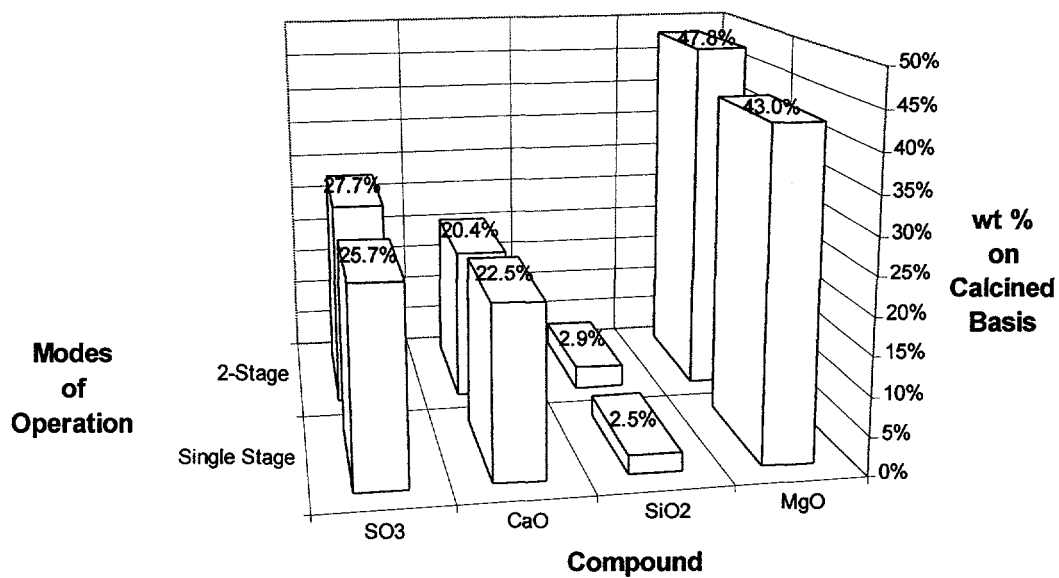


Figure 23. Comparison of Single and Two Stage Crystallizer Operation - Secondary Hydroclone Overflow



c) **Conclusions from Crystallizer Testing**

While crystallizer parametric testing was conducted in as a controlled manner as possible, liquor chemistry of the feed stream to the magnesium recovery process varied with FGD operation. The direct effect of this variability was varying sulfate ion ( $\text{SO}_4^-$ ) concentration entering the crystallizer. (Figure 25 and 26) Any inconsistencies observed in the data collected during these series of tests could be a result of varying FGD operation.

For single stage precipitation, gypsum particle size increased as residence time increased. Recycling gypsum to the oxidizer or the crystallizer decreased the purity of the magnesium hydroxide in the product stream. Also, the minimum amount of gypsum in the product stream is obtained when the residence time of the crystallizer is 2.6 hours. Due to inconsistencies in the data taken during pH testing, few trends were found. Overall the best crystallizer residence time is 2.6 hours. Gypsum recycle should be used only as needed to maintain crystallizer slurry density between 5 and 6 wt. % solids. For purposes of design, a single stage crystallizer should be designed for 2.6 hours residence time and operated at a pH of 10.5.

Since no advantage was obtained with the two stage crystallizer design, this mode will not be considered for future magnesium recovery plants. Additionally process control problems (pH in the oxidizer) were encountered when recycling magnesium hydroxide slurry to the precipitation tank. Single stage crystallizer tank operation will be continued as the preferred mode of operation.

Figure 24. Crystallizer Performance for 2-Stage Precipitation Testing

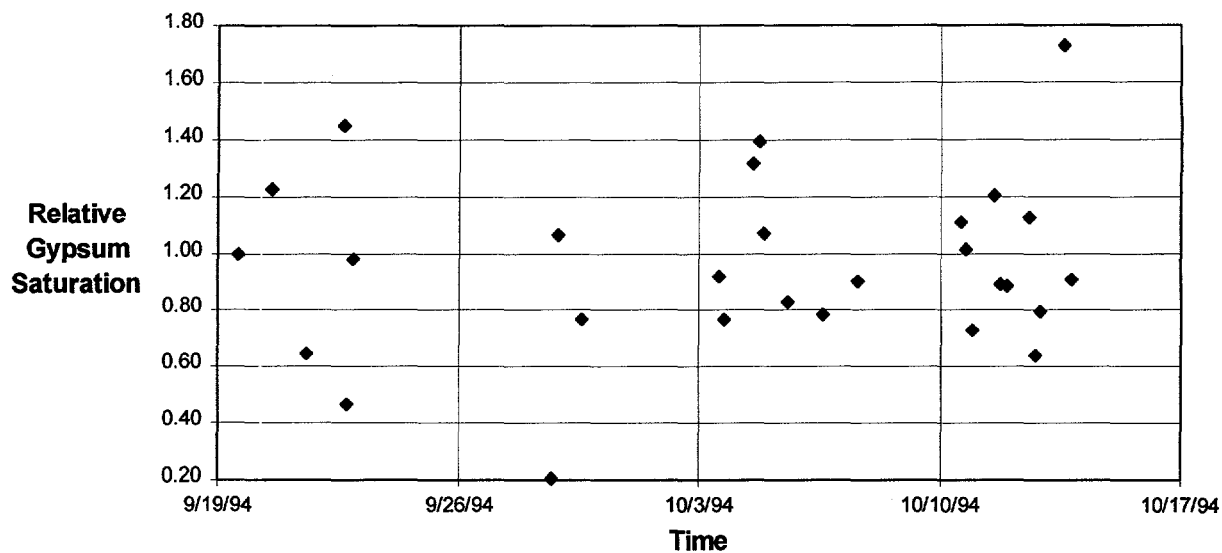


Figure 25. Oxidizer Inlet-Outlet Sulfite Concentration Profile

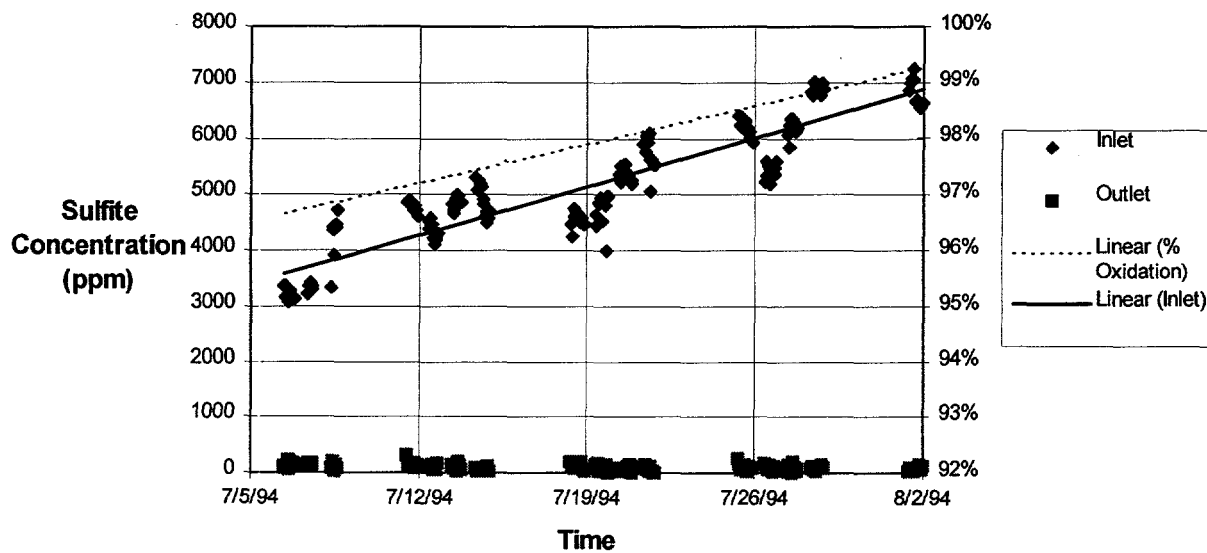
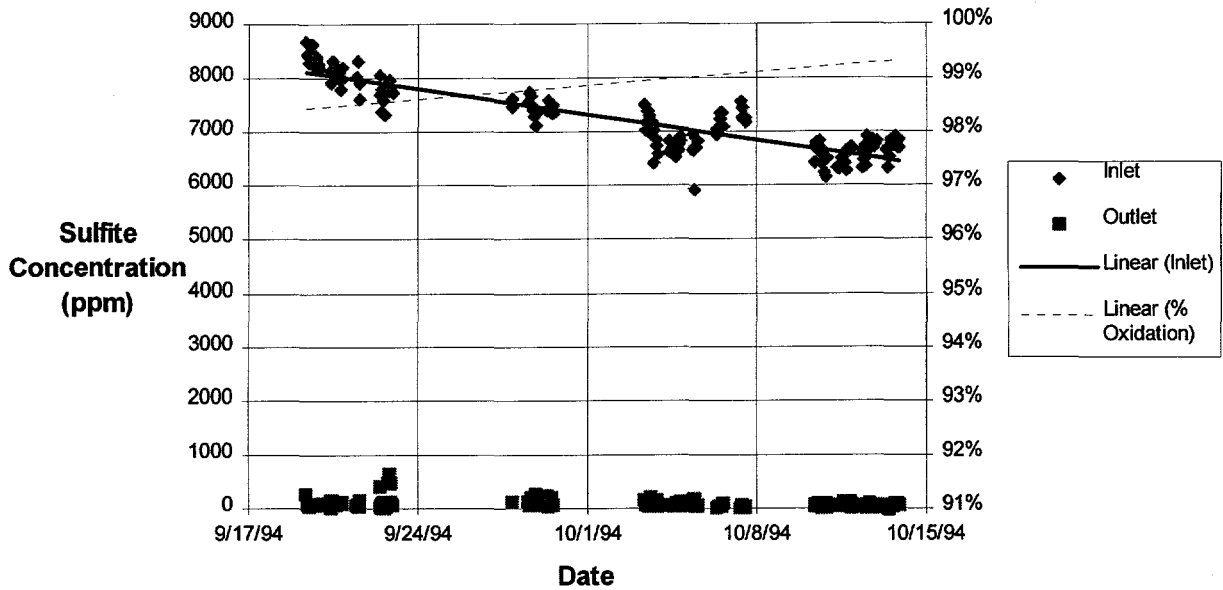


Figure 26. Oxidizer Inlet-Outlet Sulfite Concentration Profile



### 3. Hydroclone Testing

Solid separation of magnesium hydroxide and gypsum is accomplished by using hydroclones. Hydroclones separate the particles on the basis of differences in particle size and shape of two major components viz. gypsum and magnesium hydroxide. Parametric testing of the primary and secondary hydroclones was conducted to quantify the impact the hydroclone banks have on the purity of the magnesium hydroxide and gypsum products streams. A mass balance around the entire hydroclone system and each individual bank was performed. Hydroclones were tested in a series configuration in which the overflow from the first hydroclone bank was the feed for the second hydroclone bank. This test configuration was intended to increase the purity of the magnesium hydroxide in the overflow. The optimal operating conditions of the hydroclones are presented.

One inch vortexes were installed in the primary hydroclones. The performance of the hydroclones with these vortexes will be evaluated. These results will be compared to results of the hydroclones in normal operation with 5/8 inch vortexes. The primary hydroclones were evaluated with 1 inch vortexes and 1/4 or 3/8 inch apexes at flowrates of 100 and 120 GPM.

Purity and recovery of magnesium hydroxide will be evaluated and compared to the 5/8 inch vortexes used previously.

a) **Mass Balance**

The mass balance equations are shown in Table 10 along with a diagram of the areas considered for each mass balance. The mass balance is only on the solids' portion of each stream. The basis for the solids mass balance assumed that the flows of all streams were constant through the testing period. The split fractions for the hydroclone banks were also assumed to be constant. For example, a 100 GPM total feed to five primary hydroclones would result in the total hydroclone overflow and underflow being 89.7 and 10.3 GPM, respectively. Also for a 100 GPM feed to five secondary hydroclones, the total hydroclone overflow and underflow are 91.2 and 8.8 GPM, respectively. The split fractions were based on flow measurements of the hydroclone underflows at similar conditions. If the inlet flow would change, so would the overflow and underflow flow rates using the same split fraction.

An assumption also made was that Total Suspended Solids (TSS) would be constant for the testing period. (Table 11) The mass balance was found to be statistically highly dependent on the feed and HCOF TSS for each hydroclone bank. Due to the mass balance not closing, the values for TSS were adjusted by a reasonable factor. This factor was found not to be the same for all testing. Different constants were used to close the magnesium hydroxide mass balance for each testing period. Since the product stream's flow was not measured, its flow was a variable to close the overall mass balance. (Table 11) Another assumption inherent in the mass balance equations was that there was no accumulation in each system. On the other hand, the gypsum mass balance was difficult to close. Usually, there was a trade-off between the gypsum balance and the magnesium hydroxide balance. Since the magnesium hydroxide has higher importance, its balance was closed. Also, the constant that closed the gypsum balance usually made TSS values invalid.

The flowrate of the measured streams could also be a source of error. Using the data generated from the control software, the assumption of the flowrate being constant was challenged. As shown in the Appendix VI, the flowrates were fairly close to that assumed and would not be a source of error. The pressure of the feed streams were also considered. This was to see if there were any physical signs of any problems that could have occurred during the testing. No relevant trends were found.

Physical evidence of gypsum precipitating in the hydroclone overflow lines lead to the belief that equilibrium between the solid phase gypsum and liquid phase gypsum can be disturbed during hydroclone separation. Accumulation of gypsum in the system is indicated in the gypsum mass balance. Therefore, the  $Mg(OH)_2$  balance was used for the basis of the system.

Gypsum accumulation in the hydroclone overflow line can affect the  $Mg(OH)_2$  balance as well. During formation of the gypsum crystal, some  $Mg(OH)_2$  crystals can become attached, if particle charges make them attract one another. If this the case, the  $Mg(OH)_2$  balance method would show an imbalance on the low side while the gypsum balance would be on the high side. In spite of these issues, the results of the mass balance do show trends in the configuration and operation of the hydroclones.

The mass balance shows a considerable increase in magnesium hydroxide purity by running the secondary hydroclones. From the magnesium hydroxide mass balance, magnesium hydroxide recovery increased from between 80-88% to 90-95%. (Table 12) To show the economic relevance of operating the secondary hydroclones a rough cost analysis was performed. The analysis shows that running the secondary hydroclones recovers between \$10,000 and \$30,000 each year based on an operating cost to produce magnesium hydroxide of \$90/ton. This includes the operating cost of the secondary hydroclones.

Due to the unagitated dilution tank between the primary hydroclones and the secondary hydroclones, the solids from the primary hydroclones tend to settle on the bottom of the dilution tank. (Figure 27) During shut down periods the dilution tank was cleaned of accumulated solids. When the unit was restarted after cleaning, the mass balance did not close until the solids stopped accumulating. The operating conditions for the testing period were conducted only after accumulation was determined to have stopped, so that the mass balance could be determined accurately.

Changes were made in the number of hydroclones and also in the internals of the hydroclones. The number of hydroclones ranged from 4 to 6 primary hydroclones and 4 to 5 secondary hydroclones. The internals for both banks were set at either 3/8 inch apexes or 1/4 inch apexes. The hydroclones performed best with 1/4 inch apexes. Changing from 1/4 inch to 3/8 inch apexes decreased magnesium hydroxide recovery and purity. However, use of the 1/4 inch apexes tended to plug more easily and create higher inlet pressure. Operating 5 primary hydroclones and 5 secondary hydroclones with 1/4 inch apexes had the highest magnesium hydroxide recovery of 95%. These operating conditions recovered an additional 1.81 lbs. magnesium hydroxide per minute. Operating 5 primary hydroclones and 5 secondary hydroclones had the highest product purity reaching 70% magnesium hydroxide in the solids' portion of the product. Another excellent operating condition was 4 primary hydroclones and 5 secondary hydroclones with 1/4 inch apexes. These operating conditions recovered 94% of the magnesium hydroxide and had close to 70% magnesium hydroxide in solids' portion of the product. These two operating conditions are close in product purity and magnesium hydroxide recovery. Running 5 primary hydroclones and 5 secondary hydroclones with 1/4 inch apexes is the best option. Running 5 primary hydroclones instead of 4 will increase the amount of magnesium hydroxide produced without sacrificing quality.

Figure 27. Dilution Tank

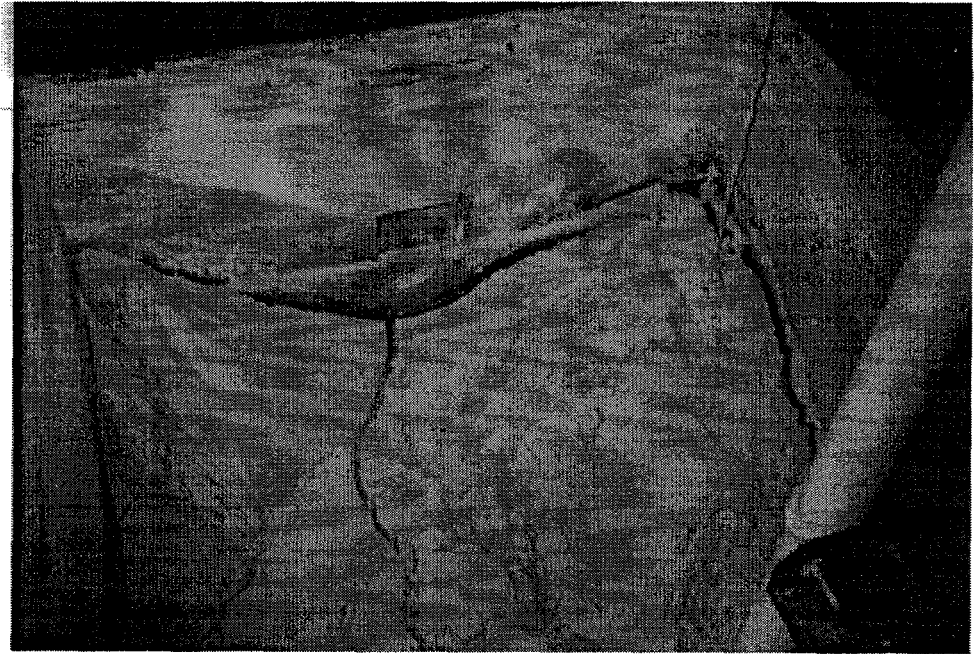
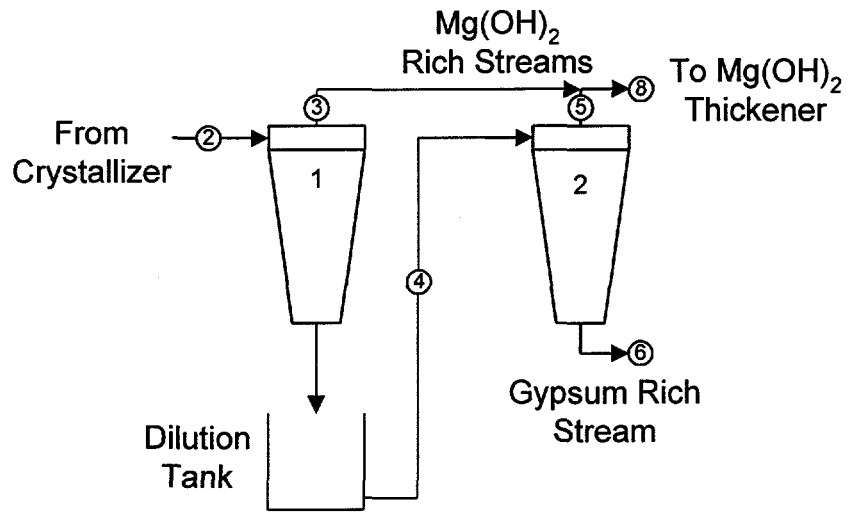


Table 10

**Solids Mass Balance Diagram**



Stream Table	
Number	Name
2	Crystallizer
3	HCOF#1
4	HCUF#1
5	HCOF#2
6	HCUF#2
8	Product

**Solids Mass Balance Equations**

Overall Solids Mass Balance

$$2 - 6 - 8 = \text{Accum.} = 0$$

Mass Balance of Primary Hydroclone

$$2 - 3 - 4 = \text{Accum.} = 0$$

Mass Balance of Secondary Hydroclone

$$4 - 5 - 6 = \text{Accum.} = 0$$

### Component Balances

(Where  $X_i^j$  is the percent of component  $i$  in the  $j$  stream)

#### Gypsum Balance

##### Overall Balance

$$(2 \times X_{\text{GYP}}^2) - (6 \times X_{\text{GYP}}^6) - (8 \times X_{\text{GYP}}^8) = 0$$

##### Primary Hydroclone

$$(2 \times X_{\text{GYP}}^2) - (3 \times X_{\text{GYP}}^3) - (4 \times X_{\text{GYP}}^4) = 0$$

##### Secondary Hydroclone

$$(4 \times X_{\text{GYP}}^4) - (5 \times X_{\text{GYP}}^5) - (6 \times X_{\text{GYP}}^6) = 0$$

#### Mg(OH)<sub>2</sub>

##### Overall Balance

$$(2 \times X_{\text{Mg(OH)}_2}^2) - (6 \times X_{\text{Mg(OH)}_2}^6) - (8 \times X_{\text{Mg(OH)}_2}^8) = 0$$

##### Primary Hydroclone

$$(2 \times X_{\text{Mg(OH)}_2}^2) - (3 \times X_{\text{Mg(OH)}_2}^3) - (4 \times X_{\text{Mg(OH)}_2}^4) = 0$$

##### Secondary Hydroclone

$$(4 \times X_{\text{Mg(OH)}_2}^4) - (5 \times X_{\text{Mg(OH)}_2}^5) - (6 \times X_{\text{Mg(OH)}_2}^6) = 0$$

### Percent Recovery Equations

#### Overall

$$\% \text{Rec}_{\text{Mg(OH)}_2} = \frac{8 \times X_{\text{Mg(OH)}_2}^8}{2 \times X_{\text{Mg(OH)}_2}^2} \times 100$$

$$\% \text{Rec}_{\text{GYP}} = \frac{6 \times X_{\text{GYP}}^6}{2 \times X_{\text{GYP}}^2} \times 100\%$$

#### Primary Hydroclones

$$\% \text{Rec}_{\text{Mg(OH)}_2} = \frac{3 \times X_{\text{Mg(OH)}_2}^3}{2 \times X_{\text{Mg(OH)}_2}^2} \times 100$$

$$\% \text{Rec}_{\text{GYP}} = \frac{4 \times X_{\text{GYP}}^4}{2 \times X_{\text{GYP}}^2} \times 100\%$$

#### Secondary Hydroclones

$$\% \text{Rec}_{\text{Mg(OH)}_2} = \frac{5 \times X_{\text{Mg(OH)}_2}^5}{4 \times X_{\text{Mg(OH)}_2}^4} \times 100$$

$$\% \text{Rec}_{\text{GYP}} = \frac{6 \times X_{\text{GYP}}^6}{4 \times X_{\text{GYP}}^4} \times 100\%$$

