PRODUCT DEVELOPMENT AND UTILIZATION OF ZIMMER STATION WET FGD BY-PRODUCTS

FINAL REPORT

VOLUME 1: EXECUTIVE SUMMARY

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1.0 INTRODUCTION

About 30 electric utility units with a combined total of 15,000 MW utilize magnesium enhanced lime flue gas desulfurization (FGD) systems. A disadvantage of this and other inhibited or natural oxidation wet FGD systems is the capital and operating cost associated with landfill disposal of the calcium sulfite based solids. Fixation to stabilize the solids for compaction in a landfill also consumes fly ash that otherwise may be marketable. This Executive Summary describes efforts to dewater the magnesium hydroxide and gypsum slurries and then process the solids into a more user friendly and higher value form.

To eliminate the cost of solids disposal in its first generation Thiosorbic® system, the Dravo Lime Company developed the ThioClear® process that utilizes a magnesium based absorber liquor to remove SO_2 with minimal suspended solids. Magnesium enhanced lime is added to an oxidized bleed stream of thickener overflow (TOF) to produce magnesium hydroxide [$Mg(OH)_2$] and gypsum ($CaSO_4 \cdot 2H_2O$), as by-products. This process was demonstrated at the 3 to 5 MW closed loop FGD system pilot plant at the Miami Fort Station of Cinergy, near Cincinnati, Ohio with the help of OCDO Grant Agreement CDO/D-91-6. A similar process strictly for recovery and reuse of $Mg(OH)_2$ began operation at the Zimmer Station of Cinergy in late 1994 that can produce 900 pounds of $Mg(OH)_2$ per hour and 2,600 pounds of gypsum per hour. This by-product plant, called the Zimmer Slipstream Magnesium Hydroxide Recovery Project Demonstration, was conducted with the help of OCDO Grant Agreement CDO/D-921-004. Full scale ThioClear® plants began operating in 1997 at the 130 MW Applied Energy Services plant, in Monaca, PA, and in year 2000 at the 1,330 MW Allegheny Energy Pleasants Station at St. Marys, WV.

Product evaluation for various market uses was performed for both by-products throughout the project. The Zimmer gypsum, both loose and agglomerated, was successfully used in full scale production of hydraulic portland cement and as a soil conditioner / amendment for agriculture and mine reclamation per experiments by The Ohio State University (OSU). Dried, pulverized, and high brightness gypsum was produced for use as a mineral filler in manufacturing plastic products.

Magnesium hydroxide was evaluated for treating wastewater from industry and from municipalities. Its reactivity in neutralizing acid favorably compared with other neutralizing reagents while producing less sludge. Zimmer $Mg(OH)_2$ powder was studied by the University of Cincinnati where they are evaluating its utility in treating municipal wastewater in the biological aerobic and anaerobic sludge processes to facilitate solids removal and precipitate nutrient pollutants: ammonia and phosphates. Samples of washed $Mg(OH)_2$ powder were submitted to two refractory manufacturers of calcined magnesia (MgO). Both reported a concern with remaining impurities. Other uses for this lower grade MgO, such as flux, fertilizer, and animal feed supplement may be economically feasible. Its use as a feedstock may not be economical for magnesium chloride but may be economical for producing magnesium sulfate.

2.0 OVERALL PROJECT OJBECTIVES

The goal of Phase 1 of this by-product utilization project was to recover the Zimmer demonstration plant by-products and develop them into salable products for the gypsum and magnesium markets. Besides the familiar uses of gypsum in the construction industry as wallboard and plaster, it also is needed in the portland cement industry to control the setting time and in agriculture to improve soil quality and productivity. The magnesium hydroxide market includes acid neutralization, agriculture as fertilizer and animal feed, and as a feedstock for magnesium chemicals, refractories and the magnesium metal industry. A new use is as a fuel additive or sorbent to inject in a furnace to enhance boiler performance and control emission opacity. The market value of 95% technical grade magnesium hydroxide [>95% $Mg(OH)_2$, as 55% solids slurry, bulk quantity] is nearly $200 per dry ton. The value of uncalcined gypsum for hydraulic portland cement production and for agriculture is reportedly about $10 per ton. Wallboard manufacturers pay less.

Industry has not been responsive to reuse of FGD by-products because, as removed from the plant, they are difficult to handle. This difficulty stems from high moisture content and solids fineness. This program has evaluated dewatering and agglomeration processes so that the separately recovered gypsum and magnesium hydroxide will be acceptable for commercial use. Successful demonstration by-product recovery will permit the supplemental income from their sale and thereby improve the overall scrubbing economics of the highly efficient magnesium enhanced lime FGD scrubbing process for SO_2 emission control. Combustion of local high sulfur coal will be encouraged rather than fuel switching to low sulfur western coals.

Industrial by-product gypsum in other areas of the United States has been demonstrated successfully for various markets, but none yet in Ohio. Large quantities of both by-products can be made available to various markets, such as the portland cement industry and agriculture.

Phase 2 and Phase 3 of this proposed project were conducted by The Ohio State University (OSU), School of Natural Resources. In these experiments FGD gypsum by-product solids were evaluated as a soil conditioner for use in agriculture and mine land reclamation.

One objective of Phase 2 is a laboratory and greenhouse study to evaluate the effects of this unique by-product gypsum on soil physical and chemical properties. One sample of the gypsum by-product for the greenhouse study was formulated to contain 6% to 8% magnesium hydroxide [$Mg(OH)_2$] upon the recommendation of the Agricultural Research Service of the USDA. A separate objective of Phase 2 was a laboratory investigation on the effect of calcium sulfite FGD solids to control pyrite oxidization in order to suppress acid mine drainage formation. This demonstration is related somewhat remotely to the first objective of Phase 2, as explained further.

Based on the Phase 2 greenhouse study, Phase 3 conducted test crop response on several different soils and mine spoils in field experiment plots. For mineland reclamation a comparison was made with conventional agricultural limestone (aglime) and borrow soil as well as supplements of compost and biosolids. The spreading of the agglomerated gypsum granules on land was evaluated.

3.0 GYPSUM BY-PRODUCT

3.1 Project Objectives – Phase 1 – Gypsum

The objectives for this product development study on this type of FGD gypsum from the magnesium enhanced lime scrubbing were as follows:

- Evaluate several means of dewatering the gypsum solids from a secondary hydrocyclone containing 1% to 6% $Mg(OH)_2$. Samples were submitted to vendors before selecting units for pilot plant testing.

- Gain understanding on the aspects of material handling that affect transportation and storage unit operations.

- Evaluate several means of agglomerating to produce both small and large size products for selected markets. A small size would be a micropellet or granule (1 x 4 mm or 4 x 10 mesh) for use in agriculture and soil conditioning. Larger or macropellets (0.5 x 2 inch) would be a rock-like substitute for natural gypsum rock, particularly the rare naturally white gypsum ore.

- Another project objective added afterward was to make a mineral filler or an industrial plaster product that has higher value due to high brightness of this FGD gypsum (whiteness) as compared to limestone scrubbed FGD gypsum and most natural gypsum.

3.2 Sources Of Gypsum Samples

At the ThioClear® pilot plant at Miami Fort the gypsum slurry can be filtered after the oxidizer at pH of 5 to 6 prior to raising the pH to precipitate the $Mg(OH)_2$ so that the gypsum only contains about 1% $Mg(OH)_2$. The Zimmer facility is designed to recover $Mg(OH)_2$ from the gypsum with a two-stage hydrocylone system. The gypsum product typically contains 3% to 5% $Mg(OH)_2$, which for agricultural purposes can be beneficial according to research at the Agricultural Research Service of United States Department of Agriculture (USDA) and The Ohio State University (OSU). The Miami Fort ThioClear® pilot plant completed testing 1994 so most of this work on gypsum solids recovery and conversion was performed on the Zimmer gypsum source. More tests at Miami Fort on a vacuum rotary drum filter and a horizontal belt filter were performed in 1999. Some tests were on the Applied Energy Services (AES) Beaver Valley gypsum and $Mg(OH)_2$ when Zimmer material was not available. A chemical analysis is seen in Table 1. Scanning electron microscopic (SEM) photographs of both gypsum sources are seen in Figure 1 and 2. The Zimmer gypsum in Figure 1 shows the presence of smaller amorphous $Mg(OH)_2$ where as the Miami Fort gypsum in Figure 2 does not show any $Mg(OH)_2$.

3.3 Summary – Dewatering Gypsum

After the FGD gypsum is crystallized from solution in the oxidizer, it is first separated from the process flow with hydrocyclones to at least 25% to 30% solids. Magnesium enhanced lime FGD gypsum slurry from two of Cinergy's coal fired power plants has been evaluated for further dewatering by several mechanical devices: vacuum filtration, basket and decanter centrifuges, and a belt press. Dewatered product could then be evaluated for agglomeration into micro or macro pellets for several potential markets. Early results on both the Miami Fort ThioClear® and the Zimmer Station Recovery plant gypsum slurries exhibited high brightness and purity but were difficult to dewater due to crystal shape and size. The presence of about 1% to 5% $Mg(OH)_2$, depending on the process design, can enhance the gypsum's value for agricultural and mineland soil restoration but was expected to adversely impact dewatering efficiency.

Table 1

Comparison of Zimmer and Miami Fort ThioClear® FGD Gypsum

	Zimmer Slurry	Zimmer Bird Centrifuge Solids	Miami Fort Slurry	Miami Fort Eimco Filter Cake	Miami Fort Eimco Filter Cake
Date	July, 1994	June, 1996	August, 1994	August, 1994	March, 1999
$CaSO_4 \cdot 2H_2O$	90.3 – 93.0	95.7	89.6	94.6	98.7
$CaSO_3 \cdot \frac{1}{2}H_2O$	0.6 – 2.4	1.1	0.4	0.3	0.3
$Mg(OH)_2$	2.1 – 4.0	2.9	6.1	1.0	<0.5
$MgSiO_3$	0.28 – 0.56	0.7	0.4	0.3	<0.5
$CaCO_3$	0.8 – 1.2	2.6	1.1	0.1	<0.1
Particle size, mv	57 – 79		63 – 75		69
Particle shape	needles		needles		needles
Aspect ratio	4 - 10		4 - 10		4+
Specific gravity	1.13 – 1.24	2.3		2.3	

3.3.1 Belt Press

In order to produce timely quantities of Zimmer magnesium enhanced gypsum for the OSU Phase 3 Field Tests, a portable belt press was employed to dewater about 200 tons. A flocculent was necessary to keep the solids on the belt and produce a respectably clear filtrate. Only 60% to 70% solids was attained in the dewatered cake.