Lab#	SpID1	SampleID	SpID2	SpID3	CaO	CO <sub>2</sub>	MgO	SiO <sub>2</sub>	Total Susp. Solids (wt %)	Microtrac MV (microns)	Mg(OH) <sub>2</sub> (calc.)	CaSO <sub>4</sub> 2H <sub>2</sub> O (calc.)	MgSiO <sub>3</sub> (calc.)	Spec. Gravity	Flowrate Gall/min	Flowrate Lbs/min	Mg(OH) <sub>2</sub> Lbs/min	CaSO <sub>4</sub> 2H <sub>2</sub> O Lbs/min	Mass Balances Where In - Out = 0		Constant	% Mg(OH) <sub>2</sub> Recovery	% CaSO <sub>4</sub> 2H <sub>2</sub> O Recovery	
																			Total	Mg(OH) <sub>2</sub>				
941859	Crystallizer	2	5/27/94	8:30					5.1	23.1				1.021	100.0	850.99								
941899	Crystallizer	2	6/7/94	14:30					5.5	30.3	25.28	63.10	1.50	1.023	100.0	852.59	12.21	29.32			-3.2			
942103	Crystallizer	2	6/15/94	12:00	22.54	1.06	18.88	0.72	1.07															
942109	Crystallizer	2	6/16/94	14:00	22.17	1.31	20.31	0.74	1.19	4.7	34.5	28.24	60.94	1.67	1.019	100.0	848.86	11.22	24.21	0				
942115	Crystallizer	2	6/17/94	13:00	22.31	1.22	20.02	0.85	1.14	5.6	42.5	27.86	61.42	1.60	1.024	100.0	853.36	13.34	29.41	0.5				
942205	Crystallizer	2	6/22/94	14:00	22.28	1.06	19.44	0.51	0.95	5.4	38.8	27.21	62.87	1.33	1.023	100.0	852.35	12.52	28.94	-2.5				
942199	Crystallizer	2	6/28/94	14:00	22.32	1.08	19.42	0.55	1.02	6.7	41.5	27.11	62.81	1.43	1.031	100.0	858.78	15.67	36.30	1.1				
942193	Crystallizer	2	6/28/94	20:00	22.38	1.81	19.67	0.46	1.05	10.5	39.6	27.44	60.38	1.47	1.052	100.0	876.93	25.22	55.49	-3.1				
942187	Crystallizer	2	6/29/94	18:00	22.18	1.12	19.89	0.78	1.10	5.1	43.2	27.71	61.60	1.54	1.021	100.0	851.09	12.12	26.95	0.1				
942177	Crystallizer	2	6/30/94	13:30	22.76	1.11	19.13	0.66	1.10	6.8	35.5	26.61	63.74	1.54	1.031	100.0	859.03	15.50	37.13	-2.3				
942183	Crystallizer	2	6/30/94	20:00	24.11	1.20	16.70	0.89	0.87	9.4	41.5	23.32	66.92	1.22	1.046	100.0	871.56	19.05	54.65	-3.5				
942309	Crystallizer	2	7/5/94	14:00	22.20	1.00	19.66	0.40	0.94	4.7	40.1	27.54	63.16	1.32	1.019	100.0	849.06	11.04	25.31	-2.4				
942315	Crystallizer	2	7/5/94	18:00	21.61	1.22	20.89	0.45	0.98	6.5	38.0	29.28	60.35	1.37	1.029	100.0	857.48	16.22	33.43	3				
942319	Crystallizer	2	7/5/94	22:00	23.02	1.02	18.11	0.28	0.86	8.6	33.5	25.37	65.92	1.21	1.042	100.0	867.98	19.01	49.38	-3				
942325	Crystallizer	2	7/5/94	13:00	21.01	0.94	21.32	0.36	1.06	3.4	40.5	29.82	59.85	1.49	1.011	80.0	674.09	6.81	13.68	0				
942331	Crystallizer	2	7/5/94	20:00	20.98	1.13	21.34	0.49	1.07	6.8	42.1	29.84	58.66	1.50	1.031	100.0	858.88	17.30	34.01	2				
942337	Crystallizer	2	7/7/94	14:00	21.67	0.90	20.04	0.52	1.02	5.9	45.7	28.01	61.60	1.43	1.026	120.0	1025.60	16.89	37.15	0.8				
942343	Crystallizer	2	7/8/94	14:00	21.66	1.05	20.55	0.38	1.10	5.8	27.2	28.67	61.36	1.54	1.025	80.0	683.31	11.30	24.19	-0.7				
941796	HCOF#1	3	5/19/94	12:15	10.63		41.73	0.33	2.43	11.9	58.03	31.74	3.41											
941797	HCOF#1	3	5/19/94	12:15	9.56		44.75	0.37	2.78		62.06	28.35	3.90											
941860	HCOF#1	3	5/27/94	8:30						7.3														
941895	HCOF#1	3	6/7/94	14:50	8.15	2.08	48.44	0.70	2.66	11.6	67.51	15.00	3.73											
942104	HCOF#1	3	6/15/94	12:00	7.28	1.97	48.04	0.57	2.46	1.9	7.1	67.13	13.11	3.45	1.003	89.7	749.12	9.76	1.90	0.0	0.30	0.36	79.89%	
942116	HCOF#1	3	6/16/94	14:00	6.68	2.36	50.76	0.54	2.72	1.7	4.7	70.81	9.82	3.82	1.002	89.7	748.20	9.17	1.27	0.0	0.08	-0.55	0.05	81.72%
942206	HCOF#1	3	6/17/94	13:00	7.59	2.26	49.77	0.72	2.51	2.2	29.8	69.58	12.52	3.52	1.004	89.7	750.11	11.33	2.04	0.0	0.09	3.18	-1.6	84.91%
942206	HCOF#1	3	6/27/94	14:00	11.90	1.86	38.88	0.47	2.00	2.6	19.4	54.32	27.99	2.81	1.007	89.7	751.98	10.62	5.47	0.0	0.08	2.19	-0.6	84.81%
942200	HCOF#1	3	6/28/94	14:00	7.40	1.94	48.29	0.60	2.27	2.6	18.0	67.68	13.51	3.18	1.007	89.7	752.07	13.33	2.86	0.0	0.17	10.12	-0.1	85.10%
942184	HCOF#1	3	6/28/94	20:00	6.85	1.08	49.22	0.10	2.34	4.3	7.7	68.95	14.11	3.28	1.016	89.7	759.14	22.25	4.55	0.0	0.01	20.81	0.3	88.20%
942186	HCOF#1	3	6/29/94	18:00	6.04	1.88	50.87	0.88	2.48	1.9	5.3	71.21	8.82	3.48	1.002	89.7	748.90	10.08	1.25	0.0	-0.05	9.98	-1.5	83.13%
942178	HCOF#1	3	6/30/94	13:30	7.23	2.42	49.60	0.50	2.54	2.5	4.5	69.31	11.38	3.56	1.006	89.7	751.50	12.97	2.13	0.0	-0.07	15.24	0	83.67%
942184	HCOF#1	3	6/30/94	20:00	7.89	2.03	48.22	0.54	2.20	3.2	5.0	67.64	15.13	3.09	1.010	89.7	754.41	16.13	3.61	0.0	0.02	19.03	0	84.67%
942316	HCOF#1	3	7/5/94	14:00	8.04	1.88	47.06	0.22	2.05	1.8	8.0	66.11	16.73	2.88	1.002	89.7	748.68	9.11	2.31	0.0	0.08	0.07	-0.8	82.52%
942320	HCOF#1	3	7/5/94	18:00	8.29	2.00	47.20	0.38	2.00	2.7	7.0	66.38	16.60	2.81	1.007	89.7	752.37	13.43	3.36	0.0	0.06	0.29	0.15	82.81%
942326	HCOF#1	3	7/6/94	22:00	6.84	1.91	49.33	0.08	2.13	3.0	7.5	69.32	13.31	2.99	1.009	89.7	753.85	15.83	3.04	0.0	0.30	15.51	0.8	83.31%
942332	HCOF#1	3	7/6/94	13:00		1.78		0.33		1.3	12.3			0.999	71.7	597.21								
942332	HCOF#1	3	7/6/94	20:00	6.75	1.69	48.02	0.38	2.25	2.9	14.5	67.30	13.09	3.16	1.008	89.7	753.11	14.50	2.82	0.0	0.12	1.16	0.4	83.79%
942338	HCOF#1	3	7/7/94	14:00	7.00	1.52	46.38	0.41	2.18	2.4	21.1	65.00	14.44	3.06	1.005	107.6	901.28	14.00	3.11	0.0	0.09	0.46	0.37	82.89%
942344	HCOF#1	3	7/8/94	14:00	7.24	1.83	48.90	0.34	2.37	2.3	13.8	68.46	14.15	3.32	1.005	71.7	600.40	9.29	1.92	0.0	0.13	0.05	0.2	82.18%
941798	HCOF#1	4	5/19/94	12:15	30.31		4.08	0.33	0.41		29.8	5.51	92.15	0.58										
941858	HCOF#1	4	5/27/94	8:30						49.6														
941857	HCOF#1	4	5/27/94	9:30	29.88	0.55	5.00	0.27	0.38		47.8	6.87	88.84	0.53										
941897	HCOF#1	4	6/7/94	14:50	28.33	0.66	7.64	0.27	0.61	14.4	36.6	10.46	83.65	0.86	1.075	10.3	92.70	1.40	11.19					
942105	HCOF#1	4	6/15/94	12:00	29.50	0.60	5.07	0.49	0.41	30.9	66.9	6.94	86.89	0.58	1.171	10.3	100.92	2.16	27.06					
942111	HCOF#1	4	6/16/94	14:00	29.50	0.67	5.31	0.65	0.47	27.5	62.3	7.23	86.18	0.86	1.151	10.3	98.23	1.97	23.49					
942107	HCOF#1	4	6/17/94	13:00	29.58	0.65	5.10	0.46	0.47	28.0	76.9	6.92	87.02	0.66	1.154	10.3	98.47	1.92	24.19					
942207	HCOF#1	4	6/27/94	14:00	29.35	0.65	5.38	0.38	0.38	25.1	61.6	7.42	86.53	0.53	1.137	10.3	98.03	1.82	21.27					

Table 11. Mass Balance for Perimetric Hydrochlorone Testing

Lab#	SpI ID1	SpI ID2	SpI ID3	CaO	CO <sub>2</sub>	MgO	SiO <sub>2</sub>	Total Susp. Solids (wt %)	Microtrac MV (microns)	Mg(OH) <sub>2</sub> (calc.)	CaSO <sub>4</sub> 2H <sub>2</sub> O (calc.)	MgSiO <sub>3</sub> (calc.)	Spec. Gravity	Flowrate Gal/min	Flowrate Lbs/min	CaSO <sub>4</sub> 2H <sub>2</sub> O Lbs/min	Mass Balances Where In - Out = 0	Constant	% Mg(OH) <sub>2</sub> Recovery	% CaSO <sub>4</sub> 2H <sub>2</sub> O Recovery						
942201	HCUF#1	4	6/28/94	14.00	28.97	0.62	5.69	0.55	0.42	27.8	57.9	7.83	85.02	0.59	1.153	10.3	99.41	2.17	23.52	1.5						
942195	HCUF#1	4	6/28/94	20.00	28.87	0.69	6.08	0.54	0.49	34.7	66.2	8.32	84.47	0.69	1.193	10.3	102.84	2.97	30.12	0.3						
942189	HCUF#1	4	6/29/94	18.00	27.94	0.72	7.89	0.54	0.55	20.2	65.7	10.88	81.49	0.77	1.109	10.3	95.58	2.10	15.72	3						
942179	HCUF#1	4	6/30/94	13.30	28.29	0.76	7.88	0.54	0.56	24.5	63.1	10.86	82.41	0.79	1.134	10.3	97.75	2.60	19.76	2						
942185	HCUF#1	4	6/30/94	20.00	29.25	0.68	5.59	0.90	0.44	36.4	66.7	7.66	84.70	0.82	1.203	10.3	103.72	2.90	32.01	0						
942311	HCUF#1	4	7/5/94	14.00	29.17	0.53	4.94	1.13	0.35	27.4	67.5	6.81	84.43	0.49	1.151	10.3	99.19	1.85	22.94	0						
942317	HCUF#1	4	7/5/94	18.00	29.20	0.64	5.70	0.43	0.40	33.8	70.9	7.86	85.97	0.56	1.188	10.3	102.41	2.72	29.78	0						
942321	HCUF#1	4	7/5/94	22.00	28.98	0.61	5.74	0.35	0.35	35.0	64.7	7.97	85.63	0.49	1.195	10.3	102.98	2.87	30.83	0						
942327	HCUF#1	4	7/6/94	13.00	29.33	0.56	5.49	0.55	0.37	25.0	68.5	7.59	86.36	0.52	1.137	8.3	78.41	1.49	16.96	0						
942333	HCUF#1	4	7/6/94	20.00	29.15	0.61	5.54	0.52	0.37	34.2	65.9	7.66	85.69	0.52	1.190	10.3	102.58	2.68	30.03	0						
942339	HCUF#1	4	7/7/94	14.00	29.44	0.64	5.25	0.48	0.38	31.9	72.1	7.23	86.57	0.53	1.176	12.4	121.76	2.80	33.57	0						
942345	HCUF#1	4	7/8/94	14.00	29.33	0.59	5.33	0.58	0.42	31.8	70.6	7.31	86.16	0.59	1.176	8.3	81.11	1.88	22.22	0						
941896	HCUF#2	5	6/7/94	15.05	8.24	2.02	48.29	0.32	2.66		11.8	67.30	16.53	3.73												
942106	HCUF#2	5	6/15/94	12.00	16.91	1.48	29.23	0.48	1.58	0.5	15.9	40.76	44.82	2.22	0.994	91.2	755.50	1.51	1.66	0.0	0.02	6.32	-1	69.83%	70.51%	
942112	HCUF#2	5	6/16/94	14.00	16.12	0.56	30.87	0.42	2.22	0.3	11.4	42.23	46.16	3.11	0.993	91.2	754.80	1.05	1.15	0.0	0.05	1.59	-0.2	53.39%	88.33%	
942118	HCUF#2	5	6/17/94	14.00	16.18	0.56	30.23	0.36	2.19	0.3	18.2	41.62	46.51	3.07	0.993	91.2	754.84	1.07	1.19	0.0	0.02	1.27	-0.05	55.49%	89.82%	
942208	HCUF#2	5	6/27/94		16.05	1.27	31.24	0.38	1.49	0.4		43.76	45.28	2.09	0.994	91.2	755.15	1.35	1.34	0.0	-0.17	0.31	-1.3	74.30%	92.26%	
942202	HCUF#2	5	6/28/94		10.64	1.48	41.47	0.63	1.98	0.4		58.09	25.18	2.78	0.994	91.2	755.02	1.67	0.72	0.0	-0.87	2.18	-2.3	76.97%	87.65%	
942190	HCUF#2	5	6/29/94		17.61	1.48	28.36	0.59	1.39	0.5		39.69	46.68	1.95	0.994	91.2	755.41	1.41	1.66	0.0	0.39	0.03	0	47.48%	94.40%	
942180	HCUF#2	5	6/30/94		8.75	1.59	45.89	0.39	2.07	0.3		64.40	19.59	2.90	0.993	91.2	754.84	1.65	0.50	0.0	-0.80	-10.40	-1.3	78.73%	163.00%	
942312	HCUF#2	5	7/5/94		12.67	1.59	37.73	0.50	1.99	0.4		52.67	31.33	2.79	0.994	91.2	755.24	1.71	1.02	0.0	-0.67	-10.70	-0.2	65.68%	149.01%	
942322	HCUF#2	5	7/5/94		NES	1.44	NES	0.28	NES	0.9		13.9			0.997	91.2	757.35						0			
942328	HCUF#2	5	7/6/94		NES	1.59	NES	0.22	NES	0.5		15.2			0.994	91.2	755.41						0			
942334	HCUF#2	5	7/6/94		NES	NES	NES	0.38	NES	0.3		13.9			0.993	72.9	603.59						0			
942340	HCUF#2	5	7/7/94		NES	NES	NES	0.42	NES	0.3		17.3			0.993	91.2	754.71						0			
942346	HCUF#2	5	7/8/94		NES	1.52	NES	0.44	NES	0.6		19.2			0.995	91.2	755.99						0			
941898	HCUF#2	6	6/7/94		NES	1.38	NES	0.41	NES	0.4		14.2			0.994	72.9	604.08						0			
942107	HCUF#2	6	6/7/94	15.05	30.73	0.42	2.59	0.21	0.36	27.2	45.5	3.40	92.12	0.51	1.149	8.8	84.49	0.78	21.18							
942113	HCUF#2	6	6/15/94	12.00	30.89	0.47	2.29	0.56	0.27	25.0	72.5	3.05	91.47	0.38	1.136	8.8	83.53	0.64	19.08							
942119	HCUF#2	6	6/16/94	14.00	30.57	0.56	2.84	0.53	0.34	27.2	69.2	3.78	90.22	0.48	1.150	8.8	84.49	0.87	20.75							
942209	HCUF#2	6	6/17/94	13.00	30.83	0.52	2.67	0.40	0.34	28.0	78.7	3.53	91.52	0.48	1.154	8.8	84.82	0.84	21.73							
942203	HCUF#2	6	6/27/94	14.00	31.20	0.39	2.26	0.43	0.24	25.2	71.0	3.04	93.09	0.34	1.138	8.8	83.63	0.64	19.63							
942197	HCUF#2	6	6/28/94	14.00	30.04	0.50	4.36	0.56	0.42	27.5	59.0	5.90	88.75	0.59	1.151	8.8	84.59	1.37	20.62							
942181	HCUF#2	6	6/29/94	20.00	30.77	0.50	2.94	0.41	0.31	35.5	64.1	3.95	91.12	0.43	1.197	8.8	88.01	1.23	28.44							
942313	HCUF#2	6	6/30/94	13.30	30.31	0.51	3.52	0.51	0.35	37.0	60.6	4.75	89.67	0.49	1.207	8.8	86.68	1.56	29.45							
942323	HCUF#2	6	7/5/94	14.00	30.67	0.50	2.88	0.41	0.25	25.3	72.6	3.93	91.08	0.35	1.139	8.8	83.68	0.83	19.31							
942329	HCUF#2	6	7/5/94	22.00	30.47	2.16	3.09	0.46	0.26	37.9	69.9	4.22	83.84	0.36	1.208	8.8	88.79	1.40	27.75							
942335	HCUF#2	6	7/6/94	13.00	30.51	0.46	2.80	0.56	0.26	33.9	74.0	3.80	90.35	0.36	1.130	7.1	86.47	0.60	14.36							
942341	HCUF#2	6	7/6/94	20.00	30.39	0.48	2.84	0.57	0.26	39.0	70.6	3.86	89.87	0.36	1.218	8.8	89.52	1.35	31.38							
942347	HCUF#2	6	7/7/94	14.00	30.69	0.45	2.56	0.62	0.25	34.7	75.8	3.46	90.78	0.35	1.193	8.8	87.66	1.05	27.57							
941855	Product	8	5/27/94		6.30	1.50	50.15	0.51	3.00		4.1	69.66	12.10	4.21												
941856	Product	8	6/2/94		7.36	1.43	48.90	0.49	2.81		3.9	68.03	15.68	3.94												
941894	Product	8	6/7/94		7.44	1.35	49.56	0.45	2.72		6.0	69.03	16.35	3.82												
Overall Mass Balance																		For Mg(OH) <sub>2</sub>		For Gypsum						
																		Strm2 - Strm6 = Strm8		Strm3 + Strm5 = Strm8						

Table 11. Mass Balance for Perimetric Hydroclorone Testing (continued)

Lab#	Spl ID1	SampleID	Spl ID2	Spl ID3	CaO	CO <sub>2</sub>	MgO	SO <sub>2</sub>	SiO <sub>2</sub>	Total Susp. Solids (wt %)	Microtrac MV (microns)	Mg(OH) <sub>2</sub> (calc.)	CaSO <sub>4</sub> 2H <sub>2</sub> O (calc.)	MgSiO <sub>3</sub> (calc.)	Spec. Gravity	Flowrate Gall/min	Flowrate Lbs/min	Mg(OH) <sub>2</sub> Lbs/min	CaSO <sub>4</sub> 2H <sub>2</sub> O Lbs/min	Mass Balances Where In - Out =0	Constant	% Mg(OH) <sub>2</sub> Recovery	% CaSO <sub>4</sub> 2H <sub>2</sub> O Recovery
942108	Product	8	6/15/94	12:00	7.35	1.89	49.42	0.55	2.69	18.4	4.0	68.90	13.69	3.77	1.088	10.0	91.50	11.57	2.30	11.58	3.56	94.74%	7.84%
942114	Product	8	6/16/94	14:00	7.26	1.81	50.36	0.43	2.70	18.5	4.8	70.25	14.05	3.79	1.099	8.6	78.76	10.25	2.05	10.35	2.42	91.36%	8.46%
942120	Product	8	6/17/94	13:00	7.32	1.71	50.27	0.44	2.70	18.5	3.2	70.12	14.60	3.79	1.099	10.5	96.13	12.44	2.59	12.50	3.23	93.29%	8.81%
942210	Product	8	6/27/94	14:00	7.32	1.65	49.83	0.46	2.62	22.6	14.0	69.56	14.78	3.68	1.123	8.1	75.79	11.92	2.53	11.88	6.81	95.18%	8.75%
942204	Product	8	6/28/94	14:00	7.46	1.66	49.73	0.94	2.63	20.7	11.6	69.41	13.88	3.69	1.111	10.8	100.03	14.94	2.87	14.30	3.38	91.54%	7.90%
942198	Product	8	6/28/94	20:00	7.49	1.70	49.90	0.55	2.65	20.0	5.4	69.64	14.86	3.72	1.108	18.5	170.77	23.81	5.08	23.99	6.21	94.39%	9.16%
942192	Product	8	6/29/94	18:00	7.51	1.70	49.89	0.41	2.63	20.6	4.6	69.64	15.30	3.69	1.111	8.2	75.92	10.89	2.39	10.88	1.75	89.79%	8.87%
942186	Product	8	6/30/94	13:30	8.14	1.93	48.91	0.87	2.49	16.4	4.0	68.36	15.10	3.49	1.087	13.8	124.96	13.99	3.09	13.94	3.15	90.26%	8.32%
942314	Product	8	7/5/94	14:00	8.37	1.92	48.48	0.13	2.34	13.6	5.3	67.88	17.63	3.28	1.070	12.0	107.03	9.86	2.59	10.20	21.38	89.34%	10.23%
942318	Product	8	7/5/94	18:00	8.30	1.89	48.43	0.29	2.34	13.6	5.7	67.81	17.30	3.28	1.070	17.5	156.09	14.37	3.67	14.82	24.11	88.63%	10.97%
942324	Product	8	7/5/94	22:00	8.24	1.96	48.30	0.13	2.33	13.7	7.6	67.63	17.28	3.27	1.071	20.2	180.27	16.66	4.26	18.40	24.77	87.76%	8.63%
942330	Product	8	7/6/94	13:00	8.20	1.82	48.59	0.33	2.35	14.0	7.3	68.03	17.16	3.30	1.073								
942336	Product	8	7/6/94	20:00	8.25	1.93	48.63	0.39	2.35	14.3	12.2	68.09	16.72	3.30	1.074	18.3	163.84	15.92	3.91	16.25	23.43	92.01%	11.50%
942342	Product	8	7/7/94	14:00	8.27	1.94	48.42	0.38	2.34	14.5	13.0	67.90	16.77	3.28	1.076	17.3	155.10	15.28	3.78	16.33	31.55	90.45%	10.18%
942348	Product	8	7/6/94	14:00	8.23	1.98	48.20	0.31	2.32	14.7	14.4	67.50	16.68	3.25	1.077	11.9	106.76	10.56	2.61	11.30	27.54	93.39%	10.79%
930148	DOW Prod.	#N/A			0.85		65.27	0.00	0.40			94.06	2.61	0.56									

Table 11. Mass Balance for Perimetric Hydrocclone Testing (continued)

Date	Time	Primary HC		Secondary HC		Product Stream		Basis		HC Cost Power Req. = \$0.05/kWhr = 3.73 kWhr	# of HC's	Apex Size			
		% Mg(OH) <sub>2</sub> Recovery	% CaSO <sub>4</sub> 2H <sub>2</sub> O Recovery	% Mg(OH) <sub>2</sub> Recovery	% CaSO <sub>4</sub> 2H <sub>2</sub> O Recovery	Mg(OH) <sub>2</sub> Savings (lbs/min)	\$ / Yr	HCOF Micron Size	HCOF Micron Size				Micron Size	Percent Mg(OH) <sub>2</sub>	
6/15/94	12:00	79.89%	92.29%	69.83%	70.51%	94.74%	7.84%	1.81	\$32,970.28	7.1	15.9	4.0	68.9	5-5	1/4-1/4
6/16/94	14:00	81.72%	97.04%	53.39%	88.33%	91.36%	8.48%	1.08	\$19,140.96	4.7	11.4	4.8	70.3	5-5	1/4-1/4
6/17/94	13:00	84.91%	82.27%	55.49%	89.82%	93.29%	8.81%	1.12	\$19,819.80	29.8	18.2	3.2	70.1	5-5	1/4-1/4
6/27/94	14:00	84.81%	73.51%	74.30%	92.28%	95.18%	8.75%	1.30	\$23,258.46	19.4	Not Availabl	14.0	69.6	5-5	1/4-1/4
6/28/94	14:00	85.10%	64.79%	76.97%	87.65%	91.54%	7.90%	1.01	\$17,775.71	18.0	Not Availabl	11.6	69.4	5-5	1/4-1/4
6/29/94	20:00	88.20%	54.29%	47.48%	94.40%	94.39%	9.16%	1.56	\$28,206.87	7.7	Not Availabl	5.4	69.6	4-5	1/4-1/4
6/29/94	18:00	83.13%	58.32%	78.73%	163.00%	89.79%	8.87%	0.81	\$13,965.11	5.3	Not Availabl	4.6	69.6	5-5	3/8-1/4
6/30/94	13:30	83.67%	53.23%	65.68%	149.01%	90.26%	8.32%	1.02	\$18,017.66	4.5	Not Availabl	4.0	68.4	4-5	3/8-1/4
6/30/94	20:00	84.67%	58.68%			89.53%	7.51%	0.93	\$16,183.48	5.0	Not Availabl	4.2	67.2	5-0	1/4-0
7/5/94	14:00	82.52%	90.62%			89.34%	10.23%	0.75	\$12,906.13	8.0	13.9	5.3	67.9	4-5	1/4-1/4
7/5/94	18:00	82.81%	89.10%			88.63%	10.97%	0.94	\$16,521.36	7.0		5.7	67.8	5-0	1/4-0
7/5/94	22:00	83.31%	62.43%			87.76%	8.63%	0.85	\$14,678.36	7.5	15.2	7.6	67.6	5-5	1/4-1/4
7/6/94	13:00									12.3	13.9	7.3	68	4-4	1/4-1/4
7/6/94	20:00	83.79%	88.29%			92.01%	11.50%	1.42	\$25,578.24	14.5	17.3	12.2	68.1	5-5	1/4-1/4
7/7/94	14:00	82.89%	90.38%			90.45%	10.18%	1.28	\$22,836.33	21.1	19.2	13.0	67.80	6-5	1/4-1/4
7/8/94	14:00	82.18%	91.87%			93.99%	10.79%	1.27	\$22,637.67	13.8	14.2	14.4	67.5	4-4	1/4-1/4

Date	Time	Crystallizer		Primary HC		Secondary HC		HCOF#2	Constant	HCOF#2	Constant	HCOF#2	Constant
		TSS	Constant	HCOF#1	Constant	HCOF#1	Constant						
6/15/94	12:00	8.65	-3.2	2.14	-0.2	29.86	1	1.5	-1	24.97	N/A	N/A	N/A
6/16/94	14:00	4.68	0	1.68	0.05	27.47	0	0.5	-0.2	27.22	N/A	N/A	N/A
6/17/94	13:00	5.11	0.5	3.77	-1.6	27.95	0	0.4	-0.05	27.99	N/A	N/A	N/A
6/27/94	14:00	7.9	-2.5	3.2	-0.6	24.08	1	1.7	-1.3	25.21	N/A	N/A	N/A
6/28/94	14:00	5.63	1.1	2.72	-0.1	26.33	1.5	2.7	-2.3	27.46	N/A	N/A	N/A
6/28/94	20:00	13.58	-3.1	3.95	0.3	33.78	0.9	0.5	0	35.46	N/A	N/A	N/A
6/29/94	18:00	5.04	0.1	3.39	-1.5	17.18	3	1.6	-1.3	32.57	N/A	N/A	N/A
6/30/94	13:30	9.08	-2.3	2.49	0	22.53	2	0.6	-0.2	37.03	N/A	N/A	N/A
6/30/94	20:00	12.87	-3.5	3.16	0	36.44	0	0.91	0				
7/5/94	14:00	7.12	-2.4	2.64	-0.8	27.39	0	0.47	0	25.33	N/A	N/A	N/A
7/5/94	18:00	3.46	3	2.54	0.15	33.83	0	0.26	0				
7/5/94	22:00	11.63	-3	2.23	0.8	34.96	0	0.31	0	37.28	N/A	N/A	N/A
7/6/94	13:00	3.39	0	1.34	0	25.04	0	0.60	0	23.92	N/A	N/A	N/A
7/6/94	20:00	4.75	2	2.46	0.4	34.16	0	0.40	0	39	N/A	N/A	N/A
7/7/94	14:00	5.08	0.8	2.02	0.37	31.85	0			34.65	N/A	N/A	N/A
7/8/94	14:00	6.47	-0.7	2.06	0.2	31.8	0			24.4	N/A	N/A	N/A

Table 12. Summary of Mass Balances Results for Testing Period

b) One Inch Vortexes

The 1/4 inch apexes were unable to operate in this configuration for either flowrates. Therefore, the testing for the 1/4 inch apexes was discontinued.

The 3/8 inch apex testing occurred on 11/21/94 with a flowrate of 100 GPM. The magnesium hydroxide purity in the HCOF#1 was 65 wt %. Also the magnesium hydroxide purity for HCOF#2 was 38 wt %. Due to the lag time in the thickener, the product results were not used for this analysis. The recovery of magnesium hydroxide in the primary and secondary hydroclones was 76% and 67% respectively. The overall magnesium hydroxide recovery for both hydroclone overflows was 84%. Overall gypsum recovery from the secondary hydroclone underflow was 92%. The gypsum balance around the primary and secondary hydroclone system indicates more solid gypsum leaving than entering. Gypsum scale was forming in the hydroclone overflows due to the separation of the saturated solution from solid gypsum. This was particularly evident in the primary overflow streams, even though the gypsum saturation was calculated to be 1.00. Thus, the solid gypsum leaving the system is larger than what enters.

The 3/8 inch apex testing occurred on 11/22/94 with a flowrate of 120 GPM. The magnesium hydroxide purity in the HCOF#1 was 67 wt %. Also the magnesium hydroxide purity for HCOF#2 was 17 wt %. The recovery of magnesium hydroxide in the primary and secondary hydroclones was 82% and 51% respectively. The overall magnesium hydroxide recovery for both hydroclone overflows was 90% with 24% of the gypsum being recovered also. The overall gypsum recovery from the secondary hydroclone underflow was 79%.

Comparing the two flowrates for 3/8 inch apex, 100 GPM should be the operational flowrate. A flowrate of 120 GPM could be employed to recover more magnesium hydroxide. However, the 100 GPM flowrate condition achieves higher magnesium

hydroxide purity in the secondary bank. If recovery is more important than purity then the 120 GPM flowrate is more suited for operation.

Comparing the previous hydroclone system with 5/8 inch vortexes to the hydroclones with 1 inch vortex, there was no apparent difference in product purity for the two. A calcined basis was used to analyze the two modes of operation. The average purity of the magnesium hydroxide in the product was found to be the same for both modes of operation. Figure 28 illustrates MgO wt % was approximately 74% for both modes. Considering that there may be a lag time involved in the product stream, the primary hydroclone overflow, HCOF#1, was evaluated. (Figure 29) The 5/8 inch vortexes had a higher magnesium hydroxide purity of 76% while the 1 inch vortexes had a magnesium hydroxide purity of 72%.

The secondary hydroclone overflow, HCOF#2, was evaluated also. A similar effect on magnesium hydroxide purity was found. The secondary hydroclones had a higher magnesium hydroxide purity of 43%, during the 5/8 inch vortex operation than the 1 inch vortex operation where magnesium hydroxide purity was 27%. (Figure 30)

Comparing the two modes of operation on the basis of recovery, the hydroclones with 5/8 inch vortexes recover more magnesium hydroxide overall. The primary hydroclones recover approximately the same amount of magnesium hydroxide at about 78% for both size vortexes. (Figure 31) However, the secondary hydroclones recover more with the 5/8 inch vortexes. The 1 inch vortexes recover only 59% of the magnesium hydroxide while the 5/8 inch vortexes recover most, if not all of the magnesium hydroxide coming from the primary hydroclone underflow. The recovery for the secondary hydroclones in the 5/8 inch vortex operation is shown over 100%. This could be due to saturated magnesium hydroxide in solution precipitating when the primary hydroclones separate most of the solid magnesium hydroxide from the solution in the underflow. The issue of compounds dropping out of solution is discussed elsewhere in this report. Overall, the

5/8 inch vortexes recover 97% of the magnesium hydroxide while the 1 inch vortexes recover only 87%.

Figure 28. Comparison of Magnesium Hydroxide Product for Different Hydroclone Vortex Sizes

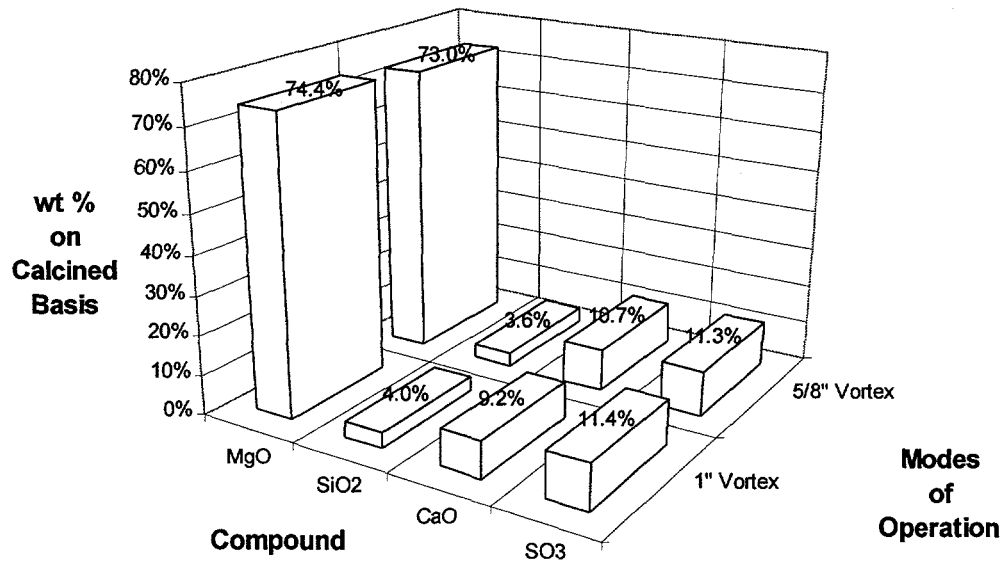


Figure 29 Comparison of Primary Hydroclone Overflow for Different Hydroclone Vortex Sizes

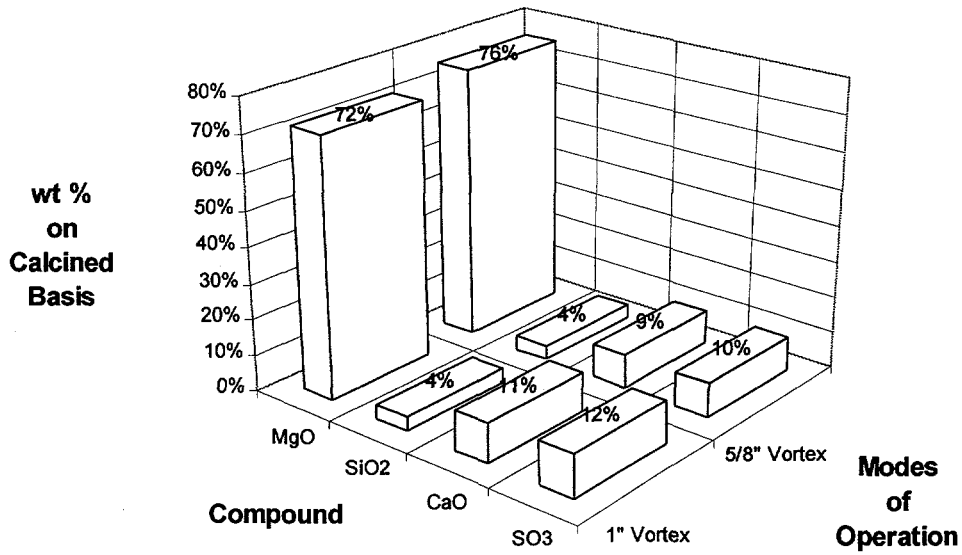


Figure 30 Comparison of Secondary Hydroclone Overflow for Different Hydroclone Vortex Sizes

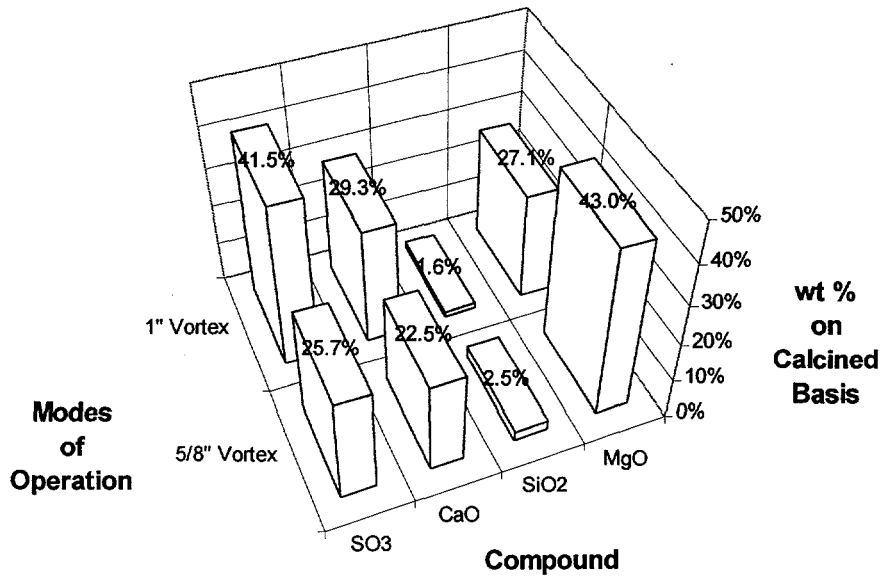
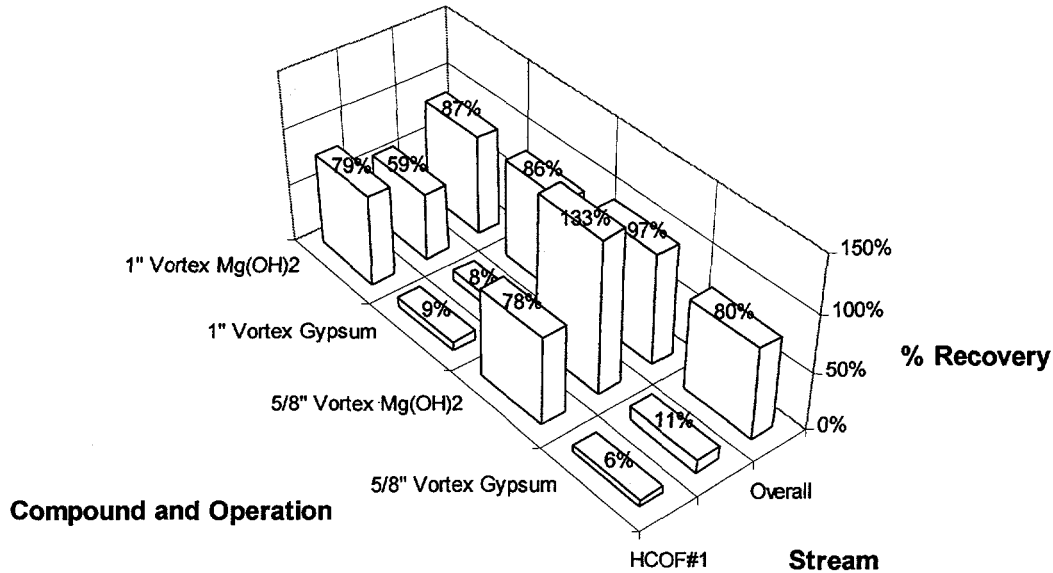


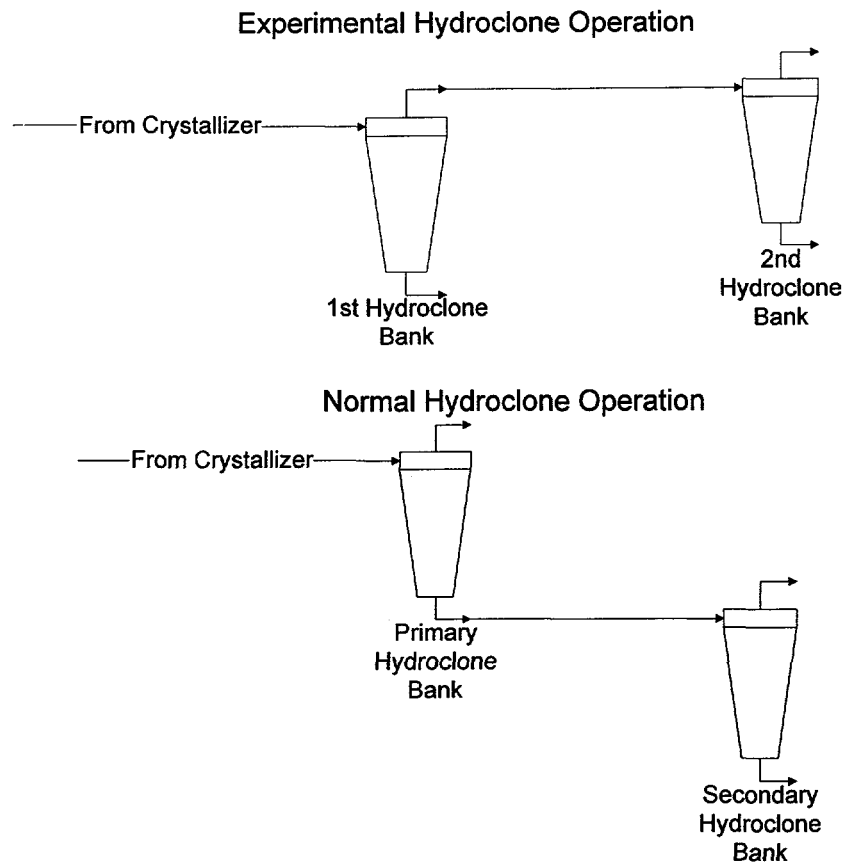
Figure 31. Recovery of Mg(OH)<sub>2</sub> and Gypsum with Different Hydroclone Operation



c) Hydroclones in Overflow Series

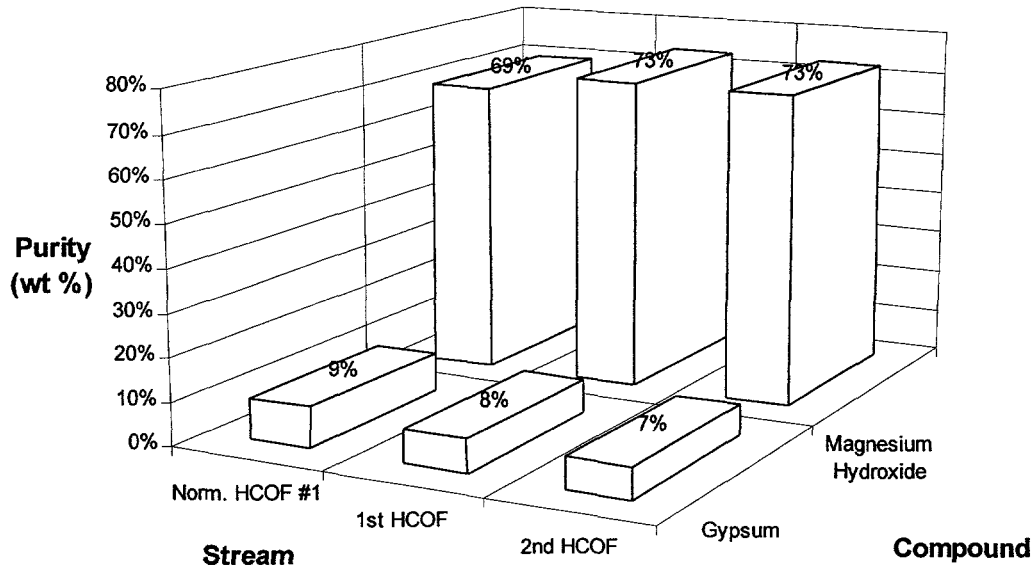
Also tested was taking a hydroclone from its original design and using it as shown in Figure 32. This hydroclone arrangement was tested to improve magnesium hydroxide purity by separating the magnesium hydroxide from any gypsum particles left in the primary hydroclone overflow streams. The chemical analysis and particle size of the solids were used to evaluate the hydroclone setup.

Figure 32



As shown in Figure 33, the purity of the magnesium hydroxide did not significantly increase from the first to the second hydroclone bank. Although the first hydroclone does have a 4 wt. % higher purity (non-calcined basis) than the control sample taken that day, normal primary hydroclone overflows have achieved as high as 73 wt. % magnesium hydroxide purity. The gypsum impurity in the second hydroclone overflow was 7 wt. % instead of 8 wt. % gypsum in the first hydroclone. As seen in the difference in the particle size distributions, there is only a small amount of the larger gypsum particles that are being separated from the smaller magnesium hydroxide particles.

Figure 33. Hydroclone Operation Study



Using hydroclones in series as shown in Figure 32 does not increase the purity of magnesium hydroxide or decrease the gypsum impurity by any significant amount. Also the amount of magnesium hydroxide that would be lost in the gypsum could be recovered using the original design, making the recovery unit more economical.