Figure 1

SEM Photo of Zimmer Gypsum Crystals before Dewatering

Figure 2

SEM Photo of Miami Fort Gypsum Crystals before Dewatering

3.3.2 Centrifuge

A 40 HP solid bowl decanter centrifuge was chosen and about 150 tons from Zimmer were processed using a 25% solids slurry feed coming from hydrocyclone underflows. This quantity was required to evaluate agglomeration unit processes. At the same time parametric testing of operating variables found the optimum percent solids to be near 80%, less than data reported for limestone FGD gypsum using vacuum filtration. However, the sticky and thixotropic centrifuge product exhibits self-hardening behavior. The nearly 1,800 "G" force shears the needle shaped crystals causing them to consolidate and re-knit. Upon aging, the centrifuged solids reaches compressive strengths over 500 psi. After several weeks in an open-air stockpile, the centrifuge moist cake-like product can be agglomerated by high-pressure extrusion at about 15% moisture. Higher moistures would be too wet. Some moisture, i.e. 6% to 12%, is desirable for agglomeration.

Vacuum filter solids at about 70% to 80% solids from Miami Fort did not exhibit self-hardening behavior but an auger extruder test found that at about 85% to 90% solids it could also be formed into self-hardening pellets. We found that the high pressure extrusion process also shears needle-like crystals which then harden after a few days in ventilated, ambient air.

3.3.3 BSO® Vacuum Filter Tests

Since the 1996 tests on centrifuges and early 1994 - 1995 ThioClear® tests on the Miami Fort 10.5 square foot Eimco horizontal vacuum belt filter, the FGD gypsum industry has installed mostly horizontal belt vacuum filters and most are able to achieve at least 90% solids at limestone FGD scrubbers. Limestone forced-oxidized gypsum, according to Baker Process, personnel is designed for 200 dry pounds per hour per square foot for a typical system.

An extensive investigation was conducted by Dravo Technology with Baker Process engineers on vacuum filtration at the Miami Fort pilot plant in early 1999 with FGD gypsum from the BSO® (Bleed Stream Oxidation) version of magnesium enhanced lime scrubbing. BSO® scrubbing is a new variation of ThioClear® that should lead to improved economics and operating options. Basically, the lime is added to the scrubber recycle tank instead of the regeneration tank. Very pure gypsum properties with less than 1% $Mg(OH)_2$ are seen in Table 1. These tests were conducted to design for dewatering wallboard quality gypsum at Zimmer Station for Lafarge Corporation to meet a 90% solids specification.

Tests on the 1999 Miami Fort BSO® gypsum compared rotary drum vacuum filtration with horizontal belt vacuum filtration. First, two different types of pilot-scale drum filters were found inadequate because the agitator rakes in the feed vats provided insufficient agitation for maintaining the gypsum in suspension.

Then, tests on the Miami Fort 10.5 square foot Eimco horizontal belt vacuum unit averaged 86.5% cake solids while making 50 tons. Cake product production rates were varied from 70 to 300 dry pounds per square foot. Two main conditions hampered better results. First, the hydrocyclone operation was inconsistent and caused variation in the feed solids to the filter. This was due to the agitator in the filter feed tank being inadequate to keep suspended the large plus 70 micron gypsum crystals which resulted in stratification of the gypsum slurry to the hydrocyclone.

Second, the large gypsum crystals resulted in a porous filter cake which are beneficial in promoting high filtration rates, which according to Baker Process engineers exceed those typically found with FGD gypsum. Large crystals made a porous cake which create air voids. The porous cake reduces the air stripping velocity required to remove the moisture adhering to the gypsum particles.

Equipment and process design can compensate for this. Using experimental techniques, bench scale vacuum filter leaf tests produced cake solids over 90%. Based on these tests and their other experience Baker Process made the following conclusions:

- Leaf tests and pilot tests are routinely used to size full-scale equipment. Leaf test data will match full-scale filtration.
- Cake thickness adversely impacts cake moisture to some degree. In all cases thicker cakes increases cake moisture.
- Higher airflows reduce cake moistures.
- Cloth washing is very important to prevent blinding from impurities.
- Higher feed solids results in lower cake moistures.

In summary, based on the vacuum filter leaf testing and several weeks of production on the 10 square foot unit, Baker recommended for the new horizontal belt filters to be installed at Zimmer a design figure of 300 dry pounds per hour per square foot, which is about 1.5 times greater than loading design rates for a typical limestone forced oxidation gypsum.

3.3.4 Dewatering Costs

The cost comparison information on dewatering among the four main unit processes was supplied by Baker Process personnel. Baker Process manufactures each of these process units and reports their cost as dollars per dry ton per hour (TPH) of feed solids, based on their ten years marketing to the FGD gypsum industry. The primary market for FGD gypsum from a large power plant, i.e.

1,000 MW or more, is wallboard gypsum which customer specification limits the resultant dewatered gypsum to 10% moisture and less than 100 ppm chlorides. Chlorides and other soluble salts need to be efficiently washed from the cake after it forms. The other markets for gypsum (cement, agriculture, and mineral filler) will accept lower quality but at a likely economic penalty. The horizontal vacuum belt filter (HBF) appears be the least capital intensive and most economical solution.

Decanter centrifuges are not going to be chosen because of their inability to achieve 10% moisture and inability to wash the cake of soluble salts. Baker Process estimates their cost at greater than $30,000 per dry TPH of feed solids. However, basket centrifuges can achieve the above specifications with the ability to work, but according to Baker Process these units will cost approximately $45,000 per dry TPH of feed solids due to their batch style of operation.

Rotary vacuum drum filters (RDF) lack efficient means to wash the cake and historically have not consistently met moisture levels less than 12%. Since Zimmer already had Eimco RDF's for FGD calcium sulfite, it was desirous to convert them to filtering gypsum. This study showed the RDF would not meet the moisture and chloride specification. Baker Process estimated the cost of RDF for a Zimmer size operation would have been over $30,000 per dry TPH even if these product specifications could be met.

Baker Process states generally the HBF is the lowest cost equipment at approximately $19,000 per dry TPH of feed solids and can produce solids meeting all specifications.

3.4 Summary – Agglomeration Of Gypsum

3.4.1 *Auger Extrusion of Macropellets* - An auger extruder with capacity to make approximately 1 ton per hour, using a quad spiral, live bottom feeder, was rented to produce about 70 tons of 1 inch diameter by 2 inch pellets to agglomerate the aged and clay-like gypsum that was dewatered by the decanter centrifuge. This was to demonstrate a more user-friendly product for storage and material handling that is customary for handling natural gypsum ore. Two applications are to intergrind with portland cement clinker and grind into mineral filler products of 10 to 30 micron size in order to replace natural white gypsum rock that is in short supply. See a pictorial description in Figure 3.

A testing program found the pellets could be made at relatively high moisture (15%) but at a much faster rate using bentonite or fly ash as a lubricant. Pellet strengths and abrasion resistance were found equivalent to natural gypsum rock.

Samples of the cylindrical pellets were placed and measured for unconfirmed compressive strengths. An example, shown in Figure 4, described how the pellet strengths without any additives increased as their moisture content decreased while curing in the open air at ambient fall weather temperature. The strength gained to 500 psi after 11 days while the moistures dropped to less than 2 percent. Pellets made with 0.5% to 2.0% bentonite exhibited similar results.

An abrasion resistance test to predict durability during material handling and transport was simulated by the confined tumbling of pellets rubbing against each other and walls of the tumbling device. This "attrition" test was improvised with a laboratory grinding ball mill without the balls. As the pellets aged, a sample was tumbled for fifty revolutions. Results were recorded by measuring the loss in weight of fines removed passing a ½ inch sieve opening. A typical test result of weight loss is seen in Figure 5. There was a weight loss of about 10% after 4 days curing and at 12% moisture content. The same pellets had about 1% weight loss after 11 days and 1.4% moisture. For comparison the extruded Zimmer gypsum pellets withstood the abrasion loss or attrition test as well as a sample of natural gypsum rock used for production of portland cement.

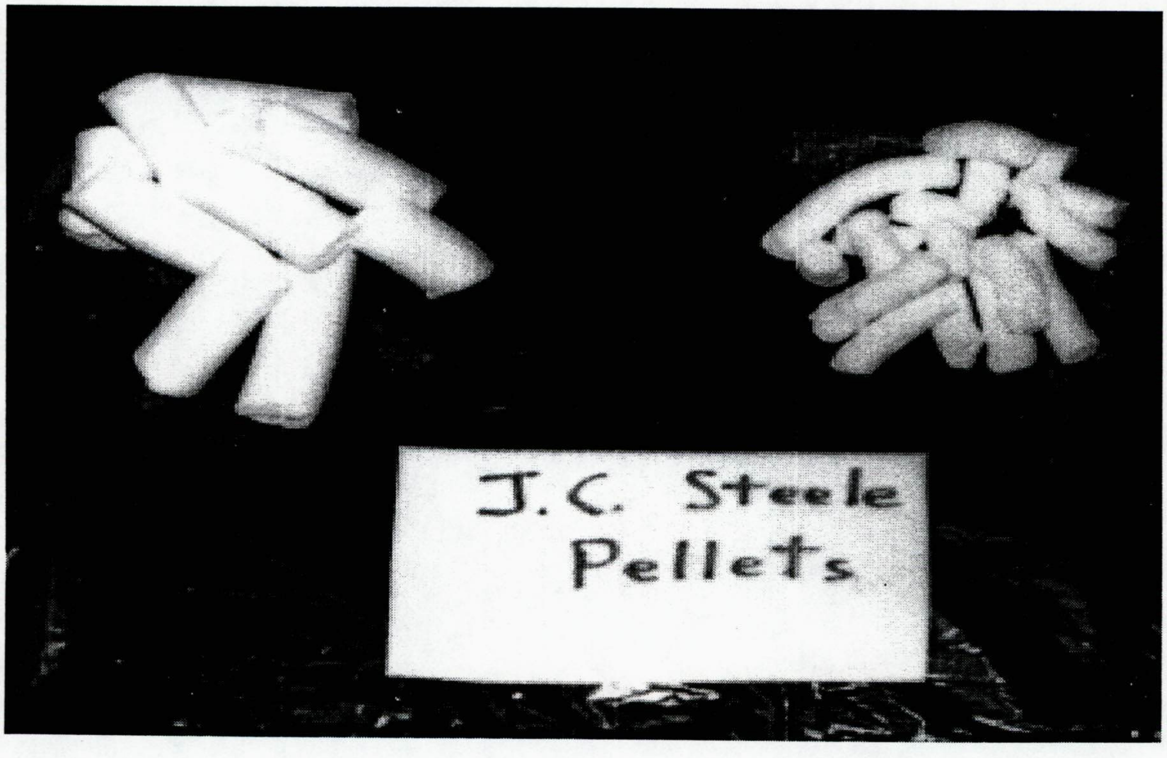


Figure 3

Gypsum Macropellets Made By Auger Extrusion
Used To Feed The ABB Raymond Roller Mill