#### d) Conclusions from Hydroclone Testing

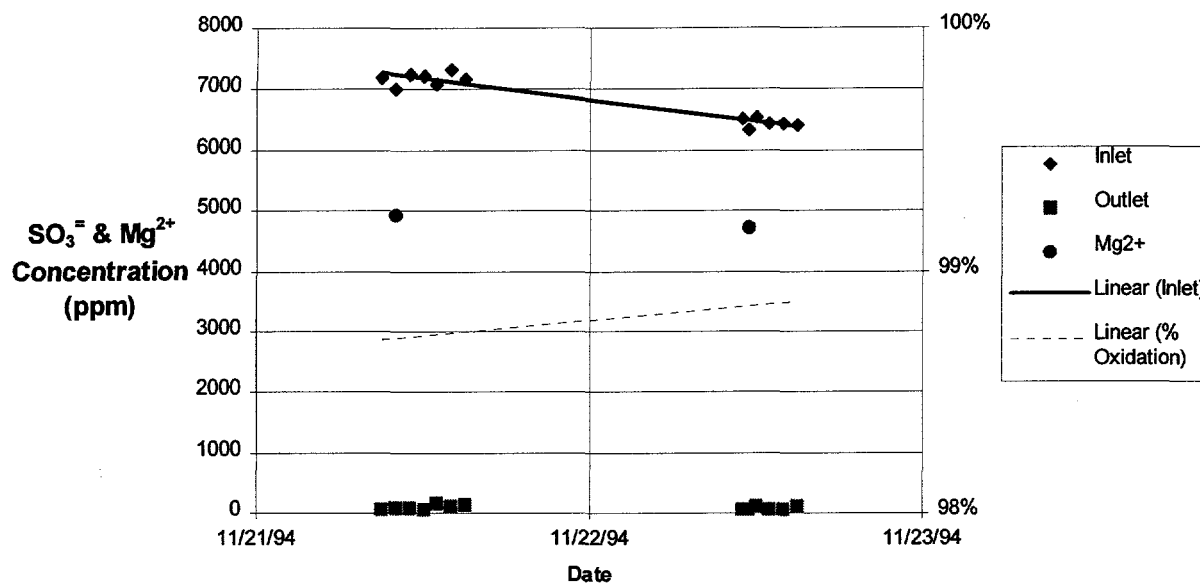
It was difficult to close both the gypsum and magnesium hydroxide balances simultaneously. The magnesium hydroxide balance was closed since magnesium hydroxide has higher value and the constant for closing the gypsum balance made TSS values invalid. Also, there is accumulation in the system when there is not any build up of gypsum in the bottom of the dilution tank. During the conditions that the hydroclones tests were run, the accumulation in the system was zero. The 1/4 inch apexes had higher percent recoveries than the 3/8 inch apexes. The secondary hydroclones show beneficial

effects on the unit with an annual magnesium hydroxide savings of up to \$32,000 resulting from better recovery. The secondary hydroclones increased magnesium hydroxide recovery from 80-88% to 90-95%. (Table 12) The optimal arrangement of both hydroclone banks was 5 primary and 5 secondary with 1/4 inch apexes. Running 4 primary hydroclones does not effect product purity or recovery drastically, but production is smaller due to smaller flows for 4 hydroclones. Running 6 hydroclones had detrimental effect on product recovery, too.

Liquor chemistry of the feed stream to the magnesium recovery process depends on FGD operation. While 1 inch hydroclone testing was conducted in as a controlled manner as possible, liquor chemistry of the feed stream to the magnesium recovery process remained relatively steady through the testing period as illustrated in Figure 34.

The flowrate for 1 inch vortexes should be 100 GPM for purity and a 120 GPM for recovery. The magnesium hydroxide purity for the 100 GPM case was 65% and 38% for the primary and secondary hydroclones respectively. The magnesium hydroxide recovery for the 120 GPM case was 82% and 51% for the primary and secondary hydroclones. The overall magnesium hydroxide recoveries for the 100 and 120 GPM cases were 84% and 90%.

Figure 34. Sulfite and Mg<sup>2+</sup> Concentration Profile



Comparing the two modes of operation, there is a considerable benefit in using 5/8 inch vortexes in the primary hydroclones. Since there is a long lag time due to the thickener volume, there was no apparent increase in product purity from the testing. However, the 5/8 inch vortexes show considerable increases in purity of both the primary and secondary hydroclones. Also the overall recovery of the 5/8 inch vortexes at 95%, is higher than that of the 1 inch vortexes, which was 90%. Therefore, the 5/8 inch vortexes remained the primary mode of operation.

Running hydroclones in series with the overflow of the first being the feed for the second, as shown in Figure 32, was found not to increase the purity of the magnesium hydroxide or decrease the impurity of the gypsum by any significant amount. The use of hydroclones in this manner only decreases the amount of magnesium hydroxide available to be recovered sending more magnesium hydroxide through the underflow.

#### 4. Magnesium Hydroxide and FGD Solids Thickening

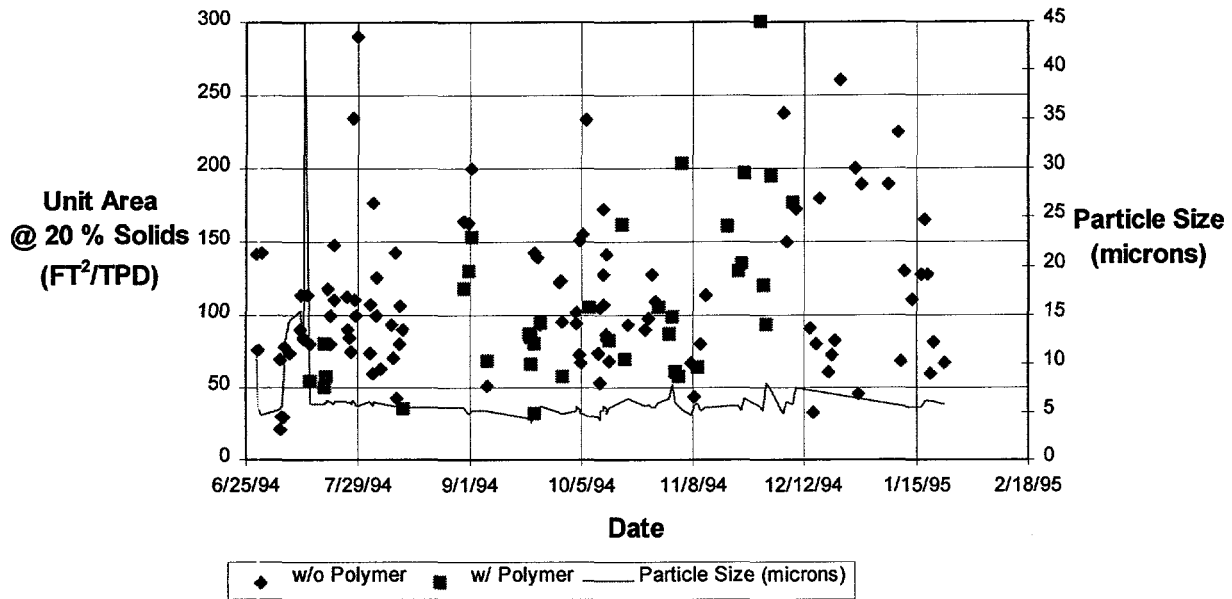
Magnesium hydroxide thickening and the FGD Thickener were areas of concern from a design standpoint. The values of unit area for both were observed for any effects from the recovery unit. The magnesium hydroxide thickener was evaluated for polymer addition to try to improve the settling rate of the magnesium hydroxide. The FGD Thickener settling rate of calcium sulfite solids was investigated for the effects of the recovery unit.

##### a) Magnesium Hydroxide Thickener

The magnesium hydroxide settling data is shown in graphical form to observe any changes in the settling rate due to the testing conducted. Changes in the thickening rate of magnesium hydroxide were observed due to by the problems that occurred upstream. Problems such as plugging hydroclones had an adverse affect on the settling rate. Thus, when 1 inch vortexes were used in the hydroclones, the settling rate appeared to decrease. This is due to the increased amount of gypsum contamination in the magnesium hydroxide product stream. However, crystallizer testing and oxidizer testing had no effects on the settling rate of magnesium hydroxide. The settling rate of magnesium hydroxide under normal conditions was roughly 100 ft<sup>2</sup>/TPD. (Figure 35)

The settling rate was not effected by the 24 hour testing. The addition of polymer to the magnesium hydroxide thickener does not increase the settling rate or ultimate dewatering of magnesium hydroxide. Polymer, at best, insures a clear thickener overflow.

Figure 35. Magnesium Hydroxide Thickener Settling Rate



**b) FGD Thickener**

The FGD solids settling rate decreased when the magnesium hydroxide recovery unit came on line. The FGD settling rate started at 32 ft<sup>2</sup>/TPD. Once it lowered during the operation of the magnesium hydroxide unit, it was constant throughout the testing and showed no affects from the recovery unit. The FGD settling rate was approximately 20 ft<sup>2</sup>/TPD while the magnesium hydroxide recovery unit was in 24 hour operation.

The settling rate in terms of unit area for a base case FGD Thickener was determined to be approximately 30 ft<sup>2</sup>/TPD. (Figure 36) The SEM pictures in Figures 37 - 40 allow more detailed comparisons of calcium sulfite crystals in the FGD thickener. Upon inspection of the SEM pictures, the particles appear to have remained the same throughout the operation of the magnesium hydroxide unit.

Figure 36. FGD Thickener Settling Rate

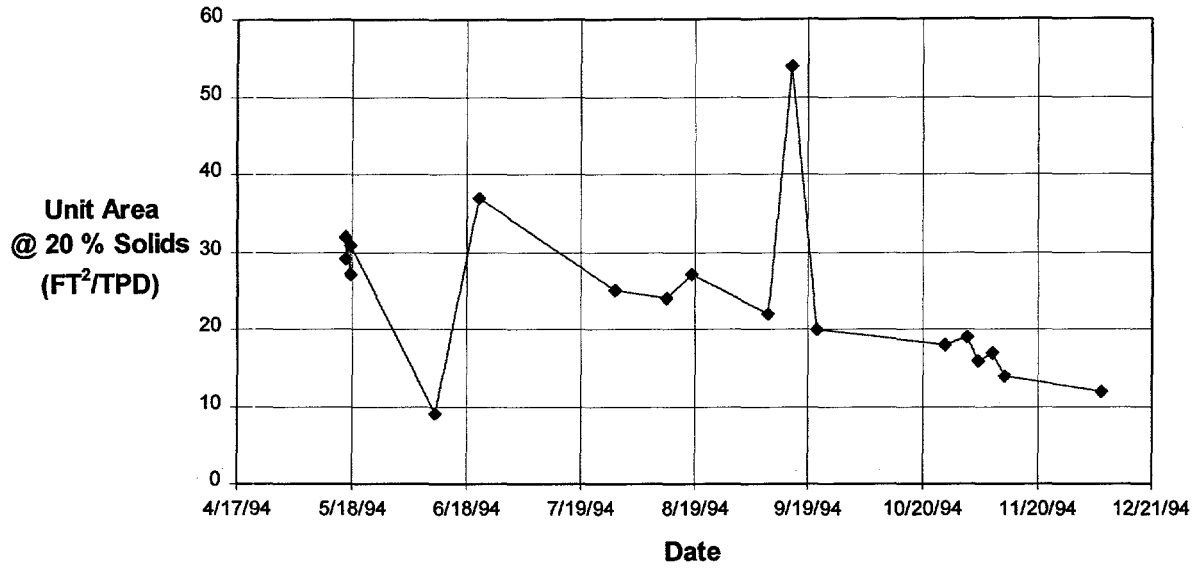


Figure 37. FGD Thickener #1 Underflow - 5-16-94

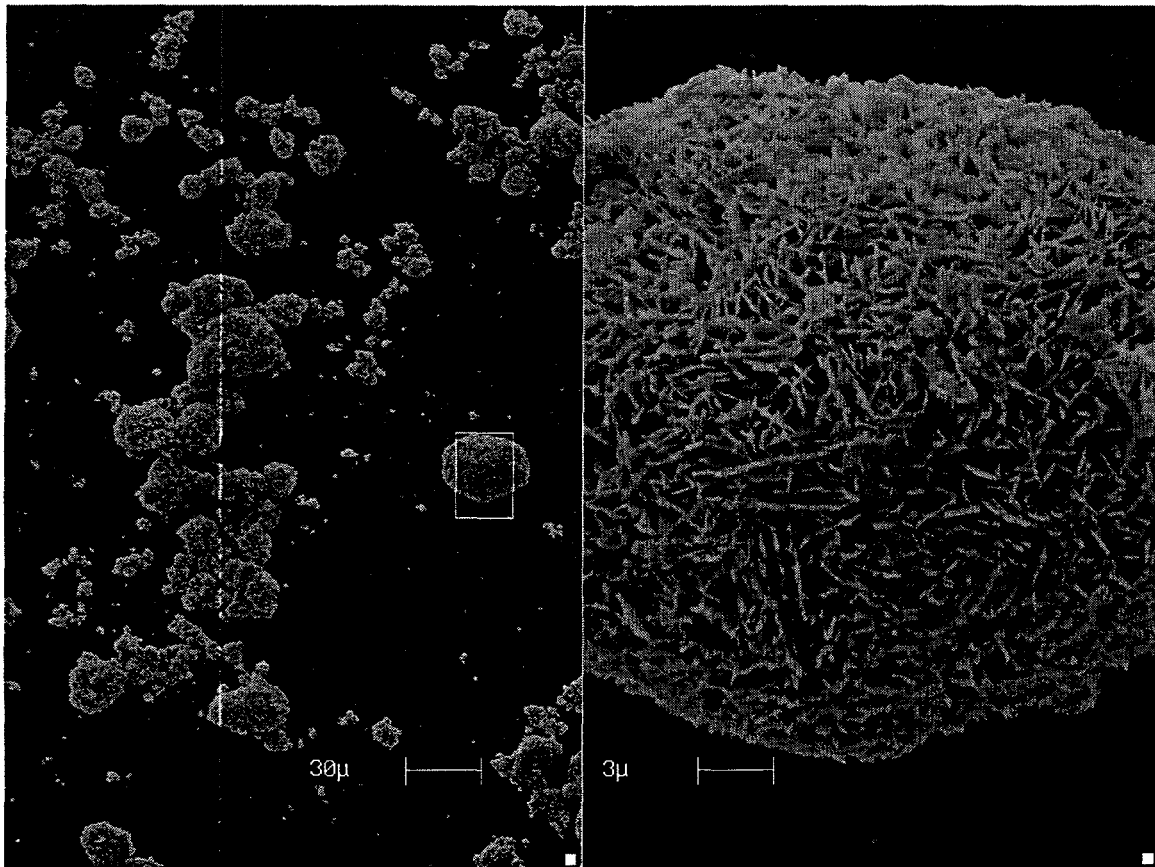


Figure 38. FGD Thickener #2 Underflow - 5/16/94

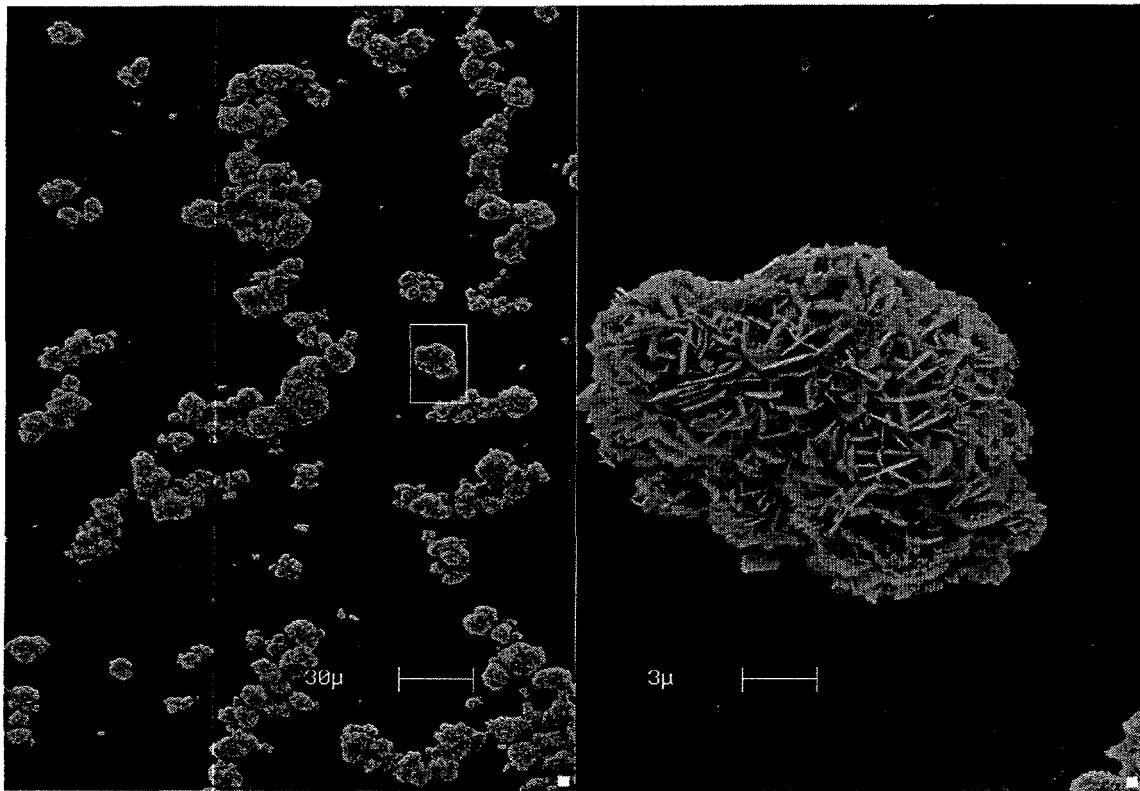


Figure 39. FGD Thickener #2 Underflow- 7/28/94

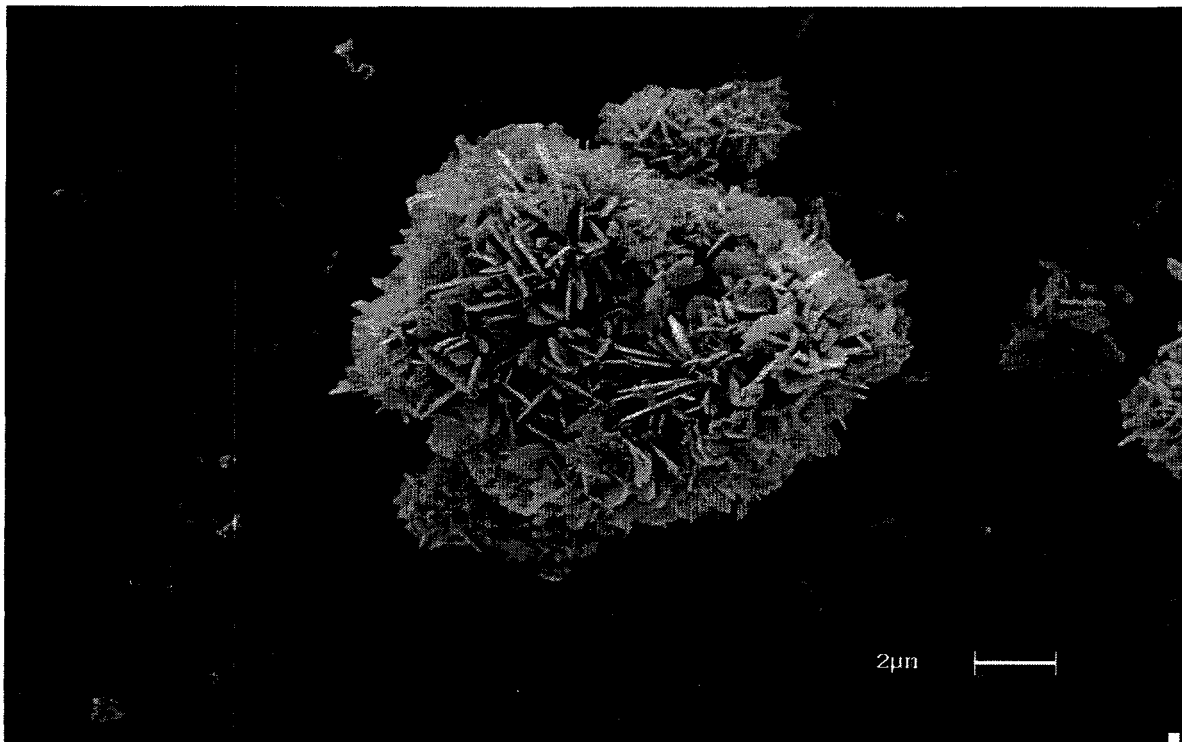
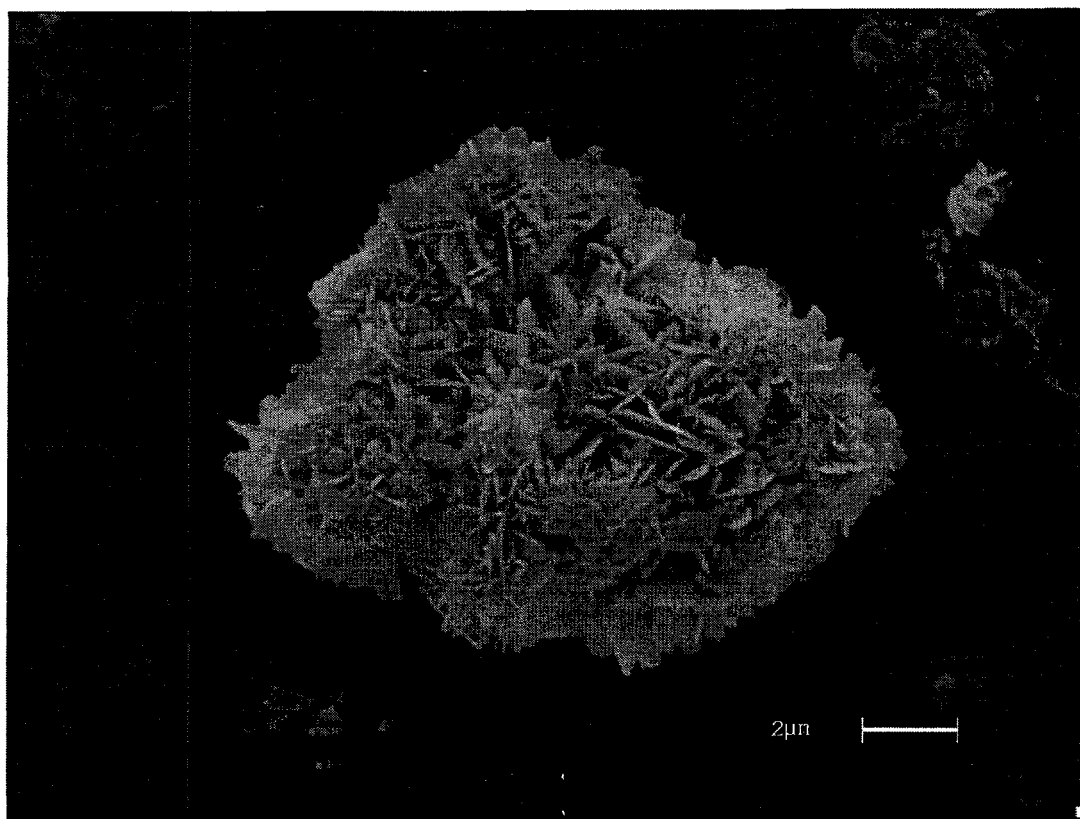


Figure 40. FGD Thickener #2 Underflow



## 5. Operations

There were testing periods devoted to study of the overall operation of the unit. Periods, such as the start-up of the unit, needed to be understood so that turning over the recovery unit to CG&E personnel could run smoothly. Also twenty-four hour testing was investigated to ensure that the relative gypsum saturation in the crystallizer would not be exceeded and lead to scaling problems.