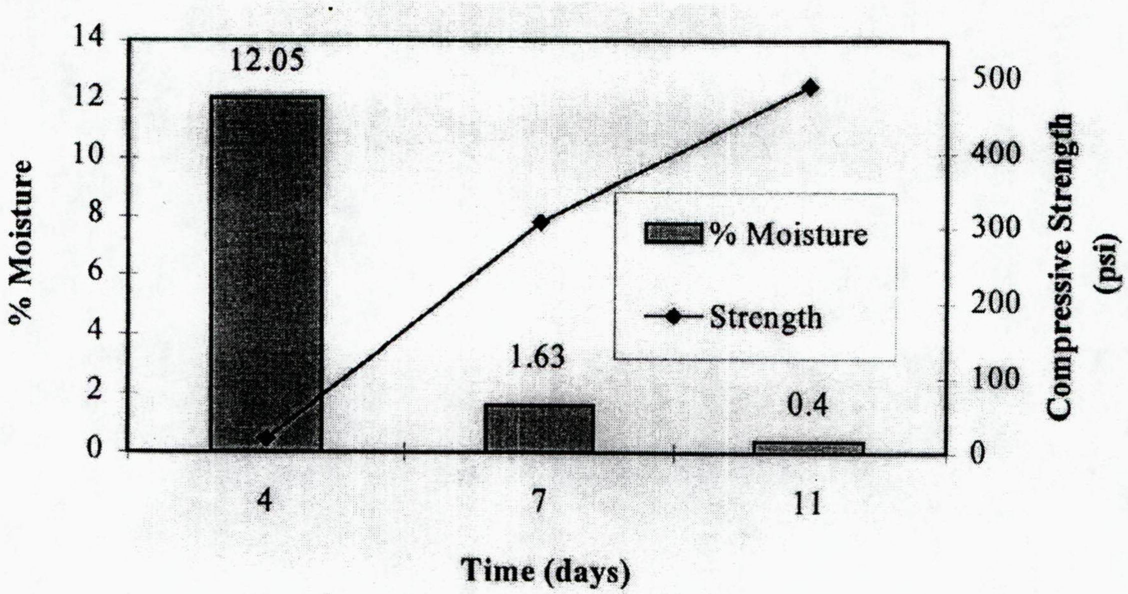


Figure 4

Effect of Curing Time and Moisture on Compressive Strength of Extruded Gypsum Pellets

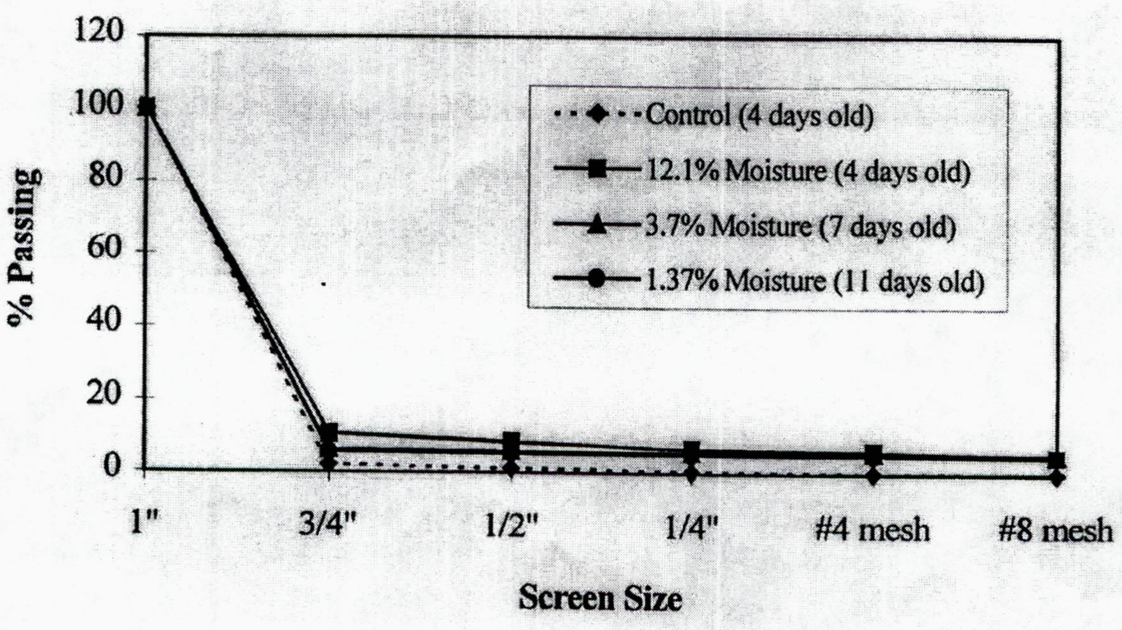


Figure 5

Effect of Curing Time and Moisture on Abrasion Resistance of Gypsum Pellets

The centrifuge shearing action and subsequent hardening effect and "wicking" or evaporation of excess moisture to allow for agglomeration avoids the need to mechanically dry the high moisture gypsum which otherwise adds significant expense and jeopardizes the quality of gypsum by forming some dehydrated calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$), called plaster, which is undesirable to make portland cement and some types of mineral filler.

The Zimmer gypsum successfully performed its chemical function of controlling the setting properties of hydraulic portland cement in full scale intergrinding tests at two portland cement plants. The typical addition rate is 5%.

The poor flow properties of non-agglomerated gypsum filter cake do not permit storage in a cement-type silo or bin as is commonly done with natural gypsum rock. Thus, a separate feeder hopper and live-bottom auger feeder, like the type demonstrated feeding the J. C. Steele and Son extruder, would be necessary to directly feed the cement grinding mill. The cost of agglomerating a product that is "ensilable" with excellent flowability would have to offset the cost of a separate feed system.

A capital cost and operating cost for a 300 ton/day extruder plant was estimated at $385,000. The operating cost with capital recovery @ 15 years and 10% interest calculates to about $6.00 per ton of product.

3.4.2 *Disc Pelletization of Micropellets* – Research, sponsored by the U. S. Department of Agriculture and The Ohio State University (OSU) is proving gypsum application to soils can improve its fertility based on several mechanisms. Fertilizer companies and limestone companies have been getting into the production of pellet lime. These plants can easily make pellet gypsum which is sized typically 6 x 16 mesh, similar to pellet lime and fertilizer. The use of lignin or other water-soluble binders is necessary to make the pellet strong and durable so that material handling is easier and less dusty, and land application is more precise and efficient.

The use of a high moisture, i.e. 20%, FGD gypsum as a feedstock to the disc or drum pelletization plant was demonstrated economically feasible both in a pilot plant and in two full-scale settings. A typical flow diagram is shown in Figure 6. The addition of dry fines (backmixing) and lignin is facilitated with the use of a high intensity mixer, i.e. pin mixer, before feeding the disc pelletizer. A higher yield of on-size product at higher productivity and less retention time on the pelletizer should result with use of the pin mixer feeding a disc or drum pelletizer than without a pin mixer. Granules all nearly the same size i.e. 6 x 16 mesh, will not segregate while being spread on land.

Mineral Processing, an Ohio based pelletizing plant produced about 7 tons of Zimmer gypsum pellets containing about 4% $Mg(OH)_2$ and 20 tons of FGD gypsum without $Mg(OH)_2$ for OSU to apply for their Phase 3 field demonstration studies. More material from Zimmer could not be pelletized as needed due to the fact that high moisture (15% to 20%) feedstock could not bypass the grinding mill to avoid plugging. OSU appraised the pellets as having sufficient quality for transporting, spreading on farmland and for storage. OSU applied the remaining gypsum in a loose form that was not processed. It was “granular” enough to flow through a drop spreader.

A 20 TPH drum pelletizer at Midstate Warehouse in Springfield, IL, was producing and selling gypsum pellets for agriculture and turf from high moisture FGD gypsum from a forced oxidized FGD limestone scrubber. This plant successfully processed four truckloads of the high moisture Zimmer Station FGD magnesium enhanced gypsum. From an outdoor stockpile having 15% to 20% moisture, the Zimmer FGD gypsum was fed at their standard rate of 20 TPH with no problems. To pelletize, a recycle or "backmixing" rate of dry fines of 1:1 was necessary to feed the pelletizer low moisture material @ 5% to 10% moisture.

Of course, less feed moisture would save drying costs, allow less backmixing and thus allow more productivity. The additional fuel to process 20% moisture feedstock @ 20 TPH versus 10% moisture feedstock can be represented by about 1.5 million Btu which @ $3 per million Btu is $4.50 per ton for fuel cost. Some drying is necessary to activate and cure the binder.

A cost analysis for a new 20 TPH plant as described briefly in this paper is estimated to be $7.82 per ton for a two shift operation and $13.12 per ton for a one shift operation. This assumes moisture contents closer to 10% to 12% in the feedstock.

An approximate price in Illinois is $35 per ton bulk and $55 per ton bagged. A market analysis of FGD gypsum in the U.S. and Ohio is discussed under Phase 2 and Phase 3 work on land application.

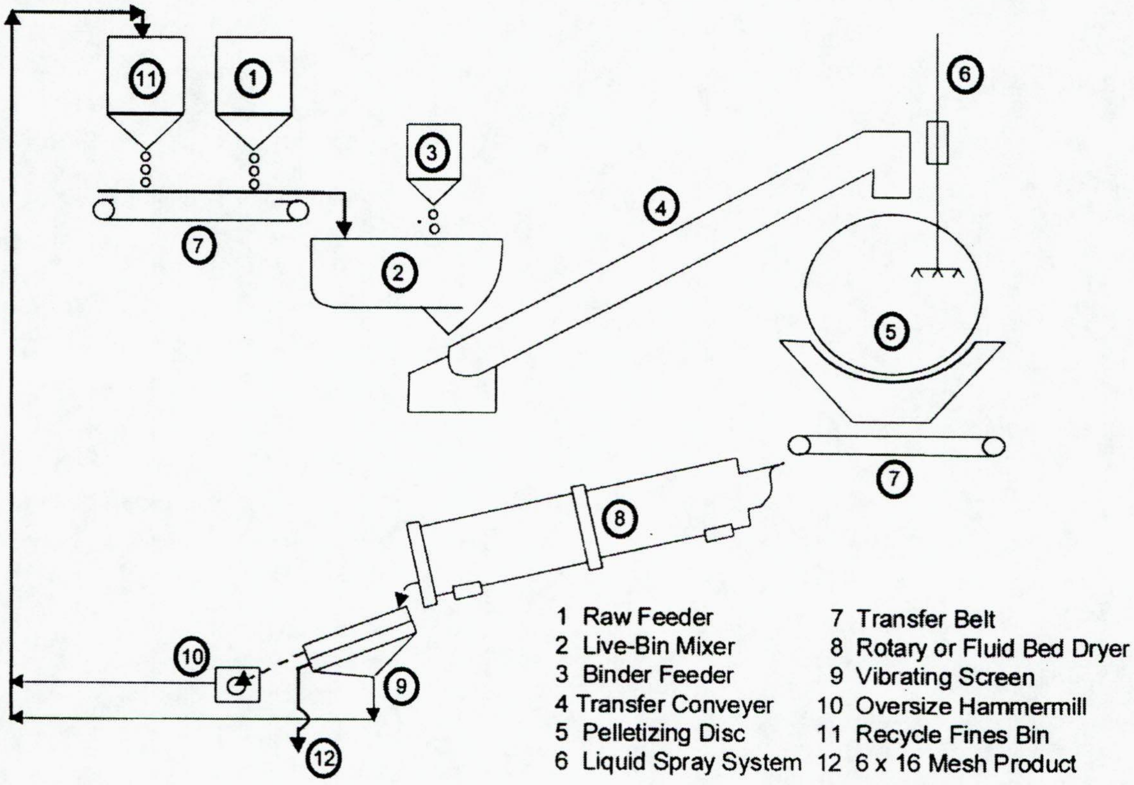


Figure 6

Plant Flow Diagram to Pelletize (Granulate) High Moisture FGD Gypsum

3.5 Drying, Grinding to Powder a Mineral Filler

3.5.1 Summary – High Brightness Gypsum for Mineral Filler and Industrial

White colored, powder-like gypsum and magnesium hydroxide are two higher value by-products that can be recovered and beneficiated to compete with natural resource based, commercial grade raw materials, using Dravo's magnesium enhanced lime advanced FGD technologies. Both as finished products should have value over $100 per ton and are as white as lime.

In the Dravo Lime FGD process gypsum and $Mg(OH)_2$ are free of discoloration impurities that are common to FGD by-product generated by scrubbing flue gas with pulverized limestone rock. In the limestone wet FGD scrubber, gypsum formation is the result of an acid base reaction of pulverized limestone ($CaCO_3$) neutralizing sulfurous acid (H_2SO_3). The impurities in the limestone are not removed in the direct acid base reaction and end up in the gypsum. These iron and clay based minerals discolor the gypsum to a buff or light gray color. A comparison is seen in Figure 7. In the Dravo Lime FGD process, these discoloration impurities are removed from the system during the manufacture of the lime during the calcination process to make quicklime from limestone and then again in the slaking process to hydrate quicklime (CaO) to hydrated lime [$Ca(OH)_2$]. High brightness in the lime-generated by-products also depends on good performance of the ESP to capture the fly ash. The gypsum should be as white as lime – above 85 dry brightness as per the ASTM C-110 measurement on a reflectometer.

Three demonstrations are reported on drying / calcining, grinding, and particle sizing classification of Zimmer converted dewatered gypsum ranging from 5% to 15% moisture into a dry mineral filler and powder-like product of specific particle fineness, i.e. 100% passing 100 mesh sieve. These processes commonly used in making industrial minerals produced a gypsum mineral filler for use in plastics, caulking compounds, and adhesives but could be likewise applied for calcining the gypsum in a higher temperature flash calciner into industrial plasters and specialty cements.

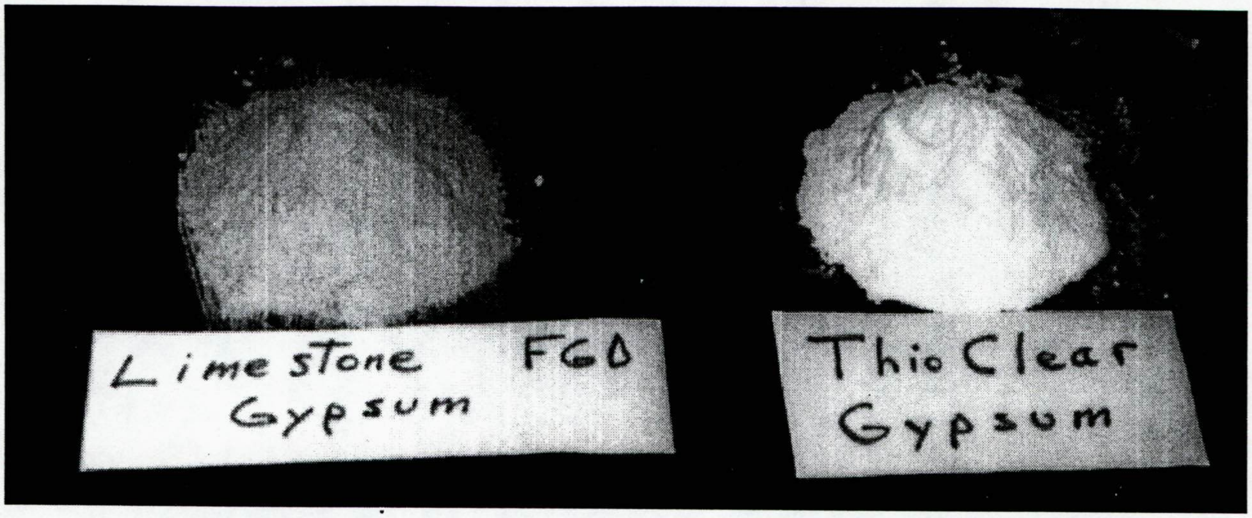


Figure 7

Compares a Limestone Scrubber FGD Gypsum Which is Typical Buff Color

First, to use an existing roller mill / flash dryer / air classifier that was designed to process natural white ore, the synthetic gypsum would preferably have to be extruded, cut, and cured into a rock-like shape. The grinding tests at ABB Raymond Research Center showed the processing of extruded shapes at least twice as much productive than natural ore.

A hammermill-like impact pulverizer process is applicable for dewatered gypsum that is not agglomerated and of higher moisture i.e. 20% to 25%. Grinding tests here were also done by ABB Research with a cage mill / flash dryer / air classifier but showed excessive horsepower was not needed. ABB proposes the lower horsepower Imp mill. An annualized direct cost amounted to $11.33 per ton based on a 6,600 ton per month plant. A third test at a full scale plant, Performance Minerals Company, with an Imp-type mill (Aztec) making mineral filler showed that the grinding rate was at least double to an equivalent fineness for the Zimmer gypsum than the natural white rock they purchase. Thus, they would expect double the productivity and less cost. In the few hours to grind 6 tons the Zimmer pellets were too easy to grind and thus resulted in the product being made too fine for their customer. The air separator was not adjusted in time. Otherwise, the Performance Mineral people were pleased with the synthetic gypsum as a potential new source of high brightness gypsum raw material for making mineral filler used for flame retardency in making plaster, i.e. polyester resin, used in making both tubs and shower stalls. The value of the mineral filler should be close to $100 per ton.

3.5.2 Gypsum – Paddle Dryer Tests

Indirect heat transfer is believed an effective method to accomplish drying high moisture gypsum, and an investigation with a Komline-Sanderson (K - S) paddle dryer was initiated. Two objectives were 1) determine feasibility to dry high moisture gypsum filter cake to meet wallboard producers specification over 90% solids, 2) determine feasibility to produce a "beta" hemihydrate plaster powder product. The task was to feed their Nara paddle dryer that has 29.8 square foot of heat transfer surface area at a specific rate and monitor the drying through five zones each (70 inches total length) with a thermocouple. From the process data a heat transfer rate coefficient of 44 Btu/hr. • ft.^{2} • °F was determined for objective 1 from tests rates of 360 and 720 pounds/hour. For objective 2 at a feed rate of 240 pounds/hour, transfer rate of 21.5 Btu/hr. • ft.^{2} • °F was found for making beta plaster.

One scenario is where the filtration device can not achieve the 90% solids specification for whatever reason. At a feed rate of 200,000 pounds/hour and feed moisture of 15% and desired product moisture of 9%, the Btu/hour demand for the necessary sensible and latent heat is theoretically 22.8 million which at $3 per million Btu's for natural gas is $68 per hour. The required area for the paddle dryer is 4,000 square feet which is priced at $1.84 million.

The fuel cost could be cut drastically if excess or "low grade" stream or waste heat via a heat exchange can be used in the paddle dryer.

4.0 MAGNESIUM HYDROXIDE BY-PRODUCT

4.1 Project Objectives – Phase 1 – Magnesium Hydroxide

The main objectives for product development of $Mg(OH)_2$ by-product focus on improving purity and solids concentration after being separated from the gypsum by hydrocyclones. At this point in the separation process, the $Mg(OH)_2$ purity is about 65% to 70% $Mg(OH)_2$ and 15% to 20% gypsum. Commercial $Mg(OH)_2$ sells at near $200/ton @ 98% purity for a variety of uses, most of which is wastewater treatment and a feedstock to make magnesium chemicals and refractories. It is sold as a powder or 55% to 60% solids slurry.

Beneficial uses in the power plant are pH control of acidic coal pile storm water runoff and bottom ash quench water. A future use being explored is injection into coal-fired boilers to neutralize sulfur trioxide (SO_3), to prevent stack gas opacity related emission problems and minimize air preheater corrosion and fouling from slag deposits. These "in-house" uses may not require any benefication. However, it is unlikely the plant can find enough uses for all or even half of the recoverable $Mg(OH)_2$. It is estimated Zimmer Station @ 1,300 MW has the capacity to recover for use outside the scrubber about 15,000 tons per year of $Mg(OH)_2$.

The specific quality objective was to make a chemical grade $Mg(OH)_2$ product that is 95% pure and a dewatered solids content of 50% to 55%. Two options were investigated to convert it into a more marketable or usable form: dry powder or pumpable slurry. Test results and economic evaluations are reported during the different process steps needed to improve the product quality: 1) dissolving or washing out the gypsum impurity 2) thickening the washed solids and using the overflow for makeup water within the FGD water balance 3) finding the best means to dewater the washed, thickened slurry and 4) repulp (reslurry) the dewatered cake into a stabilized slurry or dry it to powder. Flash drying the dewatered cake is compared to spray drying the thickened slurry.

Several applications and markets for the benefication FGD by-product $Mg(OH)_2$ were investigated ranging from uses, i.e. wastewater or "environmental", where purity may not be strict to that of making refractory grade magnesia (MgO) where the calcination process and market can not handle or remove impurities. One application objective is to study the chemical reactivity of by-product $Mg(OH)_2$. FGD $Mg(OH)_2$ is shown to have equal reactivity as an acid neutralization reagent on a $Mg(OH)_2$ molar basis to commercial $Mg(OH)_2$ products and other alkaline reagents. Its use for pH control in wastewater treatment is shown to produce a much smaller sludge volume than lime or sodium hydroxide.

A separate Zimmer $Mg(OH)_2$ research project was initiated by Dravo Technology, which is in progress by the University of Cincinnati, to treat municipal wastewater specifically for removal of ammonia and phosphate nutrient pollutants. Nearly one ton of washed material is available for their research.

The quality of magnesia, MgO, that could be made by calcination of the washed $Mg(OH)_2$ was evaluated. Samples were sent to two refractory manufacturers for their opinion.