### a) Start-up and Commissioning

Start-up occurred on May 16<sup>th</sup>, 1994. At start-up approximately 700 lbs. of gypsum was added to the dilution tank to maintain flows to the oxidizer and crystallizer tanks. This "seeds" the gypsum crystal formation. Once the accumulation of gypsum occurred in the system, this addition was terminated. Also, 1000 lbs. of dry magnesium hydroxide was

slowly added to different quadrants of the magnesium hydroxide thickener before beginning operation of the oxidizer so that the product pump could control the pH in the oxidizer. Due to the suction of the oxidizer recirculation pump being in the vicinity of the air sparger and agitation blade, slugs of air made their way to the pump. These slugs of air caused the pump's mechanical seal to fail. A packing gland type seal was installed to replace the mechanical seal.

On May 18<sup>th</sup>, 1994 the primary hydroclones were in operation and full system operation was achieved. Gypsum plugging in the primary hydroclones was a problem but resolved without any complications. Other than these minor upsets, no major problems arose from the start-up. On May 19<sup>th</sup>, 1994 the primary hydroclone overflow and underflow streams were analyzed so that the purity of both streams could be determined. The overflow solids were found to be 60 % magnesium hydroxide and 30 % gypsum with an average particle size of 12 microns. The underflow solids were found to be 92 % gypsum and only 6 % magnesium hydroxide with an average particle size of 30 microns. For start-up conditions the purity of both streams were very agreeable with design specifications. Initially, the overflow was not as pure as hoped.

**b) Secondary Hydroclone Start-up and Operation**

On June 7<sup>th</sup>, 1994, the unit started operation of its secondary hydroclone bank. The hydroclones were brought on-line one-by-one until five were operational. There is not enough data to accurately analyze their performance. However, the particle size data for this test period is available for gauging the relative performance of the primary and secondary hydroclones.

For the testing period, the particle size for the primary hydroclone overflows was approximately 11.6 microns while the particle size for the magnesium hydroxide product stream was only 6 microns. This discrepancy is likely due to the addition of 1000 lbs. of commercial powdered magnesium hydroxide at start-up. It is suspected that as the

thickener bed turns over, this measured particle size of the primary hydroclone overflow and the magnesium hydroxide thickener underflow should be in closer agreement. On the other hand, the primary hydroclone underflows had a smaller particle size, 36.6 microns, than the secondary hydroclones, which was 45.5 microns. The secondary hydroclones enhanced the separation of magnesium hydroxide from gypsum giving the gypsum stream higher purity. The content of magnesium hydroxide in the secondary hydroclone overflow stream is nearly the same as that of the primary hydroclone overflow stream. This indicates that use of the secondary hydroclone bank to achieve greater recovery of magnesium hydroxide outweighs the recovery of gypsum to the magnesium hydroxide product stream.

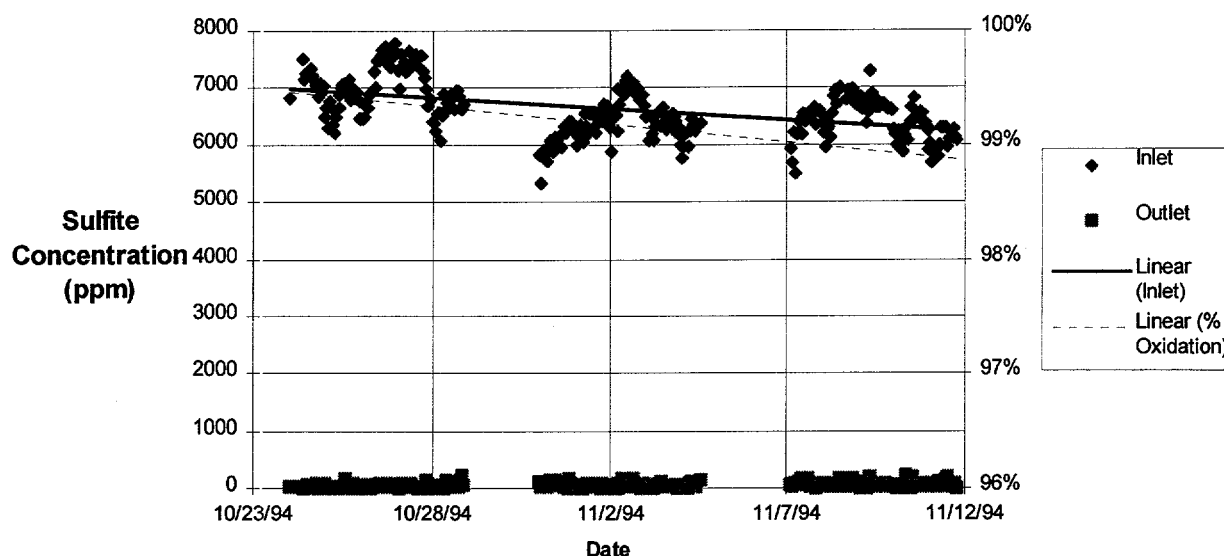
The settling data analysis shows the trends of the settling rate for the two FGD thickeners. Since testing began, measured settling rate dropped from 32 down to 9 ft<sup>2</sup>/TPD.

c) **24 Hour Operation**

The magnesium hydroxide recovery unit was operated for 24 hours a day for three consecutive weeks to evaluate its effect on the FGD unit and any scaling problems that might occur. Relative gypsum saturation was evaluated as well as the settling rate of both FGD and magnesium hydroxide thickeners.

The oxidizer, operating at a constant condition, sufficiently oxidized a changing inlet sulfite concentration. (Figure 41) The inlet sulfite concentration peaked in the middle of each week of testing with a variance of over 1000 ppm each week. The outlet sulfite concentration was rarely over 200 ppm, well below the design of 300 ppm. The oxidizer had no problems exceeding design specifications even with a varying inlet sulfite concentration.

Figure 41. Oxidizer Inlet-Outlet Sulfite Concentration Profile



The effects of scaling can be grave to the efficiency of this process. Relative gypsum saturation was calculated for the 24 hour testing period and analyzed in a graphical form. (Figure 42) The relative gypsum saturation was relatively constant through the testing period at approximately 1.00. Since scaling normally occurs when relative gypsum saturation exceeds 1.2, this process appears to operate at a safe condition. However, there was some scale evident in the primary hydroclone overflow lines after the 24 hour testing. (Figure 43) The picture shows the ports to the overflow collection tank. The ports are numbered with less than eight being the primary overflows and greater than eight being the secondary overflows. The secondary overflow ports do not have the same amount of scale as the primary overflow ports.

Figure 42. Crystallizer Performance for 24 Hour Testing

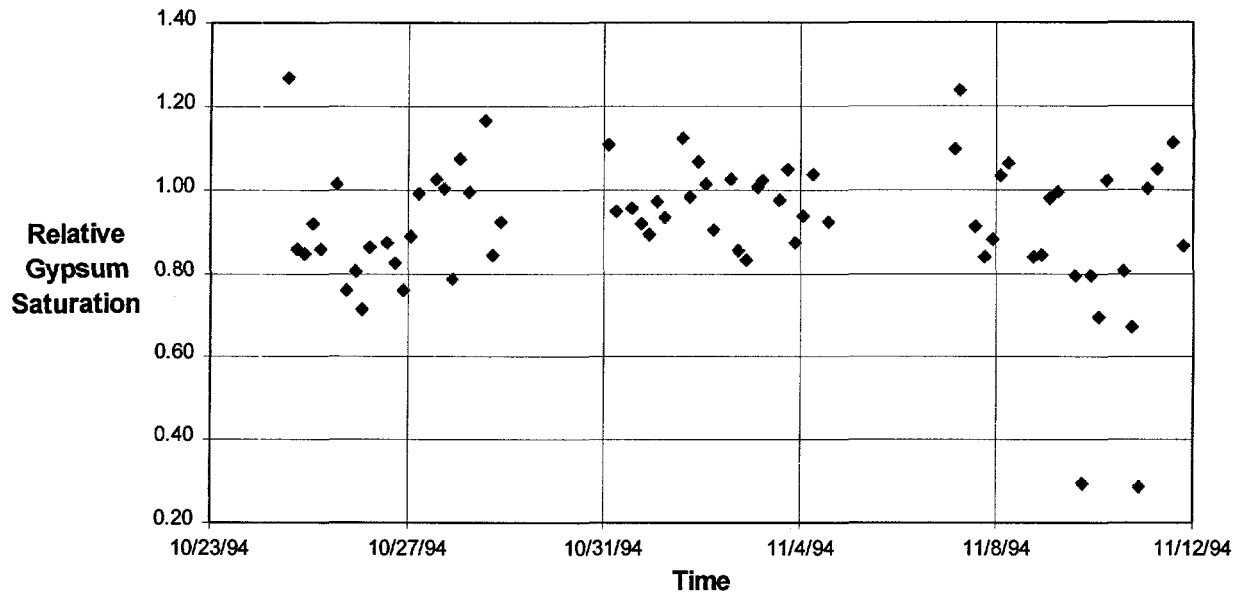
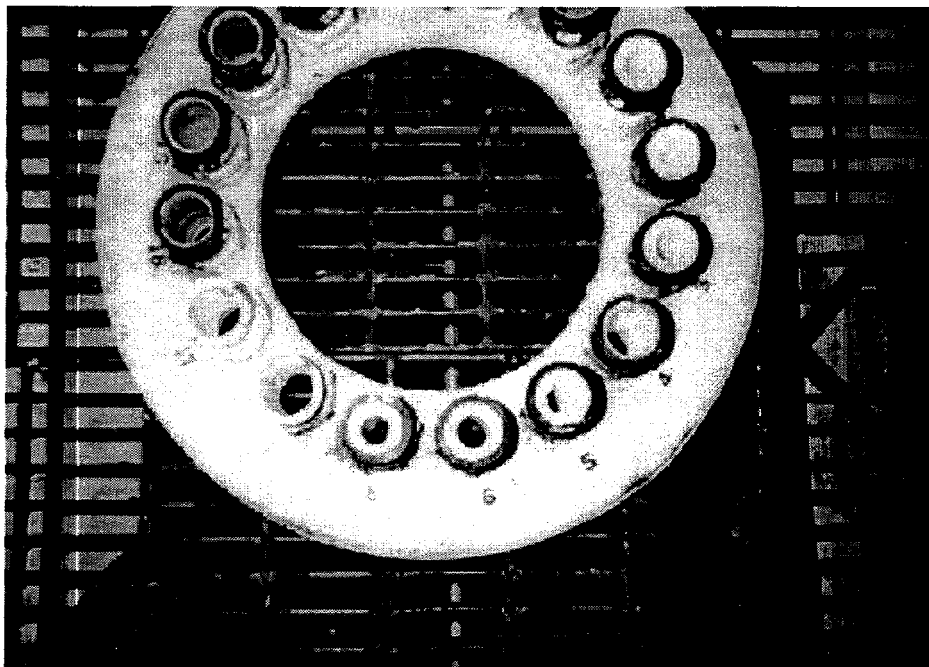


Figure 43. Ports to the Hydroclone Overflow Collection Tank



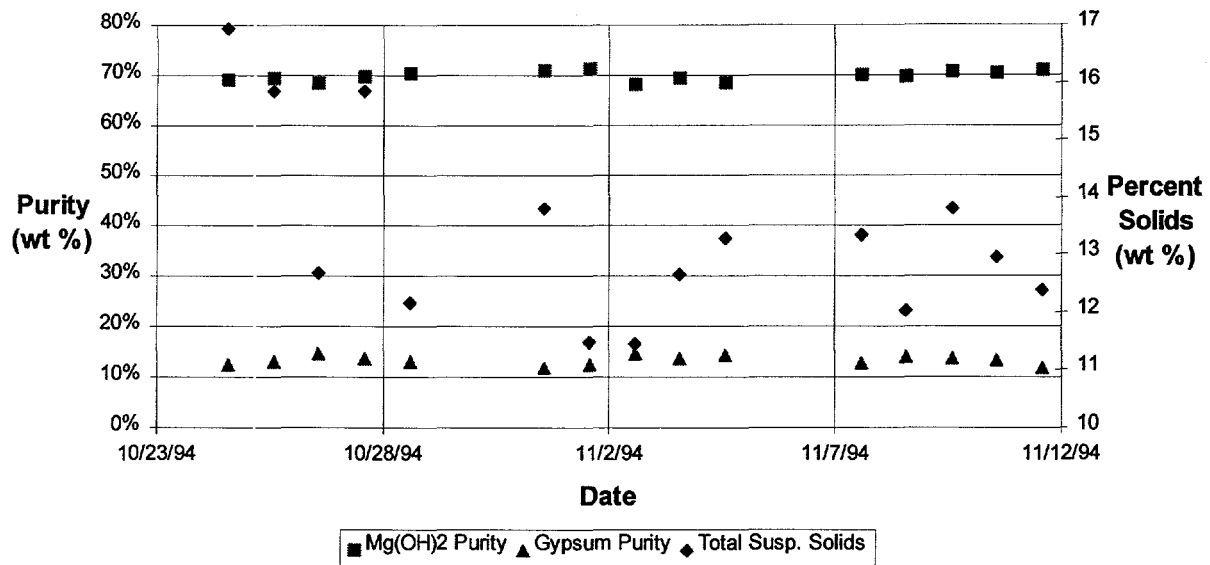
Scaling was noted to occur since July 1994 in the primary hydroclone overflow lines to the hydroclone collection tank. Scaling upstream of the primary hydroclones is not nearly as evident. Stripping away the gypsum solids from an otherwise non scaling liquor, as hydroclones do, causes soluble gypsum to drop out of solution very rapidly to form scale. The scaling that occurs is manageable as long as the scale is removed periodically. The scale in the picture was allowed to build up over a six week period that included the three weeks of 24 hour operation. The scaling of the secondary hydroclone overflow lines is not as severe as that of the primary hydroclone overflow lines. This is because the increase in solids concentration in the primary hydroclone underflow causes the liquid phase to desaturate with gypsum.

The operating performance of the hydroclones also remained consistent with steady state operating conditions. The primary hydroclones overflow magnesium hydroxide and gypsum content (wt %) ranged from 68-73 % and 9-12 % respectively. The underflow magnesium hydroxide content and gypsum purities run from 9-12 % and 83-85 %. For the secondary hydroclones, the overflow magnesium hydroxide purity and gypsum content ranged from 48-56 % and 29-38 %. The underflow magnesium hydroxide content and gypsum purity run from 3-4 % and 92-93 % respectively.

The magnesium hydroxide product was analyzed for its purity and solids content. In Figure 44, the purity of magnesium hydroxide during the 24 hour testing remained relatively constant at 70 wt %. The gypsum impurity also remained constant at 10 wt %. However, the percent solids of the stream varied. The solids started at approximately 17 percent but then varied between 11 to 14 percent solids. The variance in the percent solids of the magnesium hydroxide product, or magnesium hydroxide thickener underflow, is because of the batch operation of filling the product storage tank. There was never a continuous underflow stream during the testing period. Assuming a constant flowrate of 10 GPM for the thickener underflow and 24 hour operation of the plant, a production rate of pure dry magnesium hydroxide would be 6 tons/day. As for the production rate of gypsum, the secondary hydroclone underflow can be assumed as the

product stream. The production rate of pure dry gypsum under the same operating conditions would be 13 tons/day.

Figure 44.  $Mg(OH)_2$  Product for 24 Hour Testing



The magnesium hydroxide plant sump returns to the FGD thickener centerwell. Thus the sump chemistry was important to monitor. In Table 13 the average sump chemistry is shown. In the liquor returning to the thickener, the sulfates, chlorides, and magnesium ions are all less than when they entered. Sulfates and magnesium ions are about an order of magnitude smaller and the chlorides decreased very little. On the other hand, calcium ions increased by an order of magnitude when returning to the thickener. High calcium in a Thiosorbic process can cause scaling. However, when this stream comes in contact with a sulfite rich stream, such as the absorber blowdown, in the thickener centerwell, the calcium will drop out of solution to form calcium sulfite. The pipe which returns the recovery plant sump to the thickener is positioned towards the middle of the centerwell. This is not in proximity of any metal surfaces, where scale could form over. The calcium sulfite formed drops into the bed of thickener like any other solid particles.

Table 13. Average Magnesium Hydroxide Plant Sump Chemistry(returned to FGD Thickener)

Total Hardness (ppm)	5339
SO <sub>4</sub> (ppm)	1516
Cl <sup>-</sup> (ppm)	2494
Ca <sup>2+</sup> (ppm)	1912
Mg <sup>2+</sup> (ppm)	135
pH	10.7
Total Solids (wt %)	3.95

1) **Conclusions**

The oxidizer had no problem with a varying inlet sulfite concentration. Also, the relative gypsum saturation in the crystallizer remained relatively constant at 1.00. Scale did form on the primary hydroclone overflow piping but at a manageable rate. The primary hydroclones had overflow magnesium hydroxide purity up to 73 % and underflow gypsum purity up to 85 %. Also the secondary hydroclones had overflow magnesium hydroxide purity up to 56 % and underflow gypsum purity up to 93 %. The magnesium hydroxide thickener settling rate was not affected by increasing run time. However, because of the changeable flow from the magnesium hydroxide thickener to the magnesium hydroxide storage tank, magnesium hydroxide thickener underflow solids varied. Polymer did not show any effects on the settling rate or unit area. At best it insured a clear thickener overflow. The unit area of the FGD Solids thickener decreased to less than 20 ft<sup>2</sup>/TPD during the three week campaign. The production rate of pure dry magnesium hydroxide and pure dry gypsum were 6 and 13 tons/day respectively. The magnesium hydroxide unit decreases the sulfates and magnesium ions while increasing the calcium ions returning to the FGD plant. The location of the calcium rich stream was such that there were no problems with scaling in the FGD

system. Therefore, the magnesium hydroxide recovery unit does not detrimentally effect FGD operation.

Operation log sheets are located in Appendix VII. Training of CG&E personnel to operate the magnesium hydroxide plant ensured a smooth transition in operating personnel. The operation procedures are located in Appendix VIII.

**d) Problems**

When the magnesium hydroxide recovery unit was started up, taking feed liquid from the launder in the FGD Thickener was a problem. Not enough flow was entering the standpipe thus starving the pump. Therefore, a pipe was punched through the weir to alleviate the problem of starving the pump. The liquid is now being drawn from within the thickener and not from the weir.

Hydroclones were plugging due to insufficient retention time in the lime slaking ball mill. A bypass line strainer was installed on the inlet to the primary hydroclone bank. This would catch the large grit from the lime before it reached the hydroclones.

A Saunders diaphragm control valve was installed to control the lime feed to the crystallizer tank. This valve was unable to withstand the material passing through it. The diaphragm was tearing and wearing the body of the valve. This valve was replaced with a Clarkson sphincter valve for pH control of the crystallizer. Also another Saunders manual valve on the crystallizer recirculation line was showing the same wear problems. This valve was not replaced, but a replacement Clarkson was purchased and ready to be installed at CG&E's earliest convenience.

During the winter months, below freezing temperatures interfered with the operation of the plant. Lines coming to and going from the plant were most susceptible to freezing. The plant sump line and the lime slurry line were most problematic. These lines were not

heat traced or insulated because twenty-four hour operation was assumed to occur most of the time. When these lines were in operation they ran perfectly. It was only when the plant was shut down that these lines were problems.

## 6. Additional Solids Separation Testing

Additional testing was completed on the hydroclones at the Zimmer station along with bench scale testing of other solids separation technologies. Elutriation and Flotation were tested as alternatives to using hydroclones. Samples were sent to Krebs for testing of larger hydroclones. This will be useful in designing any magnesium hydroxide plants for full-scale production.

### a) **Roping Hydroclone Analysis**

In normal operation, the hydroclone underflow stream would have a spray pattern. There were instances when the hydroclones altered from their normal operation. For instance, the underflow stream would "rope" at times. Roping at the Zimmer station was normally caused by some form of debris becoming lodged in the apex altering the flow pattern of the underflow. Samples were taken to compare the chemical analysis of the underflow and overflow streams in the two types of flow. The results will be compared to hydroclones in normal operation.

Samples were taken of the secondary hydroclone underflow on October 20<sup>th</sup>, 1994. These samples were analyzed to see if the magnesium hydroxide contamination in the gypsum increased or decreased as compared to normal operation. The results indicated that the amount of magnesium hydroxide contamination was slightly lower than that of normal hydroclone operation. Another sample was taken of both the secondary hydroclone overflow and underflow on February 16<sup>th</sup>, 1995. Comparing the underflow of this sample to that of normal operation, the roping hydroclone had less magnesium hydroxide impurity. Normal secondary hydroclone underflow has 3-4% magnesium hydroxide. Roping hydroclone underflow has 2-3% magnesium hydroxide. However,

the amount of gypsum impurity in the overflow is much higher in a roping hydroclone than the one in normal operation. Normal secondary hydroclone overflow has 25-40% gypsum. Roping hydroclone overflow has 50% gypsum. Due to the larger amount of gypsum impurity in the roping hydroclones, the normal hydroclone operation has to be maintained for higher purity magnesium hydroxide.

**b) Alternative Methods of Separating Magnesium Hydroxide from Gypsum**

Crystallizer slurry was transferred from the magnesium hydroxide plant at Zimmer Station to the Dravo Research Center to test the separation of gypsum and magnesium hydroxide using floatation and elutriation methods. The results of the analysis of the overflow and underflow of the unit were evaluated. The elutriation testing unit is illustrated in Figure 45. The results are compared to the hydroclones operating at Zimmer Station magnesium hydroxide recovery unit.