4.2 Background on $Mg(OH)_2$ and MgO Markets

Because commercial grade $Mg(OH)_2$ is white, it is important that the FGD by-product $Mg(OH)_2$ likewise be white. Magnesium hydroxide is a major commodity product in itself at 307,000 tons shipped in 1997, excluding that used as an intermediate step in the manufacture of other magnesium compounds such as a building block for producing magnesia (MgO) and magnesium metal (Mg). Typically produced from brine or seawater, the $Mg(OH)_2$ is a feedstock to be calcined into two large markets: synthetic magnesia and refractory magnesia. Shipments and value per metric ton (MT) for the major magnesium compounds and metal appear in Table 2. Synthetic magnesia is used to make other chemicals so it must be reactive and therefore calcined by "soft burning" at a lower temperature of about 700°C to 900°C. Dead burned magnesia, used to make refractories, is $Mg(OH)_2$ calcined at higher temperatures. Magnesium hydroxide is also converted into magnesium chloride and via electrolysis is made into magnesium metal. A marketing concern is that it must compete with less expensive foreign imports of magnesia mostly from China, delivered f.o.b. New Orleans about $100 to $120/metric ton. Some of this is pressure hydrated in the U.S. and sold as $Mg(OH)_2$. Much is sold for refractories and fluxing impurities during steelmaking.

Unless the FGD recovered $Mg(OH)_2$ is beneficiated to at least 90% as $Mg(OH)_2$ and possibly 95% it may not be acceptable to some markets such as high value refractory products.

Table 2

U. S. Magnesium Compounds and Metal Shipped and Used in 1998

	Quantity, MT	Value per MT
Magnesium hydroxide	259,000	$ 186
Synthetic magnesia	170,000	442
Refractory magnesia	223,000	334
Magnesium chloride hexahydrate	-------	319
Magnesium metal	101,000	3,500

A USGS report states that after accounting for the portion to produce dead burned magnesia, 60% of the magnesium hydroxide directly used in the U.S. is consumed for environmental applications including industrial wastewater treatment, heavy metals removal, and flue gas desulfurization. Overall, 30% of the synthetic or caustic calcined MgO is used for environmental purposes.

Commercial $Mg(OH)_2$ was priced until recently over $200/metric ton and is increasingly used to replace caustic soda in neutralizing wastewaters. Advantages include safety, harmless overdosage and less sludge volume, as discussed further.

4.3 FGD Magnesium Hydroxide Product Development at Zimmer Station

In both the ThioClear® and Bleed Stream Oxidation (BSO®) process variation a large portion of recovered magnesium species is recycled back to the scrubber to capture SO_2. Depending on the Mg content of the feed lime and Mg^{+2} levels needed to maintain the scrubbing liquor alkalinity for SO_2 capture, more of the $Mg(OH)_2$ can be recovered for use within the power plant and / or beneficiated for commercial sale. In the Zimmer slipstream recovery plant $Mg(OH)_2$ is produced from the thickener overflow as needed. The BSO® process is being installed in year 2000 at the Zimmer Station in an effort between Cinergy Corporation, Babcock and Wilcox and Dravo Lime Company. The end user of the wallboard grade synthetic gypsum will be Lafarge Corporation. Although not yet committed this design maintains the future option of $Mg(OH)_2$ recovery. Approximately 15,000 tons per year could be generated.

The $Mg(OH)_2$ purity of both the ThioClear® and the Bleed Stream Oxidation (BSO®) or the slipstream type by-product is approximately 65% to 70%, and the solids concentration from the thickeners is about 14% to 16%. For on-site uses such as wastewater pH control, this level of quality and slurry concentration is satisfactory, eliminating the need to purchase more expensive commercial grade

$Mg(OH)_2$. However, this use accounts for less than 10% of the available $Mg(OH)_2$ for resale.

As stated, the major impurity in FGD recovered $Mg(OH)_2$ as it exits the hydrocyclone overflow is gypsum crystal fragments at concentrations between 12 to 23% as $CaSO_4 \cdot 2H_2O$. The other impurities are oxides of iron, aluminum, silica and calcium carbonate all of which are derived from the impurities in the lime and carry-over fly ash. The level of insoluble calcium sulfite ($CaSO_3$) should be less than 0.50% unless the oxidation process is operating at less than optimum performance. Even with impurities, the raw or unwashed $Mg(OH)_2$ can have a high brightness of near 90 unless some fly ash and carbon is escaping collection in the electrostatic precipitator.

A comparison of beneficiating FGD $Mg(OH)_2$ can be made to the production of typical commercial grade $Mg(OH)_2$. In the commercial process underground brine or seawater is first softened to remove calcium "hardness" and carbonate alkalinity with dolomitic quicklime. In a secondary reactor more dolomitic quicklime is added to precipitate $Mg(OH)_2$. Some gypsum also precipitates. A continuous flow counter current washing process using fresh water dissolves gypsum before being re-thickened and filtered.

4.4 Benefication Test Program and Results

A research program was developed to increase the purity and convert the slurry into a marketable product form. A four-step process was created: washing, rethickening, dewatering and drying or repulping (re-slurring). A schematic flow sheet of such a pilot process is shown in Figure 8.

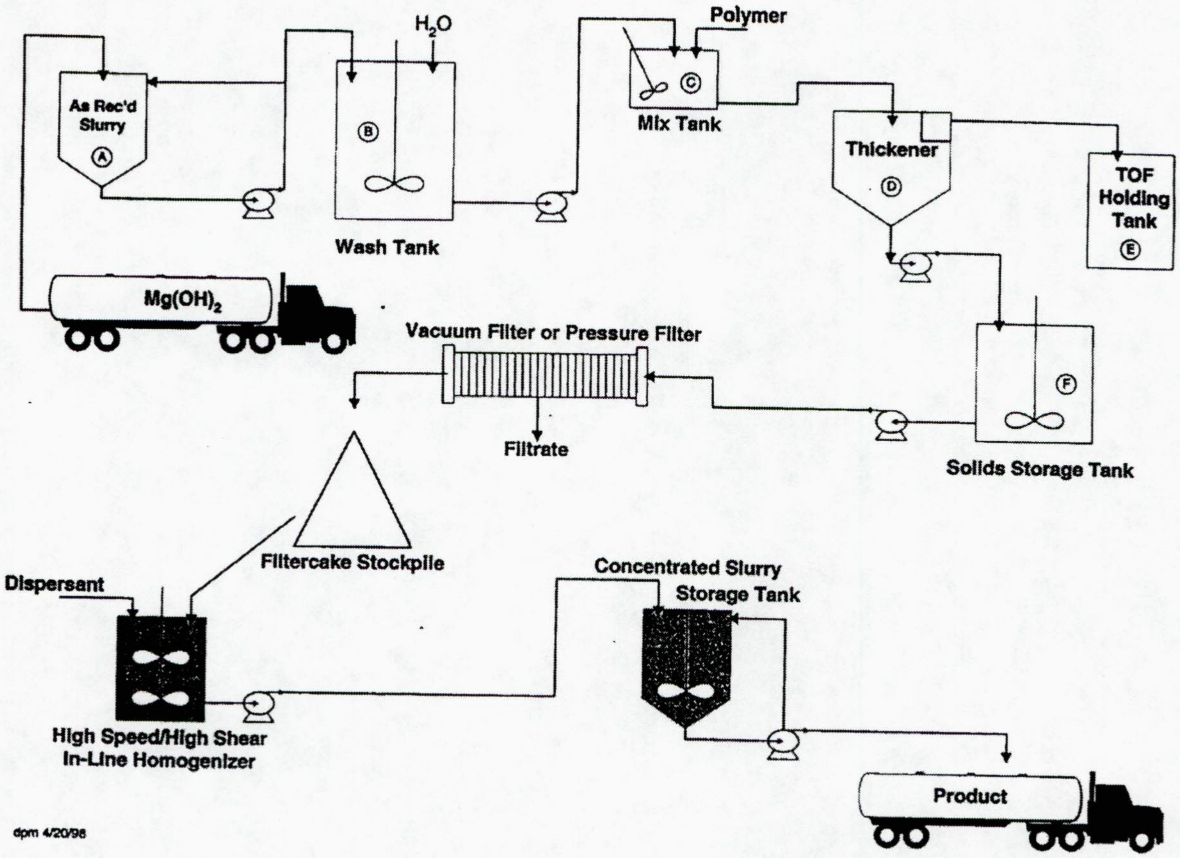


Figure 8

Pilot Process for Washing, Re-Thickening, Filtering, and Re-Slurrying ThioClear® Mg(OH)$_2$

4.4.1 _Step 1 – Washing_ – Washing refers to the dissolving of gypsum with water from the Mg(OH)$_2$ product slurry. A scanning electron microscopic (SEM) photo of the unwashed Mg(OH)$_2$ is seen in Figure 9. Contaminant gypsum needle-like crystals are seen among the smaller amorphous-like Mg(OH)$_2$ particles. Gypsum has a solubility in water at 20°C of 2,500 mg per liter as $CaSO_4 \bullet 2H_2O$. This solubility is equivalent to 48 gallons of water per pound of $CaSO_4 \bullet 2H_2O$. Based on this solubility, the theoretical wash rate or ratio in terms of gallons of water to gallons of the Mg(OH)$_2$ slurry depends on the gypsum content of the solids and the solids concentration in the slurry. Another parameter to optimize is mixing or detention time for dissolving gypsum.