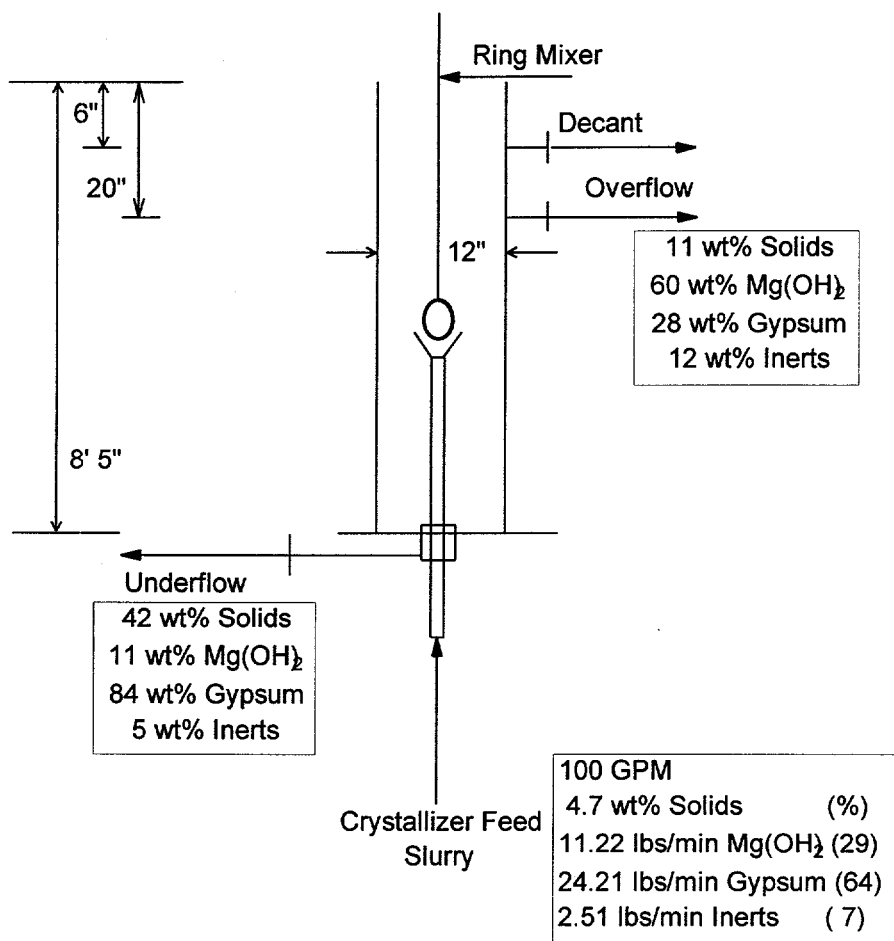
**1) Elutriation**

Elutriation refers to pumping a slurry upwards in a vertical column with an intent to cause differential settling of the particles. The forces acting on the solid particles are the upward drag due to fluid flow which tends to carry the particles up through the column, gravity, and buoyancy. The particles separation by size is controlled primarily by the velocity of the slurry so that only particles smaller than a critical size are carried in the overflow. The larger particles settle through the liquid and leave in the underflow.

Three tests were run with the elutriator. Tests 1 and 2 were run with an inlet flowrate of 1 liter per minute and approximately 5 % solids. The highest magnesium hydroxide purity obtained using the elutriator was 64 %. Test 3 ran at the same flowrate and solids' content; however, a Calgon polymer was added to the crystallizer slurry to aid in the separation of magnesium hydroxide and

gypsum. The polymer assists the separation by decreasing the static charges between the magnesium hydroxide and the gypsum particles. In this study the polymer did not aid in the separation and as a result the magnesium hydroxide purity was lower at 55 %.

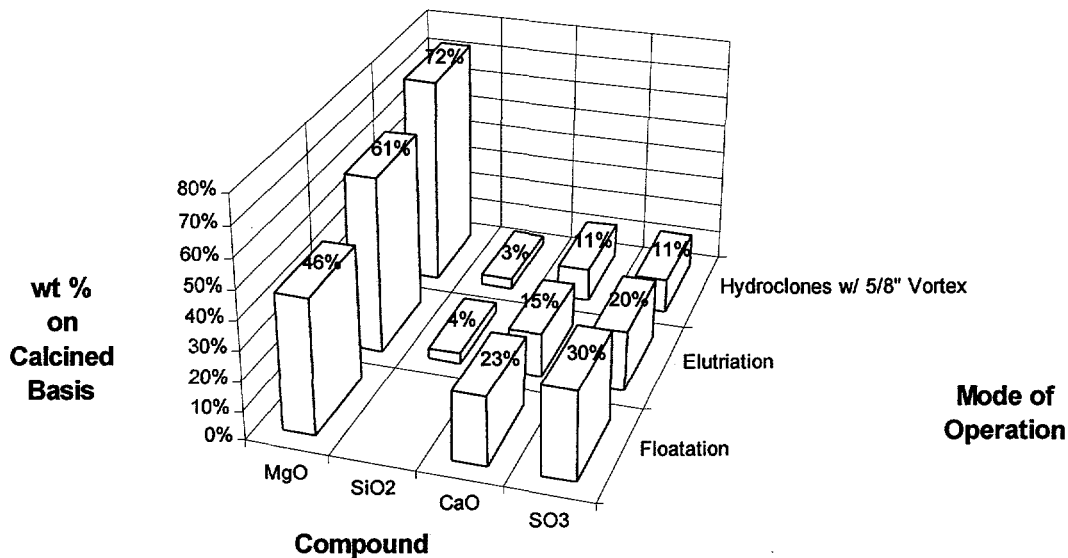
Figure 45. Elutriation Testing Unit



Comparing the elutriator to hydroclones in service at Zimmer Station, the hydroclones appear to separate magnesium hydroxide and gypsum better than elutriation. Elutriation does come close with 64 % purity magnesium hydroxide; however, the hydroclones are shown on average to produce a higher purity magnesium hydroxide. As illustrated in Figure 46, the average purity of

magnesium hydroxide in the hydroclone overflow is 10 % MgO (calcined basis) higher than the overflow of the elutriator. Also, the size of the elutriator would be of concern. The bench scale elutriator was large in relation to its feed flowrate. Scaling up of such equipment to the size required at the Zimmer Station would require an elutriator that would be prohibitively large.

Figure 46. Comparison of Overflows from Elutriation, Flotation, and Hydroclone Operation



## 2) Flotation

In flotation the surfaces of specific particles are treated with chemicals called collectors which render those particles water-repellent and susceptible to adhering to air bubbles. With vigorous agitation and aeration in the presence of a froth, a layer of froth forms at the top of the flotation machine. The particles become attached to air bubbles and rise to the surface where they collect in the froth and are skimmed off. Undesired particles remain in the liquid and leave in the underflow either by leaving their surfaces unaltered by collector absorption, or

through the use of modifying agents. Figure 47 is an example of a floatation device used in industry.

Different floatation aids were tested in the WEMCO floatation cell. The cell was set up using 1250 RPM or 1800 RPM whichever would result in foaming. Two grams of polymer were added to 998 cc of water. This was then added to 3 liters of crystallizer slurry and tested. The results are listed in Table 14. The highest magnesium hydroxide purity using the floatation cell was 48 %. As Figure 46 illustrates, low magnesium hydroxide purity in the product eliminates floatation as an alternative to hydroclones.

### 3) Conclusions from Testing

Elutriation and Floatation were found to separate magnesium hydroxide and gypsum. However, neither method appears to be a viable alternative to hydroclones. Floatation was only able to achieve 50 % magnesium hydroxide purity. Elutriation was found to have a higher magnesium hydroxide purity of 64%. Hydroclones achieve a superior magnesium hydroxide purity range of 65-75% in a more compact sized plant layout.

Lab#	Spl ID1	Spl ID2	CaO	CO <sub>2</sub>	MgO	SO <sub>2</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	Sulfur (wt %)	Total Solids (wt %)	CaSO <sub>4</sub> * CaSO <sub>3</sub> * 1/2H <sub>2</sub> O				Mg(OH) <sub>2</sub>				Total	Gypsum wt%	Purity		
											Mg(OH) <sub>2</sub>	2H <sub>2</sub> O	1/2H <sub>2</sub> O	MgSiO <sub>2</sub>	CaCO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Total				Mg(OH) <sub>2</sub> wt%	Purity
<b>Elutriation</b>																							
	Crystallizer																						
950111	Overflow Port #2	1/18/95	10.13	1.59	44.09	0.28	2.68	13.51	5.55	2.89	61.20	24.12	0.63	3.76	3.62	0.40	0.25	93.98	61%	24%			
950112	Underflow Port #10	1/18/95	22.55	0.75	18.85	0.33	1.16	31.67	12.85	5.13	26.15	65.40	0.75	1.63	1.71	0.22	0.11	95.96	26%	65%			
950222	Underflow 1 & 2	1/27/95	28.58	0.47	6.62	0.24	0.05	41.02	16.55	44.04	9.54	85.24	0.54	0.06	1.07	0.10	0.06	96.62	10%	85%			
950219	Overflow 1	1/27/95	9.60	1.56	46.00	0.34	2.75	12.86	5.32	11.18	63.90	22.45	0.77	3.86	3.55	0.40	0.22	95.14	64%	22%			
950220	Overflow 2	1/27/95	10.67	1.39	43.90	0.24	2.58	14.63	5.98	8.54	61.02	26.67	0.54	3.62	3.16	0.38	0.22	95.62	61%	27%			
950223	Underflow 3	1/27/95	27.24	0.51	9.37	0.37	0.60	38.61	15.65	37.51	12.98	80.62	0.84	0.84	1.16	0.13	0.06	96.63	13%	81%			
950221	Overflow 3	1/27/95	12.81	1.30	39.46	0.31	2.33	17.54	7.18	13.65	54.84	33.40	0.70	3.27	2.96	0.36	0.18	95.71	55%	33%			
<b>Floation</b>																							
944796	#1123L Product	12/19/94	16.10		31.41				8.49		45.45	49.42						94.87	45%	49%			
944797	#1123L Underflow	12/19/94	22.20		19.67				11.83		28.46	68.14						96.61	28%	68%			
944798	#1117L Product	12/19/94	17.20		29.74				8.61		43.03	52.80						95.83	43%	53%			
944799	#1117L Underflow	12/20/94	22.80		19.67				11.95		28.46	69.99						98.45	28%	70%			
944800	#1125L Product	12/20/94	15.50		33.51				8.23		48.49	47.58						96.07	48%	48%			
944801	#1125L Underflow	12/20/94	23.30		18.59				12.51		26.90	71.52						98.42	27%	72%			
944802	Lignosulfonate Product	12/20/94	15.20		32.05				8.07		46.38	46.66						93.03	46%	47%			
944803	Lignosulfonate Product	12/20/94	14.70		30.94				12.85		44.77	45.12						89.89	45%	45%			

Table 14. Solids' Analysis for the Testing of Elutriation and Floation

Figure 47. Typical Flootation Equipment

FLOTATION 21-67

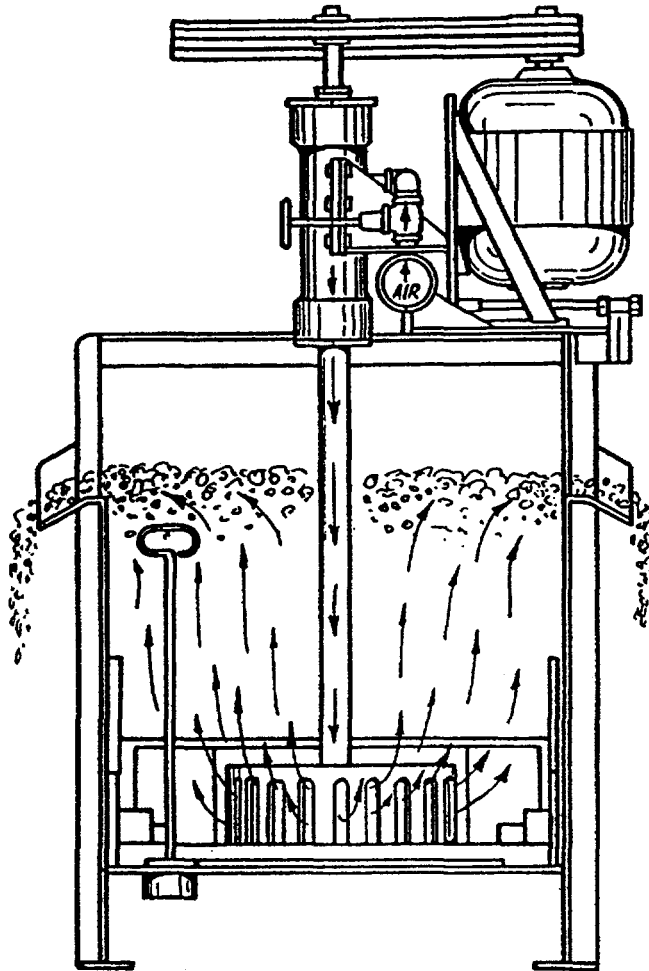


FIG. 21-96. Agitair flotation machine.

Chemical Engineer's Handbook, Perry and Chilton, 5th edition, pg. 21-67

c) **Krebs Hydroclone Analysis**

Tests were run at the Krebs Service Center in Menlo Park, California using 6" and 10" hydroclones. These units had a cyclowash feature which employs a water stream to increase separation of the two particles. The performances of the hydroclones were evaluated. The results were compared to results of the hydroclones in normal operation.

Samples were taken of regeneration tank slurry on October 27<sup>th</sup>, 1994. These samples were sent to Krebs for evaluation of their hydroclones. In return, Krebs sent back samples of hydroclone overflows and underflows for solids analysis. There were four tests conducted. Two 6" hydroclones and two 10" hydroclones were tested. For each hydroclone the cyclowash feature was utilized to increase purity of the magnesium hydroxide in the overflow. The principle of the cyclowash was to prevent fine magnesium hydroxide from exiting the hydroclone through the underflow.

These results indicate that 6" and 10" hydroclones did not have the same performance as the 3" hydroclones used at Zimmer Station. The magnesium hydroxide purity was between 36 to 48 %. Zimmer Station typically achieves between 60 to 72 %. (Table 15) Krebs felt that gypsum fines caused by the cyclowash were reporting to the overflow, contaminating the magnesium hydroxide. The underflow gypsum concentrations were relatively consistent with those of Zimmer.

Since the magnesium hydroxide needs to have a higher purity for better marketability, Krebs recommends using 4" hydroclones to improve performance, but could not give any more advice until they knew the particle size distributions for both magnesium hydroxide and gypsum.

Lab#	Spl ID1	SampleID	Spl ID2	Spl ID3	Al <sub>2</sub> O <sub>3</sub>	CaO	CO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SiO <sub>2</sub>	Total Sulfur	Total Susp. Solids (wt %)	Microtrac MV (microns)	Mg(OH) <sub>2</sub> (calc.)	CaSO <sub>4</sub> ·2H <sub>2</sub> O (calc.)
944010	Crystallizer	2	10/27/94	14:00	0.25	21.57	1.34	0.09	19.91	1.25	12.23	4.27	34.7	27.60	60.98
944011	HCOF#1	3	10/27/94	14:00	0.43	5.90	2.09	0.23	50.12	2.83	2.87	1.56	6.6	69.78	9.92
944012	HCOF#1	4	10/27/94	14:00	0.13	28.31	0.64	0.06	7.65	0.57	16.27	14.77	70.0	10.52	84.41
944013	HCOF#2	5	10/27/94	14:00	0.36	12.12	1.69	0.16	38.17	2.24	6.58	0.48	10.9	53.06	30.60
944014	HCOF#2	6	10/27/94	14:00	0.09	30.56	0.45	0.05	2.77	0.34	17.68	23.23	61.5	3.68	92.06
944015	Product	8	10/27/94	14:00	0.42	7.12	2.06	0.22	49.98	2.74	3.52	15.85	5.5	69.67	13.79
	Test 1 Cyclone UF				0.35	15.86	1.10	0.15	33.02	1.98	8.97	2.53	14.1	47.80	43.50
	Test 1 Cyclone UF				0.11	30.59	0.45	0.07	3.25	0.41	17.69	27.94	67.8	4.70	91.40
	Test 2 Cyclone UF				0.36	16.68	1.13	0.15	31.04	1.91	9.46	2.47	12.4	44.90	46.00
	Test 2 Cyclone UF				0.13	30.84	0.41	0.08	2.82	0.46	17.83	13.58	73.4	4.10	92.30
	Test 3 Cyclone UF				0.36	17.90	1.09	0.15	28.44	1.81	10.18	2.91	19.0	41.10	49.80
	Test 3 Cyclone UF				0.17	30.46	0.44	0.11	3.15	0.62	17.59	26.81	63.6	4.60	90.90
	Test 4 Cyclone UF				0.35	19.53	0.98	0.14	25.07	1.65	11.14	3.67	21.3	36.60	55.30
	Test 4 Cyclone UF				0.22	31.18	0.38	0.15	1.66	0.84	17.92	7.49	80.0	2.40	93.40
	Notes:														
	Test 1: Model D6B-12 w/o Cyclowash														
	Test 2: Model D6B-12 w/ Cyclowash														
	Test 3: Model D10B w/o Cyclowash														
	Test 4: Model D10B w/ Cyclowash														

Table 15. Solids' Analysis for the Krebs Hydroclone Testing

## 7. Testing Performed on the Dravo Lime Company 5kW Unit

### a) Lime Slaking with Zimmer Magnesium Hydroxide Plant TOF

Maysville Lime was slaked under various conditions and used to scrub simulated flue gas in the 5 kW unit at the Dravo Research Center. The 5 kW unit is a bench scale scrubber that can be used to test various flue gas conditions and scrubbing configurations. Maysville lime slaked with water containing different concentrations of magnesium hydroxide plant thickener overflow (TOF) was evaluated for the effect on SO<sub>2</sub> removal and waste solids dewatering.

Slaking lime with high pH liquor that is saturated with gypsum or magnesium hydroxide provides a coating of these compounds on the calcium hydroxide particles that forms. The thickness of the coating depends on the degree of dilution of the high pH liquor. Only as much coating on the calcium hydroxide particles is desired, that will slow its dissolution without inhibiting it altogether. Slowing dissolution of calcium hydroxide allows calcium sulfite hemihydrate crystals to form more slowly and develop with less void space and into larger particles.

Three tests were run on the 5 kW scrubber. The amount of magnesium hydroxide plant TOF used in slaking lime was varied between 25 and 50 % of the liquid needed for slaking lime. Slaking lime with 100 % magnesium hydroxide plant TOF was unsuccessful and not used in the 5 kW scrubber. Slaking lime with 100 % magnesium hydroxide plant TOF formed a gypsum coating around the outside of the lime particles. These "coated" particles appeared as grit and were unreactive and unavailable to scrub SO<sub>2</sub>.

b) SO<sub>2</sub> Removal

There were minimal differences in the removal of SO<sub>2</sub> between the tests. As can be seen in Figures 48 through 50, the SO<sub>2</sub> removals for the three tests were approximately the same. SO<sub>2</sub> removal efficiency remained over 90% throughout the testing period. In the last test the removal efficiency was low at the beginning due to a high inlet SO<sub>2</sub> concentration. Once the SO<sub>2</sub> concentration leveled off, the removal efficiency was the same as the previous tests. The stoichiometric ratio of calcium to sulfur removed remained close to normal. The range of stoichiometry was 1.02 to 1.04. (Table 16) This shows that the lime used in these tests remained reactive and was not prevented from dissolving.

Figure 48. 5 kW SO<sub>2</sub> Removal for Thiosorbic Baseline Test

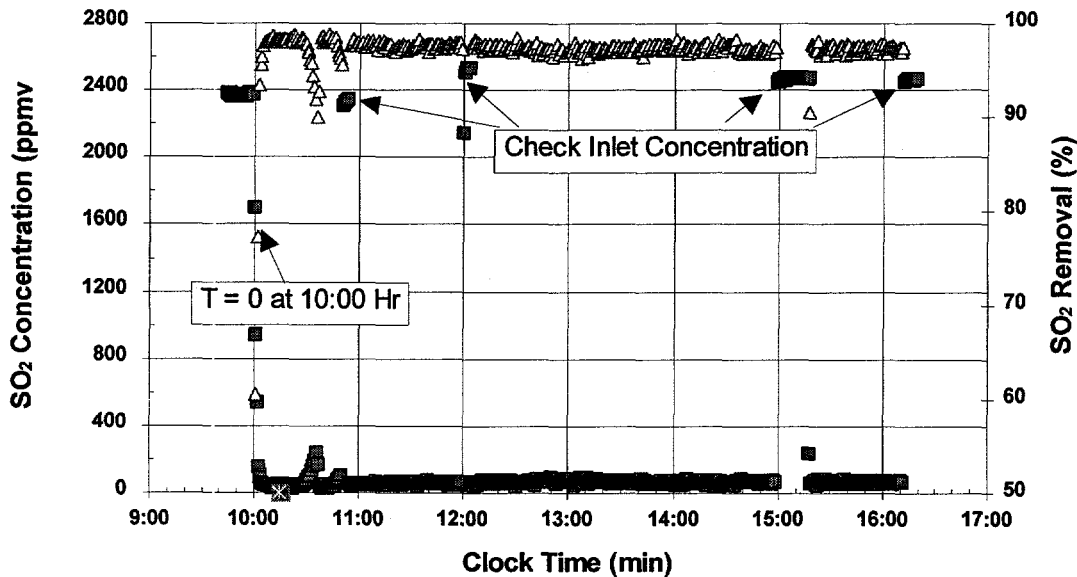


Figure 49. 5 kW SO<sub>2</sub> Removal for Lime Slaked With 25% TOF Test

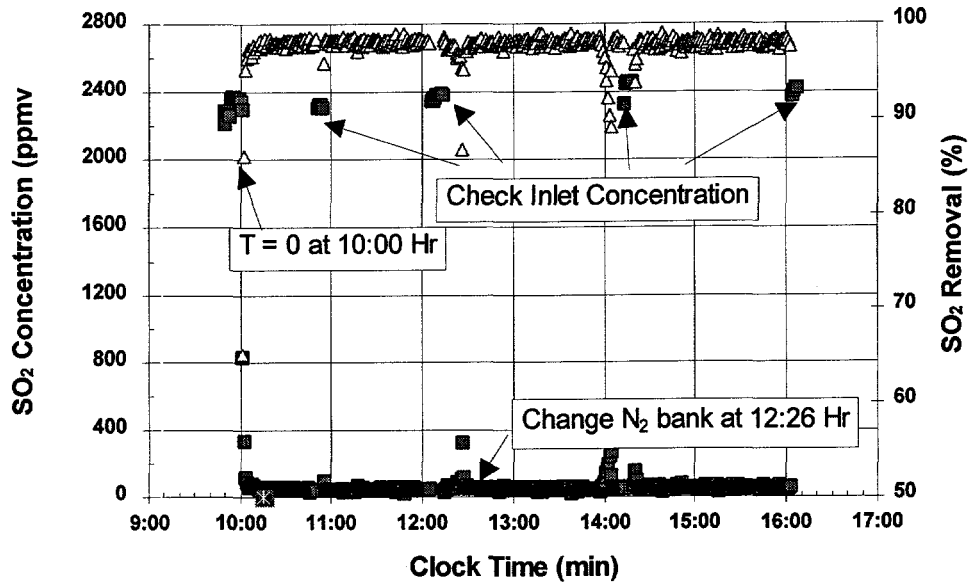
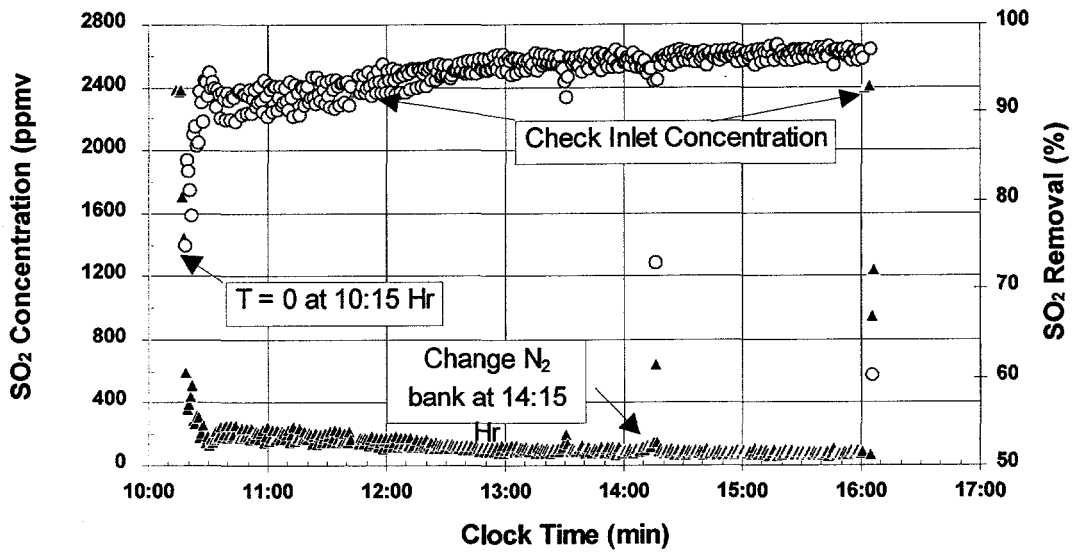