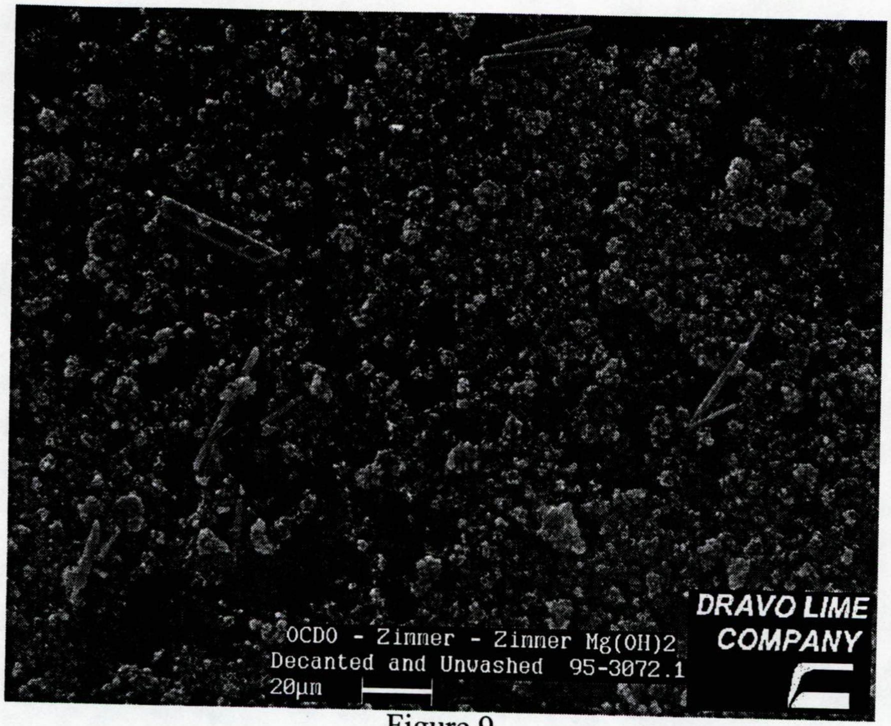


Figure 9

Zimmer $Mg(OH)_2$ - Decanted and Unwashed 95-03072.1

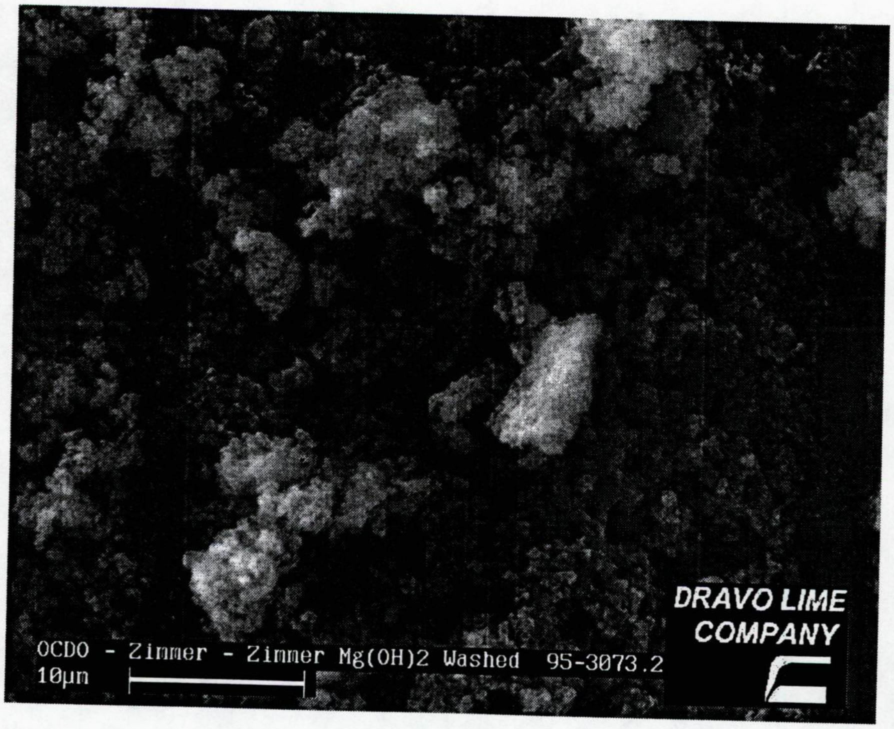


Figure 10

Zimmer $Mg(OH)_2$ – Washed to Dissolve Gypsum 95-3073.2

A bench scale single stage continuous flow reactor was used for preliminary evaluation of various wash rates and detention times. Results were encouraging in meeting the objective that at least 90% of the gypsum can be dissolved at rates near the 37 gallons per pound theoretical rate. A larger scale single stage continuous flow washing reactor capable of rates up to 30 gpm was installed followed by a 4 foot diameter thickener. Wash tests were conducted on 4,500 gallons of unwashed Zimmer slurry containing 14% solids. An analysis of the as received (unwashed) solids is 68% $Mg(OH)_2$ and 11.35% total sulfur as SO_3, most of which is in the form of gypsum. Details are shown in Table 3. There was a small amount of calcium sulfite in the unwashed $Mg(OH)_2$ that did not get oxidized to gypsum. Calcium sulfite ($CaSO_3 \bullet ½H_2O$) is very insoluble and can not be removed by washing. A SEM of the washed material is seen in Figure 10. A PSD showed a MV of 4.2 micron.

Table 3

Comparison of Unwashed and Washed $Mg(OH)_2$

Test Condition:	Actual Wash Rate	37 gallons per pound $CaSO_4 \bullet 2H_2O$
	Actual Ratio	30 gallons water: 2 gallons slurry (15:1)
	Detention Time	31 minutes

		Unwashed, %	Washed, %	Calcined, %
Chemical Analysis:	MgO	47.04	59.00 (86.0 % as $Mg(OH)_2$	90.8
	CaO	8.63	2.64	4.1
	CO_2 (not in total)	1.33	2.05	--
	Total Sulfur as SO_3	11.35	2.45	--
	SiO_2	2.01	2.62	4.0
	Fe_2O_3	0.17	0.28	0.4
	Al_2O_3	0.36	0.42	0.6
	LOI @ 1100°C	32.42	32.60	--
	TOTAL	102.00	99.9	99.9

The calcium sulfite level was higher than normal at 1.12% as SO_2. Water and slurry were pumped through the reactor at ratios below and above the theoretical solubility and various rates simulating various detention times. Consistent over four samples, the washed $Mg(OH)_2$ mixed with water near the rate of 37 gallons per pound $CaSO_4 \cdot 2H_2O$ was 86% $Mg(OH)_2$ and less than 1% residual total sulfur that was about 40% gypsum (2% $CaSO_4 \cdot 2H_2O$) and 60% calcium sulfite ($CaSO_3 \cdot ½H_2O$). Total sulfur removal was only 81% to 82% due to high levels of insoluble calcium sulfite, but calcium sulfate removal was about 91%. Residual total sulfur was 0.92% as sulfur (S). Thus, complete oxidation of the sulfite to sulfates is very important to get sufficient removal of all the sulfur bearing impurities by washing.

4.4.2 *Step 2 – Re-Thickening and Re-Use of Washwater* – Thickening of the washed slurry would yield approximately 15% solids slurry product that can be stored and used internally to 1) boost Mg levels in the scrubber liquor during a startup operation and 2) pH control of coal ash quench water and coal pile storm water runoff. A third but future use can be injection into the coal-fired boiler for SO_3 opacity control and corrosion control of the air preheaters. This step includes finding uses for the clarified washwater within the FGD system water balance.

Washed slurry was pumped to a 4 foot diameter thickener to settle the $Mg(OH)_2$ at varying rates above and below the recommended rate of 1 gpm per square foot. A flocculent was used to achieve acceptable overhead clarity. At flow rates near 15 gpm of washed slurry the dosage of 4 to 8 mg/nonionic, high molecular weight polyelectrolyte produced an overflow of 500 to 1,000 mg/L suspended solids. Without flocculent the overflow suspended solids was 5,000 to 8,000 mg/L overflow solids must be minimized to prevent losing $Mg(OH)_2$. An anionic polyelectrolyte also performed well at the 5 to 8 mg/L dosage. Underflow percent solids were 14% to 16% solids and were not affected by the use of the flocculent.

It is desirable to keep the amount of water used by the washing step within the existing water balance of the FGD system. The compatibility of water containing dissolved gypsum with the water used to slake lime and then for lime slurry dilution was investigated. As theorized there is a slight effect on slaking reactivity (temperature rise) when hydrating quicklime. However, the use for further dilution of 30% lime slurry solids to 15% to 20% slurry solids will not be a problem.

Based on a material balance, clarified washwater at a rate less than 55 gallons per pound of gypsum can be used as make up water to certain locations within the FGD system. Using this wash water eliminates the potential problem of disposal of large quantities of water with high dissolved solids. The wash tests discussed previously were satisfactory at 37 or more gallons water per pound of gypsum.

While over 90% gypsum removal is the goal, wash rates closest to 37 gallons of water is advantageous so as to minimize the size of the wash plant and volume of water to handle.

4.4.3 _Step 3 – Dewatering_ – Preliminary investigations were made to compare dewatering by centrifuge, vacuum filtration, and pressure filtration.

Centrifugation - An opportunity arose to have about 2,000 gallons of unwashed $Mg(OH)_2$ dewatered by a Bird Machine Company 18 inch diameter x 54 inch long solids bowl decanter centrifuge @ 75 HP drive having a 4,000 "G" force and 3,800 rpm. Using a cationic polyelectrolyte at 5 to 5.5 pound/ton of dry solids, Bird personnel were able to feed 20 gpm and achieve about 38% solids and overall solids recovery of 99% based on a clear centrate. The throughput was about 1,000 pound/hour. Without the polymer the feed rate was held to 8 to 10 gpm while still maintaining a clear centrate. The $Mg(OH)_2$ feed slurry was maintained at a temperature between 40°C to 50°C using heated mix tanks in order to work at optimum dewatering temperatures.

Vacuum Filtration - Using the vacuum filter leaf test procedure, both Baker Process and Dravo personnel independently simulated the vacuum filter but could not consistently achieve better dewatering than 28% solids. The effect on improving vacuum filtration from both washing out the gypsum and using polyelectrolytes to aid filtering was investigated. Both effects did not significantly change the dryness of the filter cake. Personnel from Cytec who market polyelectrolytes assisted in this study. On the same samples of washed $Mg(OH)_2$ slurry, Baker Process was commissioned to evaluate pressure filtering where results close to 40% solids were attained at their lab. Baker Process is the parent company of Eimco. Eimco makes both vacuum filters and pressure filters.

Pressure Filtration - In terms of filter cake percent solids, a choice for Task 6 and Task 8 was made to dewater the re-thickened and washed $Mg(OH)_2$, by pressure filtration using an Eimco Model 1470 rental unit having the membrane squeeze option. It was capable of processing a 90 pound batch every 10 minutes. With squeeze pressure of 225 psi and clear filtrate, cake thicknesses of 25 to 32 mm and cake solids of about 50% solids density were obtained. Filtering cycle times were shorter at 50°C and thicker filter cake resulted, however the percent solids did not improve.

For a hypothetical plant with a slurry feed of 4,400 gallons/hour and 15% solids, the pressure filter unit with the membrane squeeze would be sized at 270 cubic feet/hour. For a diaphragm dimension of 1,500 x 1,500 mm and 32 mm thick cake, this volume is equal to a processing volume of 2.1 cubic feet per diaphragm, which equates to 153 diaphragm plates.

These cake solids can be easily conveyed and stockpiled preferably under roof. Based on observations and assuming a first in / first out inventory stockpiling process with a telescopic and rotating stacking conveyor, cake solids of 65% to 70% can be achieved in a few days if exposed to air ventilation and not covered. With more time and ventilation, the cake will achieve as high as 90% solids. At cake solids concentration over 45%, the cake can easily be sold in bulk and transported by dump trucks. It has the consistency of clay.

Cost Analysis - Commercial $Mg(OH)_2$ producers seem to mostly use vacuum drum filters and attain 50% to 60% solids with their crystalline particle morphology. Based on a cost analysis with assistance by vendors, for a hypothetical dewatering plant for 15,000 dry tons per year and 4,400 gallons per hour slurry being generated, the total direct cost of vacuum filtration was $34 per dry ton versus $47 per dry ton for pressure filtration. However, the extra energy cost alone of drying 35% solids filter cake via vacuum filtration versus 50% solids filter cake via pressure filtration is $8 per ton. Thus, pressure filtration may not be less expensive overall, particularly if repulping from storage to a 20% solids slurry is the final process step. Higher moisture filter cake can be reslurried with less mix times and intensity than hardened, dry cake.

4.4.4 *Step 4 – Repulping or Drying*

– Processing the filter cake further to a marketable form entails either repulping (also called dispersing or disintegration) it into a pumpable slurry or drying to a powder. However, the dewatering and drying action causes the $Mg(OH)_2$ to agglomerate. A particle size distribution (PSD) shows that the mean volume increases to about 25 to 30 microns by forming clumps. Dispersion will be needed to disintegrate these "conglomerates" or clumps.