Figure 50. 5 kW SO<sub>2</sub> Removal for Lime Slaked With 50% TOF Test



Recycle tank chemistry for Proj-5248: DT020195 (Slaking Test No. 1)																	
Sampling Time	Liquor pH	Alkalinity (ppm)	[SO <sub>3</sub> <sup>-2</sup> ] (ppm)	[Ca <sup>+2</sup> ] by ICP (ppm)	[Mg <sup>+2</sup> ] by ICP (ppm)	[Total Fe] by ICP (ppm)	[Na+1] by ICP (ppm)	[SO <sub>3</sub> <sup>-2</sup> ] by IC (ppm)	[SO <sub>4</sub> <sup>-2</sup> ] by IC (ppm)	[S <sub>2</sub> O <sub>3</sub> <sup>-2</sup> ] by IC (ppm)	[Cl <sup>-1</sup> ] by IC (ppm)	[NO <sub>3</sub> <sup>-1</sup> ] by IC (ppm)	Filtercake Solids (wt%)	[SO <sub>4</sub> <sup>-2</sup> ] calculated (ppm)	% Oxidation by IC	Free Base as CaO at ph 8.3 (%)	Stoichiometric Ratio
10:15	6.4	1,935	4,948	118	4,779	3.15	24.65	6,633	17,770	n.d.	113	n.d.		13,226			
11:15	6.6	2,052	4,155	133	5,203	6.55	26.89	5,023	18,316	n.d.	210	n.d.	44.1	15,888	11.39	0.71	1.03
12:15	6.45	3,469	4,091	145	5,551	5.72	28.45	4,892	20,176	n.d.	279	n.d.	37.2	17,369	11.21	0.69	1.03
13:15	6.5	1,818	3,691	155	5,456	5.76	29.34	4,268	19,457	n.d.	475	47	37	17,497	14.00	0.86	1.03
14:15	6.4	1,735	3,923	203	5,811	6	29.77	4,587	21,959	n.d.	164	42	36.7	18,737	12.37	0.71	
16:00	6.35	1,735	3,795	184	6,255	6.15	31.78	4,935	26,981	n.d.	259	70	34.9	20,599	12.92	0.94	1.03
Note: (1) This is a Thiosorbic baseline test using regular 20 wt % Maysville lime slurry.																	
(2) The initial liquor source was a batch of fresh synthetic liquor.																	
(3) T = 0 at 10:00 Hr and inlet NOx, SO <sub>2</sub> , & O <sub>2</sub> (by PC) = 520 ppmv, 2,485 ppmv, & 6.0 vol%, respectively.																	
(4) At 10:53 Hr inlet NOx, SO <sub>2</sub> , & O <sub>2</sub> (by PC) = 525 ppmv, 2,450 ppmv, & 6.1 vol%, respectively.																	
(5) At 12:02 Hr inlet NOx, SO <sub>2</sub> , & O <sub>2</sub> (by PC) = 515 ppmv, 2,650 ppmv, & 6.1 vol%, respectively.																	
(6) At 12:30 Hr add 1 L water to recycle tank.																	
(7) At 14:30 Hr add 1 L water to recycle tank.																	
(8) At 15:17 Hr inlet NOx, SO <sub>2</sub> , & O <sub>2</sub> (by PC) = 530 ppmv, 2,590 ppmv, & 6.8 vol%, respectively.																	
(9) At 16:19 Hr inlet NOx, SO <sub>2</sub> , & O <sub>2</sub> (by PC) = 525 ppmv, 2,585 ppmv, & 6.1 vol%, respectively.																	
(10) The calculated [SO <sub>4</sub> <sup>-2</sup> ] was based on ion-balance calculation with Ca+2, Mg+2 and SO <sub>3</sub> <sup>-2</sup> .																	
(11) n.d. = not detected.																	

Table 15. Recycle Tank Liquor Chemistry for 5 kW Unit During Testing Period

Recycle tank chemistry for DT020295 (Project 5248 - Slaking Test No. 2)																
Sampling Time	Liquor pH	Alkalinity (ppm)	[SO <sub>3</sub> <sup>2-</sup> ] (ppm)	[Ca <sup>2+</sup> ] by ICP (ppm)	[Mg <sup>2+</sup> ] by ICP (ppm)	[Total Fe] by ICP (ppm)	[Na+1] by ICP (ppm)	[SO <sub>3</sub> <sup>2-</sup> ] by IC (ppm)	[S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> ] by IC (ppm)	[Cl <sup>-</sup> ] by IC (ppm)	[NO <sub>3</sub> <sup>-</sup> ] by IC (ppm)	Filtercak Solids (wt%)	[SO <sub>4</sub> <sup>2-</sup> ] calculated (ppm)	% Oxidation by IC	Free Base as CaO at ph 8.3 (%)	Stoichiometric Ratio
10:15	6.7	1,968	4,147	193	4,985	1.07	23	4,054	14,208	n.d.	194	105	15,181			
11:15	6.35	1,635	4,067	149	5,743	1.18	25	3,668	15,648	n.d.	158	n.d.	18,166			
12:15	6.5	1,751	3,779	168	5,952	1.11	27	3,218	15,654	n.d.	243	n.d.	19,382			
13:15	6.65	1,753	3,515	177	5,992	1.07	28	3,250	17,292	n.d.	259	34	19,879	13.63	0.70	1.04
14:45	6.4	1,568	3,771	177	6,333	1.14	31	3,965	20,812	n.d.	334	49	20,919	12.70	0.71	1.04
16:00	6.65	1,835	3,611	206	6,908	1.13	35	3,565	21,508	n.d.	379	58	23,452	11.82	0.73	1.04
Note: (1) This is a Thiosorbic baseline test using regular 20 wt % Maysville lime prepared with 25 % TOF liquor from Zimmer Mg(OH)2 plant.																
(2) The Zimmer TOF liquor chemistry: pH = 11.4, T.H., SO4-2, Cl-1, Ca+2, & Mg+2 = 5,454 ppm, 1,087 ppm, 2,414 ppm, 2,346 ppm, & 152 ppm, resp. However, new ICP analyses (95-0302) of Ca+2, Total Fe, Mg+2, & Na+1 gave 2,401 ppm, 0.02 ppm, 1.77 ppm, & 44 ppm, resp. IC analyses (95-0302) of Cl-1, SO3-2, SO4-2, & S2O3-2 gave 2,589 ppm, not detected, 1,299 ppm, & not detected, resp.																
(3) The initial liquor source was a batch of fresh synthetic liquor (10 L = 75 mL H2SO4, 1,000 mL 6% H2SO3, 140 g Mg(OH)2).																
(4) T = 0 at 10:00 Hr and inlet NOx, SO2, & O2 (by PC) = 515 ppmv, 2,450 ppmv, & 5.7 vol%, respectively.																
(5) At 10:53 Hr inlet NOx, SO2, & O2 (by PC) = 533 ppmv, 2,429 ppmv, & 5.9 vol%, respectively.																
(6) At 12:12 Hr inlet NOx, SO2, & O2 (by PC) = 535 ppmv, 2,499 ppmv, & 6.1 vol%, respectively.																
(7) At 12:26 Hr change N2 bank.																
(8) At 12:30 Hr add 1 L water to recycle tank.																
(9) At 14:02 to 14:05 Hr lost lime flow.																
(10) At 14:16 Hr inlet NOx, SO2, & O2 (by PC) = 530 ppmv, 2,567 ppmv, & 6.8 vol%, respectively.																
(11) At 16:06 Hr inlet NOx, SO2, & O2 (by PC) = 530 ppmv, 2,530 ppmv, & 6.0 vol%, respectively.																
(12) The calculated [SO4-2] was based on ion-balance calculation with Ca+2, Mg+2 and SO3-2.																
(13) n.d. = not detected.																

Table 15. Recycle Tank Liquor Chemistry for 5 kW Unit During Testing Period (continued)

Recycle tank chemistry for DT022195 (Zimmer Mg(OH)2 plant TOF slaking test 50% TOF-50% water)																	
Sampling Time (Hr-Min)	Liquor pH	Alkalinity (ppm)	[SO <sub>3</sub> <sup>2-</sup> ] y titratio (ppm)	[Ca <sup>2+</sup> ] by ICP (ppm)	[Mg <sup>2+</sup> ] by ICP (ppm)	[Total Fe] by ICP (ppm)	[Na+1] by ICP (ppm)	[SO <sub>3</sub> <sup>2-</sup> ] by IC (ppm)	[SO <sub>4</sub> <sup>2-</sup> ] by IC (ppm)	[Cl <sup>-1</sup> ] by IC (ppm)	[NO <sub>3</sub> <sup>-1</sup> ] by IC (ppm)	Itercak Solids (wt%)	[SO <sub>4</sub> <sup>2-</sup> ] calculated (ppm)	[SO <sub>3</sub> <sup>2-</sup> ] calculated* (ppm)	% Oxidation by IC	Free Base as CaO at ph 8.3 (%)	Stoichiometric Ratio
10:30	6.50	1,384	2,698	689	4,432	5	47	1,594	14,046	149	61		17,098	4,137			
11:30	6.70	1,134	2,474	491	4,746	1	34	1,831	17,121	221	n.d.	55.9	17,502	2,149			
12:30	6.70	1,268	2,426	371	4,833	<1	47	1,842	15,198	267	56	52.7	17,466	3,732			
13:30	6.70	1,351	2,754	297	5,170	<1	55	2,273	17,254	299	58	45.8	18,074	2,956	17.26	0.23	1.03
14:30	6.55	1,201	2,994	282	5,331	<1	53	2,373	16,548	311	62	39.9	18,531	4,025	16.49	0.19	1.03
15:50	6.50	1,284	3,066	247	5,631	1	56	2,250	15,464	338	71	36.3	19,742	5,815	16.42	0.15	1.02
Note:																	
(1) This is a Thiosorbic baseline test using regular 20 wt % Maysville lime prepared with 50 % TOF liquor from Zimmer Mg(OH)2 plant.																	
(2) The Zimmer TOF liquor chemistry: pH = 11.4, T.H. = 5,454 ppm, SO4-2 = 1,087 ppm, Cl-1 = 2,414 ppm, Ca+2 = 2,346 ppm, Mg+2 = 152 ppm.																	
(3) The initial liquor source was a batch of fresh synthetic liquor (10 L = 75 mL H2SO4, 1,000 mL 6% H2SO3, 140 g Mg(OH)2).																	
(4) T = 0 at 10:15 Hr and inlet NOx, SO2, & O2 (by PC) = 510 ppmv, 2,505 ppmv, & 6.3 vol%, respectively.																	
(5) At 11:45 Hr inlet NOx, SO2, & O2 (by PC) = 515 ppmv, 2,490 ppmv, & 6.3 vol%, respectively.																	
(6) At 14:15 Hr change N2 bank.																	
(7) At 16:03 Hr inlet NOx, SO2, & O2 (by PC) = 505 ppmv, 2,515 ppmv, & 6.2 vol%, respectively.																	
(8) n.d. = not detected																	
(9) The calculated [SO4-2] was based on ion-balance calculation with Ca+2, Mg+2, Na+1, SO3-2, Cl-1, and NO3-1 (cations by ICP and anions by IC).																	
(10) ADS, SA, and S2O3-2 were not detected by IC analysis.																	
(11) The data of Cl-1, SO3-2, and SO4-2 were from the same samples which were re-worked!																	
(12) The calculated [SO3-2] was based on ion-balance calculation with ICP (Ca+2, Mg+2, Na+1) and IC (SO4-2, Cl-1, and NO3-1) data.																	

Table 15. Recycle Tank Liquor Chemistry for 5 kW Unit During Testing Period (continued)

c) **5kW Filter Cake Solids**

As Figure 51 illustrates, the filter cake solids for the TOF additions started at different percent solids. The same downward trend occurred for each test was a result of the start-up of the 5 kW scrubber. The dewatering trend for the three testing periods appears to show a linear relationship between the filter cake solids and the amount of TOF used in slaking. (Figure 52) The trend suggests that as the proportion of TOF liquor used in lime slaking increases, waste solids dewatering improves.

The particle size and SEM pictures of the particles show an improvement in the crystal growth by using TOF to slake lime. Using only TOF to slake lime can cause problems as stated above, but diluting the slaked lime with TOF appeared to have positive effects on FGD Solids dewatering. The percent solids of the filter cake at the end of each testing period varied from 35 to 37 % solids. On the other hand, the percent solids for the 50 % TOF test started with the filter cake solids higher than 55 %. Figures 53 through 55 show the calcium sulfite particles of the recycle tank solids from the 5 kW scrubber obtained with the SEM. The SEM images show that as the amount of TOF increased the void space of the particles decreased while the mean diameter of the particles increased. The particle size for the solids increased as follows: 20.10, 23.22, and 25.54.

Figure 51. 5 kW Filter Cake Solids for Lime Slaked with Water and Magnesium Hydroxide Plant TOF Testing vs. Time

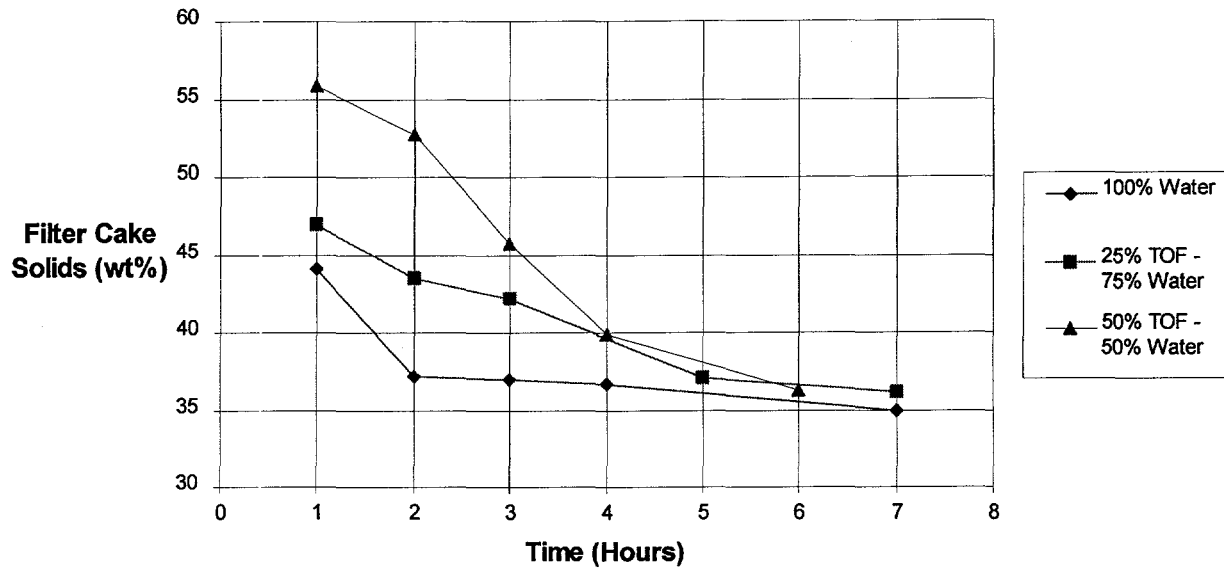


Figure 52. 5 kW Filter Cake Solids for Lime Slaking with Water and Magnesium Hydroxide Plant TOF Testing vs. % of Slaking Water as TOF

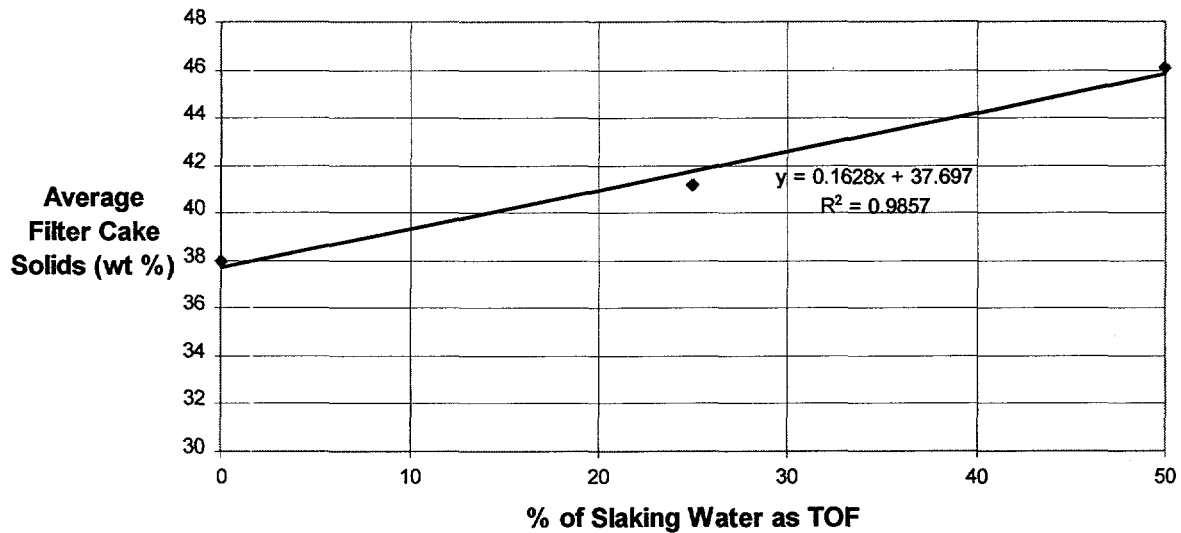


Figure 53. 5 kW Recycle Tank Final Slurry for Baseline Thiosorbic Testing

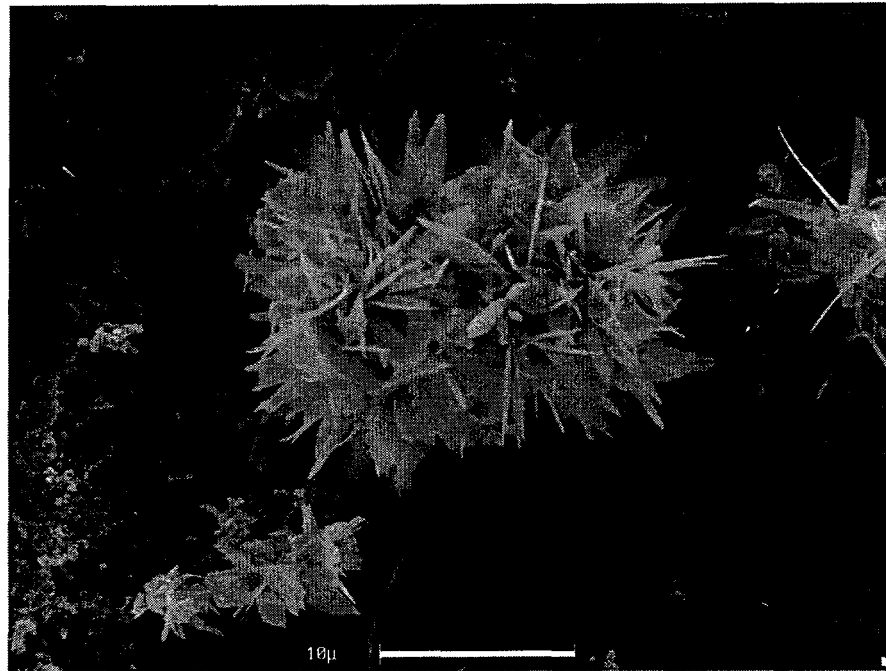


Figure 54. 5 kW Recycle Tank Final Slurry for 25% TOF Testing

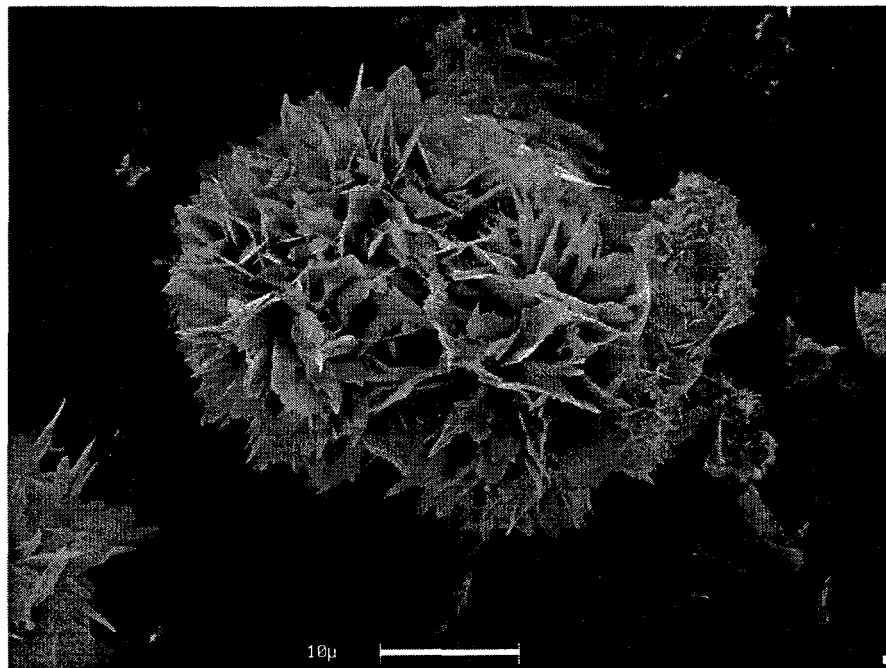
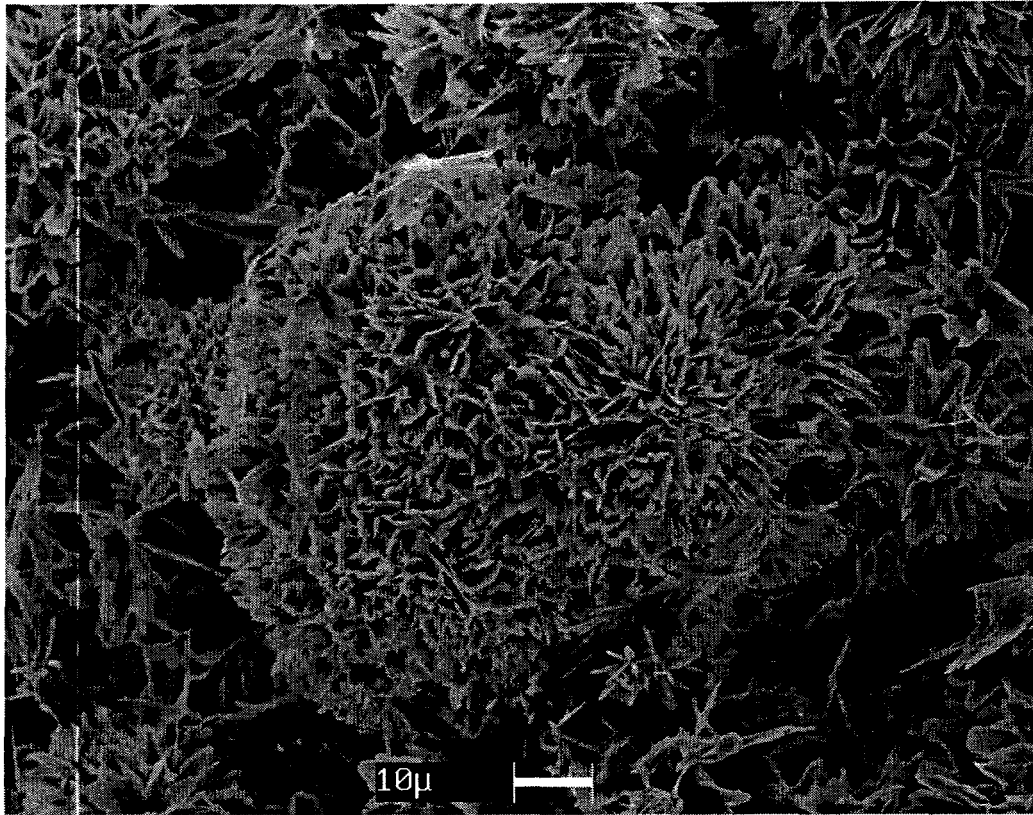


Figure 55. 5 kW Recycle Tank Final Slurry for 50% TOF Testing



d) **Conclusions from Testing**

Slaking lime with magnesium hydroxide plant TOF is not detrimental to  $\text{SO}_2$  removal.  $\text{SO}_2$  removals remained the same as did the relative stoichiometry. TOF addition can be used to improve sludge dewatering. When 100 % magnesium hydroxide plant TOF is used in slaking the lime, lime particles become excessively coated with gypsum, causing the lime to be unreactive and form grit.

Optimization of slaking lime with magnesium hydroxide thickener overflow is required. However, a trend of improved waste solids dewatering was seen with use of TOF slaked lime. Recycle tank particles increased in size from 20 to 25 microns. Also the SEM

images show particles that should dewater better with the use of magnesium hydroxide plant TOF.

## 8. Upgrade and Commercialization of Magnesium Hydroxide

The magnesium hydroxide produced from the Zimmer Station magnesium hydroxide demonstration plant is in perfect condition for in-plant use. However, if magnesium hydroxide is to be sold on the open market, it will need to meet the commercial quality standards already in place. The magnesium hydroxide product from the plant is 15-20 % solids. Commercial magnesium hydroxide is typically 58 % solids. Also, the amount of gypsum contamination would need to be decreased for commercialization. Therefore, bench scale testing was performed on the magnesium hydroxide to find the most economical method for upgrading the material to a commercial level.

Zimmer magnesium hydroxide product was washed with water under various conditions for purification at Dravo Research Center. The results of the washing have been evaluated for the purity of the magnesium hydroxide. Also comparison of the different methods of dewatering magnesium hydroxide were evaluated.

Purity data for magnesium hydroxide and gypsum on a non-calcined basis is listed in Table 17. Filtration equipment and their corresponding pressure or force requirements are listed in Table 18.

### a) Magnesium Hydroxide Washing

Magnesium hydroxide product from Zimmer Station was washed with different amounts of water and at different time intervals. The intent of washing the magnesium hydroxide was to dissolve the gypsum impurity. The initial magnesium hydroxide product was a sample taken on June 2<sup>nd</sup>, 1994 and had 68.4 % magnesium hydroxide and 22.6 % gypsum. The remaining 9 % of the sample consists of metal oxides, aluminum and iron,

magnesium silicate, and calcium carbonates and sulfites. The amount of wash water varied from 3 to 12.5 liters per 100 g of dry solids. Also the mixing duration varied from 5 to 240 minutes. As shown in Figure 56, there is an optimum amount of water and residence time that can be used for magnesium hydroxide purification. The minimum residence time that should be used in magnesium hydroxide purification is 30 minutes. In a shorter residence time, the liquid and solid phases will not reach equilibrium. The theoretical amount of water to dissolve gypsum is 6.1 liters per 100 g of dry solids. This is based on the solubility for gypsum as  $\text{CaSO}_4$  being 2600 mg per liter. Figure 56 illustrates that 8.6 liters per 100 g of dry solids is the recommended amount of water needed to remove most of the gypsum impurity. The amount of gypsum dropped to less than 5 % by washing the magnesium hydroxide using this volume of water.

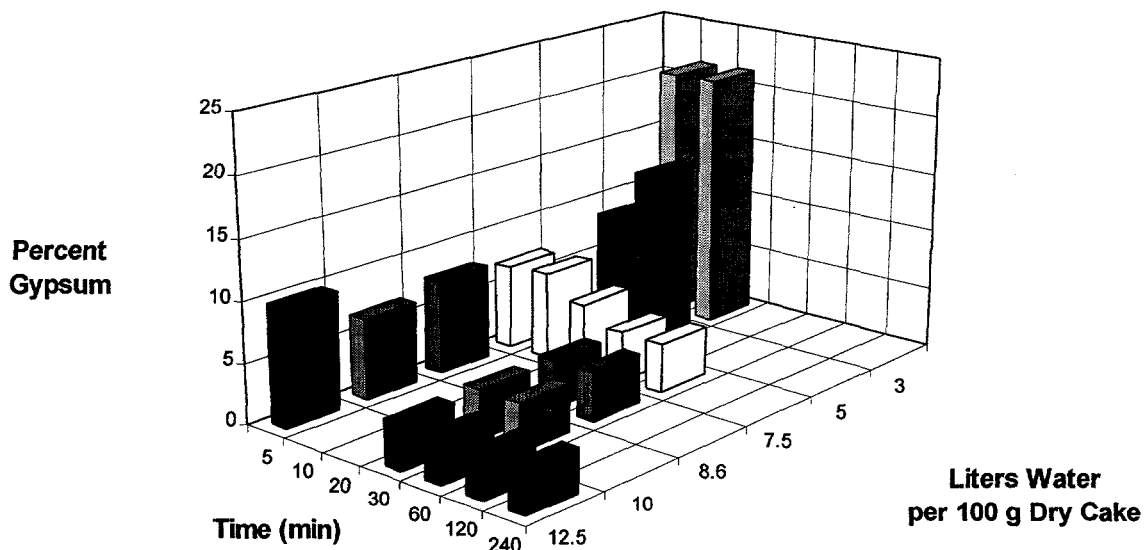
Table 17. Results of the Magnesium Hydroxide Washing Studies

<b>Percent Gypsum (non-calcined basis)</b>						
	Liters Water per 100 g Dry Filter Cake					
TIME (Min)	12.5	10	8.6	7.5	5	3
5	9.84	6.83	7.86	7.04		
10				7.3	10.31	21.48
20				5.58	14.8	21.5
30	3.74	3.99	4.04	4.12		
60	3.78	3.95	4.08	4.12		
120	3.52					
240	3.61					

<b>Percent <math>\text{Mg}(\text{OH})_2</math> (non-calcined basis)</b>						
	Liters Water per 100 g Dry Filter Cake					
TIME (Min)	12.5	10	8.6	7.5	5	3
5	75.3	72.7	71.1	75.4		
10				69.9	60.5	66.8
20				77.3	76	68.7
30	84.9	85.5	84.9	85		
60	85.2	85.2	85.1	84.5		
120	86.1					
240	86.4					

Figure 57 illustrates the corresponding magnesium hydroxide purity from the testing discussed above. The results discussed above are shown very clearly in this graph, too. When the residence time of the washing method reached 30 minutes, the purity of the magnesium hydroxide increased by 5 to 10 %. The highest magnesium hydroxide purity found was 86.4 % on an as received (non-calcined) basis for a residence time of 240 minutes using 12.5 liters of water per 100 g dry solids. However, increasing the residence time by a factor of 4 to 8 to increase purity by one percent would not be practical from a production standpoint. The tank volume needed to wash the material would be too large, and the amount of water needed would become prohibitively large. Therefore, the amount of water and residence time to be used should be the same as what was recommended above.

Figure 56. Magnesium Hydroxide Washing Tests - Percent Gypsum



Other magnesium hydroxide samples, which have been washed in the same fashion, have reached as high as 93 % in magnesium hydroxide purity on a calcined basis. Therefore, the operating conditions for a full scale magnesium hydroxide purifier using water to dissolve gypsum would need to be 8.6 liters per 100 g of dry solids, 10.3 gallons per

pound dry solid, and 30 minute residence time in the tank. Using a feed rate of 15 lb./min. (the approximate solids' flowrate from the magnesium hydroxide thickener), the size of a purification tank would be 10'  $\varnothing$  x 10' H and the required water flowrate would be 155 gpm. Other steps would have to be taken after the gypsum has been washed out, such as thickening and filtering. Samples of magnesium hydroxide slurry washed in this manner have been judged to be of commercial grade quality by suppliers of magnesium hydroxide slurry.

**b) Dewatering Magnesium Hydroxide**

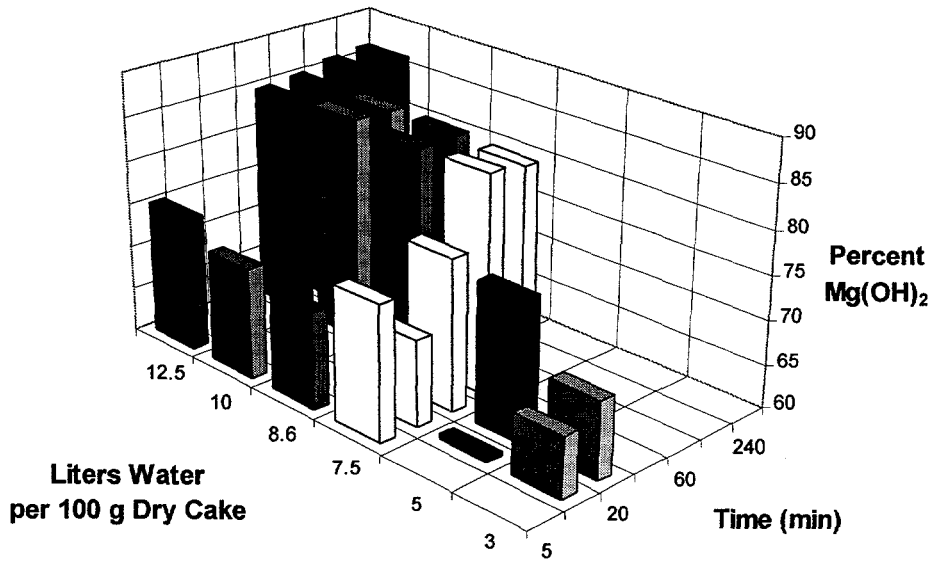
The magnesium hydroxide recovery plant can achieve up to 20 % solids in the Thickener Underflow (TUF) or magnesium hydroxide product. For commercial grade material, 50 to 60 % solids is required. Samples of magnesium hydroxide Thickener Underflow (TUF) were sent to vendors for suggestions on dewatering. Drum filtering was attempted with a sample of 10 % solids magnesium hydroxide. This method achieved 33 % solids at a filtration rate of 2 lb./hr/ft<sup>2</sup>. Pressure filtration was also attempted on the same sample. As shown in Table 18, the maximum percent solids achieved was 44 % @ 225 psig with a fill time of 50 minutes. In the pressure filtration tests, no air blowing or membrane squeezing was attempted. These methods may increase the percent solids of the cake even more.

Another magnesium hydroxide sample of 9 % solids was tested using a centrifuge and a belt filter. The maximum dewatering achieved by the belt filter was 28 %. The cloth used on this belt needed to be tight and the magnesium hydroxide filtered slowly. A spin tube test was completed on the magnesium hydroxide to determine if a centrifuge would be suitable for dewatering. Using a centrifuge, the maximum percent solids achievable would be about 55 vol. % (42 wt. %). The centrifuge did have some solids in the filtrate.

Table 18. Results from Magnesium Hydroxide Filtration Studies

Type of Filtration	Pressure/ Force	% Solids of Cake	Production Rate	Density of Cake
Drum Filtration	20" Hg	33 wt. %	2 lbs/hr/ft <sup>2</sup>	
Pressure Filtration	100 psig	40 wt. %		32.6 lbs/ft <sup>3</sup>
Pressure Filtration	225 psig	44 wt. %		37.9 lbs/ft <sup>3</sup>
Drum Filtration	15" Hg	15 wt. %	11 lbs/hr/ft <sup>2</sup>	
Centrifugal Filtration	447 psig	43 wt. %		
Centrifugal Filtration	894 psig	41 wt. %		
Decanting	476 psig	36 wt. %		
Decanting	476 psig	24 wt. %		
Belt Filter	16" Hg	28 wt. %	34 lbs/hr/ft <sup>2</sup>	

Figure 57. Magnesium Hydroxide Washing Tests - Magnesium Hydroxide Purity



A flocculant could be used but it would increase the operating costs of making magnesium hydroxide. For the magnesium hydroxide with the highest percent solids, it would take 5.4 lb. of flocculant per ton of dry feed solids. Decanting was attempted and found to give 36.3 % solids with 7.6 % solids in the effluent. Using a flocculant, the solids decreased to 23.7 % with only 0.32 % solids in the effluent. These evaluations indicate pressure filtration holds the most promise.

c) **Conclusions from Testing**

Magnesium hydroxide can be washed with water to reduce the amount of gypsum impurity in the product. Magnesium hydroxide purity of 93 % was achieved using reasonable amounts of water and tank volume. The operating conditions for the washing method should be 8.6 liters per 100 g of dry solids, 10.3 gallons per pound dry solid, and 30 minutes residence time in the tank. The washed magnesium hydroxide product was independently judged to be a commercial grade material. Considering the filtration options for obtaining a higher percent solids product, the results show that pressure filtration is the most promising filtration method. The percent solids achievable would be as high as 44 %, bringing the magnesium hydroxide close to commercial grade material. Membrane squeezing and air blowing in a pressure filtration system could raise the percent solids even higher to achieve the 50 % solids needed for commercial grade material.

Reports received from the vendors evaluating different dewatering techniques for magnesium hydroxide and addition data to support the findings from the magnesium hydroxide washing study are located in Appendix IX.

## V. MARKETING AND COMMERCIALIZATION

### A. Scale-Up of the Process to Commercial-Sized Application

Scale up of this process to commercial sized application is expected to be accomplished with few complications. This optimistic outlook is predicated upon the size of the Zimmer demonstration plant. The 100 gpm demonstration plant is capable of processing roughly 25% of the available excess magnesium from the FGD system TOF stream. This is a considerable size in lieu of the fact that Zimmer Station is rated at 1300 MW. The capacity of any commercial scale magnesium hydroxide recovery unit is determined by the available excess magnesium which is a function of water balance and the operating magnesium level in the scrubber. In the case of Zimmer, where magnesium concentration in the scrubber ranges from 4000 to 9000 mg/l, the slipstream volumetric flowrate could range from 75 to 400 gpm. Considering the likely rate of magnesium hydroxide usage and the range of magnesium oxide contained in the lime (3 to 6 wt. % MgO) delivered to Zimmer station, the plant design of 100 gpm is judged to be the maximum capacity for the site. Figure 58 shows the recovery of magnesium hydroxide as functions of MgO content in the incoming lime and the scrubber liquor chemistry.

Operation of the Zimmer demonstration plant at 100 gpm is seen to be of the same order of magnitude size as any future plant that may be designed. Modularity will have a certain appeal if hydroclones are used on a commercial scale since banks of similar-sized hydroclones will be required to effect the particle size separation of gypsum and magnesium hydroxide. Scale-up criteria for dewatering and conveying equipment and for tanks, pumps, and associated hardware are well established. Process control parameters will be established for all major process variations experienced in the demonstration plant and these parameters can be usefully applied to the wide range of process chemistry conditions expected to be encountered in any marketing effort.

Figure 58. Recovery of Magnesium Hydroxide

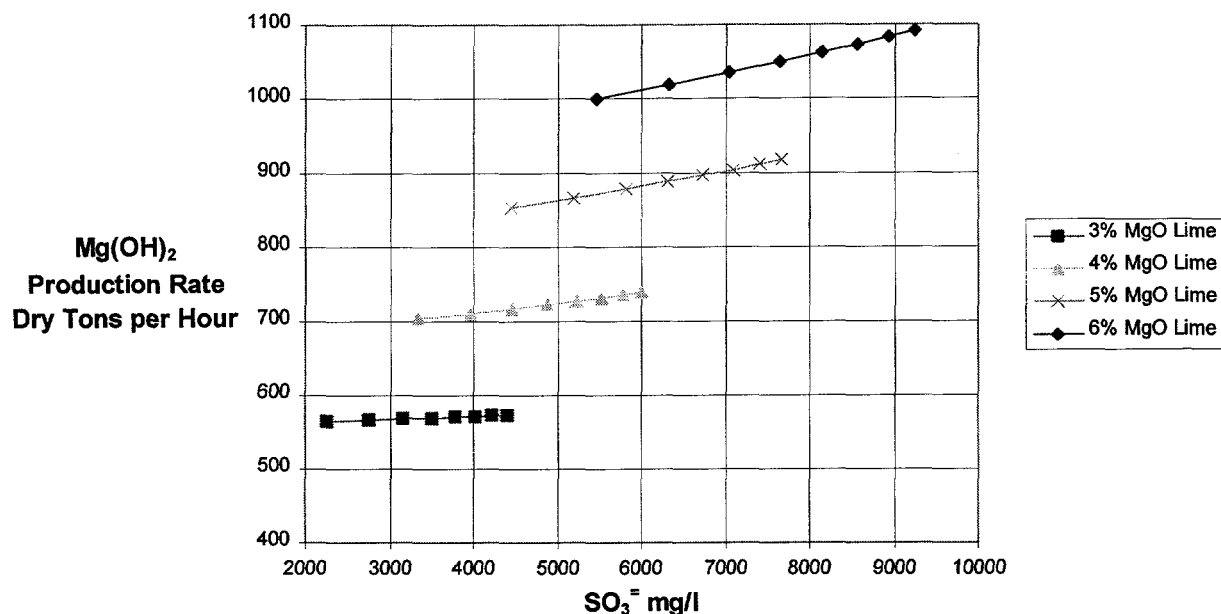


Table 19

Magnesium Oxide and Magnesium Hydroxide Prices and Specifications

Water, Waste water, & Chemical Grade:

*Dow Chemical - fob Ludington, Michigan - technical grade >95% Mg(OH)<sub>2</sub>*

liquid, bulk tanker	\$195/dry ton	(direct from factory)
solid, drums	\$680/dry ton	(direct from factory)
solid, bags	\$985/dry ton	(direct from factory)

*HVC Daly - distributor Cincinnati, Ohio*

liquid Mg(OH) <sub>2</sub> (Dow) - truckload drums @ 57.5 gallons	\$553/ton
solid MgO (M. Marietta) - truckload 50# bags	\$1,310/ton

*National Colloid - distributor Steubenville, Ohio*

solid Mg(OH) <sub>2</sub> (95-99% Dow) - 50# bags	\$1,310/ST
solid MgO (Grade 30 M. Marietta) - truckload	\$425/ST

**Table 19 - continued**

*Chemical Marketing Reporter March 1996 Prices*

Natural Magnesia, 85%	\$232/ST *
Natural Magnesia, 90%	\$265/ST *
Magnesium Chloride, 99%	\$290/ST
Magnesium Carbonate	\$1,480/ST
Magnesium Hydroxide	\$1,560/ST

\* Natural means magnesia produced from magnetite

**Animal Feed & Fertilizer Grade:**

*Purina Mills, St. Louis, MO - they possibly buy imported MgO @ Mobile AL. for \$175/ST CIF*

Their feed grade specs:

>84% MgO	<50 ppm cadmium
>97% acid soluble	<100 ppm fluoride

*Agway, Syracuse, NY (their selling prices)*

animal feed >90% MgO      whsle, 50# bag \$286/ST

fertilizer >97% MgO      whsle, 50# bag \$500/ST

*Martin Marietta 96% MgO: whsle, 50# bag \$456/ST (less than truckload)*

*Basic (now Premier) MAGOX 90% MgO: whsle, 50# bag \$370/ST (less than truckload)*

*Imports:*

Caustic Calcined MgO:	Canada	\$178/ST	(*)
	China	\$90/ST	(*)
Refractory MgO:	China	\$72/ST	(*)
	Greece	\$155/ST	(*)
Mg(OH) <sub>2</sub>	source?	\$1,568/ST	(*)

(\*) = U.S. Bureau of Mines 1989 Draft Report

*Mobile, AL CIF \$175/ST for magnesia (Purina Mills Information)*

**VI. FINAL BUDGET SUMMATION**

**Table 20**

**Total Project Budget by Major Category and Contributions of Co-sponsors**

Budget Category	Total Project Budget	Project Funds Expended				Total Expended
		DLC	OCDO	EPRI	Cinergy	
		\$	\$	\$	\$	
Personnel	\$247,263	\$38,202	\$105,843	\$68,442	\$0	\$212,487
Fringe	\$98,373	\$28,930	\$28,357	\$27,415	\$0	\$84,702
Travel	\$55,638	\$30,500	\$22,762	\$5,614	\$0	\$58,876
Equipment	\$628,870	\$257,941	\$200,465	\$0	\$143,590	\$601,997
Supplies	\$101,970	\$31,035	\$15,515	\$0	\$0	\$46,550
Contractual	\$325,497	\$122,443	\$122,443	\$0	\$0	\$244,886
Total Direct	\$1,457,611	\$509,052	\$495,385	\$101,470	\$0	\$1,105,907
Indirect	\$336,928	\$99,027	\$97,061	\$93,896	\$0	\$289,983
Total	\$1,794,539	\$608,078	\$592,446	\$195,366	\$143,590	\$1,539,480
Cinergy man-hours., fringe., & indirect.	\$50,016					
Project Total	\$1,844,555					

**Table 21**

**Expenditure of OCDO Funds By Line Item**

	Total Budget	Total Expended
Personnel	\$134,051.00	\$105,843.48
Fringe	\$34,210.74	\$28,356.60
Travel	\$24,819.00	\$22,762.38
Equipment	\$209,414.00	\$200,465.14
Supplies	\$33,986.00	\$15,514.79
Contractual	\$162,748.50	\$122,442.87
Total Direct	\$599,229.23	\$495,385.25
Indirect	\$117,171.77	\$97,060.95
Total	\$716,401.00	\$592,446.20