Repulping of filter cake is its conversion to a concentrated slurry of 40% to 50% [commercial $Mg(OH)_2$ slurry is 55 to 58% solids] solids or to a more dilute slurry of 10% to 20% solids depending on the place and time of use. The moisture in the filter cake coming from storage piles will vary. Repulping to 38% to 45%

solids has to be processed by a high shear mixing device with the aid of a dispersing agent for stabilization so as to remain homogenized yet pumpable after a period of transportation and long term storage without mixing. This was demonstrated on Premier Mill's ESD Dual Shaft Mixer. The product had a particle size distribution (PSD) of about 4 to 6 micron mean volume but a high viscosity 18,000 cps (Haake). The 38% solids product remained at that viscosity during four weeks of observation.

Another very likely scenario exists having a storage or inventory stockpile of $Mg(OH)_2$ filter cake which can be taken to another location and repulped for treatment of wastewater or injection as a sorbent into a furnace. The $Mg(OH)_2$ is preferredly fed as a dilute slurry, i.e. 20% solids or less. This slurry requirement will necessitate starting with filter cake possibly delumped into crumbles and mixing / dispersing them with water on site as needed using a skid mounted batch mixer / emulsifier using a high-speed disperser blade or a rotor-stator. Additional tests were performed at Littleford-Day and Ross Mixer.

Key criteria in specifying a mixer are the desired PSD and viscosity of the slurry product. Less than 5 micron mean volume (MV) is desirable for furnace sorbent injection to capture SO_3 gases. As the PSD becomes closer to 2 micron MV, the viscosity of a 20% slurry increases well above the desired viscosity of 1,000 cps (Brookfield). Based on tests with three vendors of high shear mixers, process development has identified three main design aspects that involve choices. First, in order to feed the filter cake to a high shear mixer, a screw feeder (single or multiple auger) with a delumper, if necessary, were investigated. Second, batch "in tank" mixing is favored over continuous "in line" rotor-stator mixing. Batch mixing permits better quality control when mixing to attain a low particle size mean volume and viscosity. The batch can be checked and sampled during recirculation before being discharged.

Third, in order to attain a finer PSD, a high degree of mixing intensity or shear rate will be necessary to perform particle size reduction. Degrees or level of shear rate is dependent on the design, complexity, and number of mixers or passes during recirculation. A laboratory study is required to make mixer choices and mixing time. Batch pre-mixing in the case of dispersing filter cake is necessary to wet or "fluidize" the cake solids with the high rpm sawtooth blade and a slow rpm sweep blade before doing any further particle size reduction with a rotor-stator or colloid mill. Likewise more recirculation or "tank turnovers" through a rotor-stator type device will result in more particle size reduction.

The degree of shear rate depends on the complexity of the disperser device. A sawtooth blade (Cowles blade) is the simplest type. A batch mix with only one sawtooth disperser blade may require an excessive mixing time and be inefficient at particle size reduction. The sawtooth blade is often referred to as the HSD (high-speed disperser) blade.

Rotor-stator type shear devices can perform more size reduction. They can be multiple units in series or designed more for size reduction at the sacrifice of throughput rate. Higher shear rates can be attained by more complex rotor-stators, called colloid mills. Even higher fineness can be achieved by high-pressure homogenizers. Dispersing aids may still be needed to keep the product from re-agglomerating.

Exhibit 1 describes the simple HSD sawtooth blade and the rotor-stator. Exhibit 1 also describes the skid-mounted model made to be portable. It is believed most appropriate and flexible for re-pulping $Mg(OH)_2$ filter cake at the point of use. It has the three mixer blades in one unit: the "mixer emulsifier" (a conventional style of rotor-stator), the high speed disperser (HSD) blade with tip speeds up to 6,000 feet per minute, and the anchor agitator or "sweep blade" @ 70 to 80 rpm to move the material to the HSD and rotor-stator. The HSD and sweep blade are required to fluidize the cake. Further mixing with the HSD and then the rotor-stator, whether in line or in tank, as shown in Exhibit 1, will provide the desired size reduction. A batch capacity of 100 to 200 gallons would be appropriate. Tests at Littleford and Ross achieved the desired fineness in about 15 minutes mixing time while making 20% solids slurry. Rotor-stator additional shearing yield a viscosity of 1,000 to 2,000 cps like thick paint. Less than 20% solids to lower the viscosity maybe appropriate.

Cost of High Shear Mixers - Budget quotations of batch style high shear mixers were received from three vendors. The 250 gallon Littleford DayMax, which is designed @ 60 HP like a Waring Blender with the HSD mounted from the bottom, is priced with stainless steel at about $100,000. This price is comparable to the Premier Mill and Ross Mixer machines of this size. A smaller 40 gallons multiple shaft mixer like that in Exhibit 1 is $60,000. A 200 gallons unit is $105,000. These 100 to 200 gallon units would be appropriate for the following application.

A 300 MW coal burning furnace desiring to treat 20 ppm sulfur trioxide (SO_3) aerosol @ a 1.5:1.0 stoichiometric ratio of $Mg(OH)_2$ to SO_3 would require 138 pounds of dry $Mg(OH)_2$ per hour (620 tons per year). As a 20% solids slurry, this equates to 1,770 gallons per day or 74 gallons per hour. For a $125,000 investment @ 15 years life and 10% interest, the capital cost per ton @ 52 tons per month is amortized to cost $26 per ton.

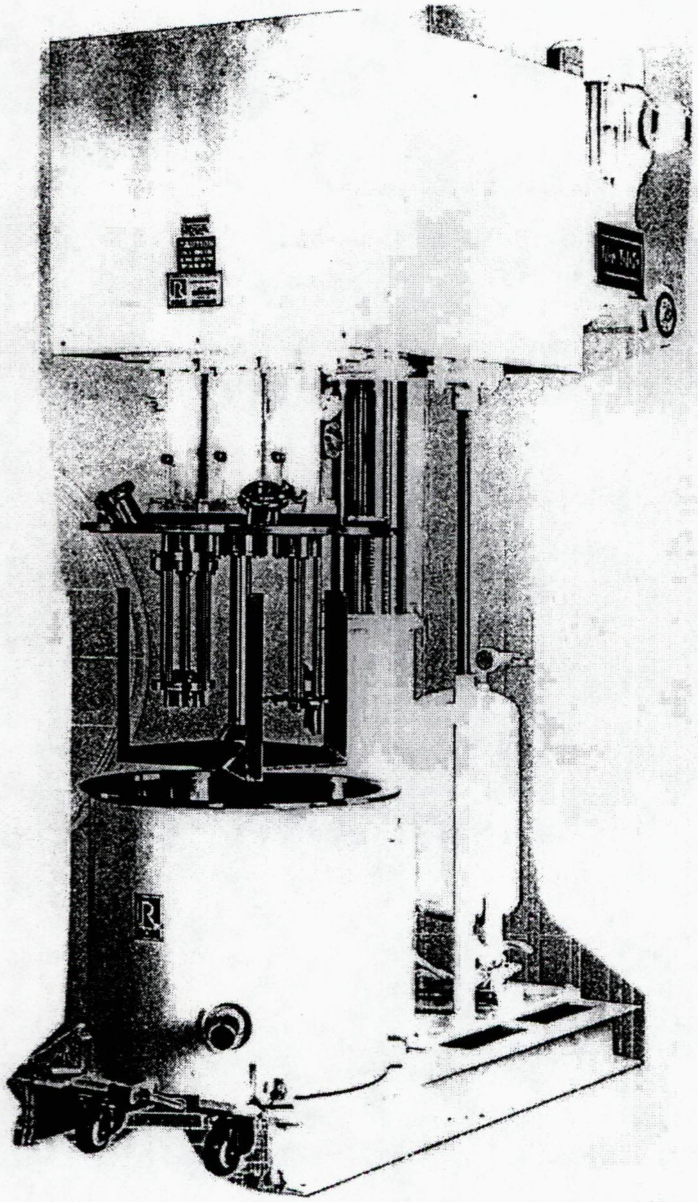
Drying – Based on pilot scale tests, production of fine, dry powder was demonstrated two ways: spray drying a thickener underflow and flash drying a filter cake. Spray drying, which bypasses the dewatering step, was successfully demonstrated using a Swenson vertical 4.50 foot diameter tube-drying chamber. A 10% solids slurry feed produced a powder at a rate of 81 pounds per hour. An inlet air temperature as low as 350°F was found to be workable. Tests were also run at 500° and 1,000°F. The hotter the inlet drying air the smaller can be the drying chamber. The product had a fineness of about 33% to 40% passing the

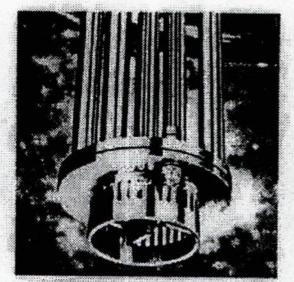
325 mesh and mean particle size of 40 microns. This increase in particle size MV to about 25 microns from 4 microns called agglomeration was also seen from flash drying as discussed below.

Flash drying of the Eimco pressure filter cake was demonstrated on a APV # 55 Spin Flash Dryer. The inlet temperature was varied from 265°F to 1,020°F with a corresponding increase in production rate. The feed rate was actually controlled by the outlet temperature to this 0.5 meter diameter and 9 meter tall drying chamber and was optimized at about 340 pounds per hour. The powder had properties much like the spray-dried product. Drying causes the fine $Mg(OH)_2$ particles to agglomerate from 3 - 5 micron MV to 25 - 30 micron MV. At 900°F a flash calciner with similar processing methodology could produce chemical grade magnesia, MgO, also called soft-burned magnesia from the filter cake.

For either the spray dryer and flash dryer there would be the opportunity to utilize waste heat via a heat exchanger to generate hot air to at least 350°F in lieu of a direct flame air heater, i.e. using exhaust gas from a lime kiln. For the next section on cost analysis an economic comparison of energy cost to spray dry versus flash dry was made using information from two vendors for a 15,000 ton/year quantity. The difference in fuel consumption to spray dry 15% solids slurry versus the 50% solids filter cake in million cubic feet (mcf) of natural gas is 245,000 mcf versus 43,600 mcf per year.

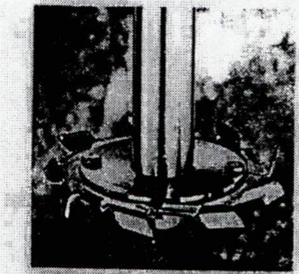
4.4.5 _Cost Analysis_ – A cost comparison, shown in Table 4 was made of producing a powder via spray drying versus dewatering the slurry via pressure filtration and then flash drying the cake to a powder. Assuming direct fired gas burners, the cost of fuel and power for drying the filter cake via the flash dryer is about $50 per ton less than the fuel and power costs of drying the slurry. This economic differential more than pays for the cost of dewatering by a pressure filter.





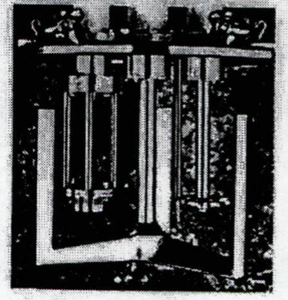
MIXER-EMULSIFIER

The high speed close-tolerance rotor and stat of this unique mixer provide a high degree of shear to all materials being passed through th rotor/stator gap. This intensive shearing action used for reducing the particle size of solids, dissolution, homogenization, and emulsificatio By itself it is best applied for materials that have a maximum viscosity of approximately 10,000 cps. In conjunction with the anchor its useful range can be extended to over 100,000



HIGH SPEED DISPERSER

The conventional shear disc dispersion blade i used to disperse solids into viscous liquid vehicles that are beyond the viscosity range of the mixer-emulsifier and anchor combination. This mixer is best applied by itself in a viscosity range to 50,000 cps, and in conjunctio with the anchor to several hundred thousand centipoise.



ANCHOR AGITATOR

The standard three wing anchor agitator is designed to provide maximum movement of product under low shear conditions within the mix vessel. It moves materials in both a radial and axial direction to feed the materials to th high speed mixer heads and to also improve heat transfer by constantly removing material from the tank wall. The anchor is designed to permit either fixed adjustable or hinged teflon wiper attachment. Since the design is of a closed triangular shape it is easy to clean and is preferred for applications that will require regular cleaning between batches.

Exhibit 1

Mixer Emulsifier / High Speed Disperser / Anchor Agitator

Table 4

Cost Comparison of Spray Drying of 15% Solids Slurry versus Flash Drying of 50% Solids Filter cake

Case: 15,000 tons/year, 3,680 gallon/hr. feed slurry

	Pressure Filter	**Flash Dryer**	**Spray Dryer**
Investment:	$1,035,000	$1,150,000	$2,000,000
$ / Ton: 12 hour operation:			
Capital Amortized @ 15 year @10% Interest	$ 8.90	$ 9.90	$ 17.20
Maintenance @ 4%	8.74	10.30	5.33
Power / Fuel	0.86	3.06	53.10
Manpower	15.00 (2)	7.50 (1)	15.00 (2)
Total $ / Ton	33.50	30.76	90.63
Combined	$ 64.26		$ 90.63

Notes:

(1) one operator per shift
(2) two operators per shift

4.5 Product Evaluation For Marketplace

4.5.1 Acidic Industrial Wastewater Neutralization Studies

For neutralization and metal precipitation of acidic wastewaters associated with coal mining, storage, and combustion, FGD by-product $Mg(OH)_2$ is a potentially superior neutralization reagent. Commercial $Mg(OH)_2$ has been given little attention and demonstration due to a combination of its delivered cost and lack of success stories in treating acid mine drainage. Some power plants have been using it for treating stormwater and plant service water associated with handling coal and bottom ash. Cinergy's Zimmer Station built their $Mg(OH)_2$ recovery plant specifically to replace commercial $Mg(OH)_2$ used for pH control of bottom ash quench water and other wastewater.

The waste acid neutralization capabilities of FGD by-product $Mg(OH)_2$ can be compared to the other common neutralization reagents as well as commercial $Mg(OH)_2$ using the ASTM C-400-92 procedure that was specifically written for high calcium and dolomitic lime products. In an actual comparison with commercial $Mg(OH)_2$ the FGD $Mg(OH)_2$ was found equivalent in neutralization capacity on an equal molar basis.

There are four advantages that all vendors of $Mg(OH)_2$ most often promote over the three commonly used reagents: sodium hydroxide (caustic soda, NaOH), sodium carbonate (soda ash, Na_2CO_3), and lime [hydrated, $Ca(OH)_2$]. There are also several disadvantages. The advantages most often emphasized are:

Less Reagent - On a mass basis, less $Mg(OH)_2$ is required than all three of the common neutralization agents to neutralize a ton of acid as follows:

Pounds of Neutralization Agent per Ton of Acid

	Hydrochloric Acid	**Sulfuric Acid**
$Mg(OH)_2$	1600	1190
NaOH	2190	1630
Na_2CO_3	2900	2160
$Ca(OH)_2$	2032	1511

Slower Rate of Reaction - Because $Mg(OH)_2$ is a solid slurry, which needs to dissolve before it can react, the neutralization is slower and thus more controllable. There is also no chance of an overdosage causing excessively high pH because it will not dissolve over pH 9.

Safer Handling - $Mg(OH)_2$ powder or slurry is less hazardous and less costly to handle than slaking lime or having to feed a strong alkali such as caustic soda.

Less Sludge Volume - An economical advantage in using $Mg(OH)_2$ is that it will make up for its higher cost since less sludge volume is produced when neutralizing acidic waste streams particularly those containing heavy metals. One vendor of commercial $Mg(OH)_2$ claims that its overall cost is much less than lime when calculating the added cost of disposing six times more sludge volume when using lime. Another major vendor claims 2.2 times more sludge when using caustic soda. The resultant sludge with using $Mg(OH)_2$ will likewise be more dense and less costly to filter per unit volume.

Major disadvantages in using $Mg(OH)_2$ would be that the slower reaction time necessitates more mixing and retention time. The maximum pH of 8.5 to 9.0 prevents sufficient removal by precipitation as a hydroxide of some heavy metals such as nickel, and cadmium. In acid mine drainage treatment, the required degree of removal of manganese is not attainable unless the pH is over 9.0. Thus, in some applications lime or caustic soda may have to supplement the required alkalinity to get higher than pH 8.5.

Demonstrations of Less Sludge - The advantage promoted that less sludge is produced when neutralizing with $Mg(OH)_2$ was demonstrated in four treatability studies on three wastewaters associated with coal fired power plants and a sample of rinse water from acid pickling of stainless steel. After neutralization and a given time for settling in a large graduated cylinder or Imhoff cone, the volume of sludge in terms of milliliters of settled hydroxide precipitate per liter of treated water, is compared in Figure 11. In each case the volume of sludge to be dewatered and filter cake to be disposed, sometimes as a hazardous waste, is much less when using $Mg(OH)_2$.

4.5.2 Treatment Of Municipal Wastewater

An original research project was awarded to the University of Cincinnati that evolved from this Zimmer By-Products Project. The idea was initiated by Dravo and offered to the Department of Civil and Environmental Engineering. It is titled *"Applications of Magnesium Hydroxide for Municipal Wastewater Treatment"* and focuses on both neutralization and nutrient removal. The City of Cincinnati Sanitary District is cooperating and hosting the site of the pilot plant and wastewater and sludge samples. Field research is in progress but early results have been reported based on laboratory experiments.

Compared with other commonly available neutralization chemicals, $Mg(OH)_2$ from Zimmer (washed) showed unique features of high neutralization capacity and large buffering intensity. The final pH did not exceed 9.0 in wastewater. If overdosed, the pH did not exceed 10.5. Second, $Mg(OH)_2$ greatly improved activated sludge settleability. The optimal dosage was approximately 20 mg Mg^{+2} per liter. Added to the samples of activated sludge aeration system $Mg(OH)_2$ showed significant potential to remove 50% ammonia and 90% phosphate via complexation and precipitation from wastewater, which removal is becoming mandated by the US EPA in many natural water bodies and streams including the Southwestern Ohio area to protect scenic river water from excessive nutrient input. Extensive research on pH control in anaerobic sludge digestion is underway and appears to be a very promising application.

For removal of ammonium and phosphate, a dosage of 100 mg/L $Mg(OH)_2$ is realistic. A 100 million gallon per day municipal treatment plant, of which there are at least three that size in the region, at a 100 mg/L dosage would demand 42 ton $Mg(OH)_2$ per day or 15,200 ton per year which is the approximate capacity of Zimmer Station.

4.5.3 Coal Fired Furnace Fuel Additive and Sorbent

The use of magnesium oxide (magnesia) and magnesium hydroxide has been accepted internationally for many years as a fuel oil additive to reduce high temperature corrosion and severe slag deposits. These problems are alleviated by treating the fuel oil with an oil dispersion of either form of magnesium or by injecting an aqueous dispersion of either form into the flame zone. A dosage of 40 kg (88 pounds) of $Mg(OH)_2$ per 100 ton of fuel oil was reported.

Recently its use as magnesium hydroxide slurry is being investigated for coal fired furnaces in a similar fashion but for additional reasons. The US EPA requirement on air toxics have moved sulfuric trioxide (SO_3) into new consideration for new control technologies. It causes formation of an acid mist in the stacks plume and affects the performance of selective catalytic reduction by forming condensates of SO_3 / ammonia products. Quantities to be treated in the flue gas are typically no more than 20 to 30 ppm.

For a SO_3 level of 20 ppm and treated at a stoichiometric ratio of 1.5 parts $Mg(OH)_2$: 1.0 parts SO_3, a 1,300 MW plant (which is the size of Zimmer Station) would demand only 7.2 tons of pure $Mg(OH)_2$ per day or 2,630 ton per year. A 20% slurry equates to 7,680 gallons per day. For an investment of $200,000 mixer that can make 1,000 gallon batches and pro-rated @ 15 years life and 10% interest, the capital cost is about $7.17 per ton, based on 300 dry tons per month usage.

For such a large furnace the heat loss from 5.33 gallons slurry per minute is insignificant. This, a 70% pure FGD recovered $Mg(OH)_2$ that is unwashed of gypsum will mean additional heat loss due more injected water and other impurities. However, a heat and material balance shows the loss is insignificant (< 1%) when added as a 20% slurry.

4.5.4 Refractories and Chemically Reactive Magnesia Feedstock

$Mg(OH)_2$ is a major source of magnesia, MgO, via calcination much like the production of lime from limestone or dolomite. Depending on the firing temperature two distinct types of magnesia are produced. High temperatures @ 1,400°C "dead burn" calcine the $Mg(OH)_2$ to a high density MgO clinker that will not react chemically but will be pure enough for use in refractory products. Temperatures @ 800°C to 900°C will "soft burn" calcine the $Mg(OH)_2$ to chemically reactive MgO. Calcined MgO of the Zimmer $Mg(OH)_2$ would be about 91% MgO and is within lower grades of MgO that may not be a quality for refractories but satisfactory for metallurgical flux, fertilizer, livestock feed, and as a feedstock to manufacture some magnesium salts.

Zimmer samples were submitted to two producers of magnesia, primarily for refractories. Harbison-Walker which possibly only buys high grade MgO i.e. >95% MgO objected to the impurities of CaO, SiO_2, and Al_2O_3. They also objected to the high level of Boron (1.1% as B_2O_3) which would attack refractories. The second company Mintek suggested the FGD generated MgO would qualify for lower grades of MgO for use in refractory spray-on protective coatings and as a flux for steelmaking. However, it must compete with inexpensive imported magnesia, listed as low as $120/ton f.o.b. New Orleans. Soft burned FGD MgO should be able to be used in fertilizer, animal feed, and environmental control uses such as acid gas fume scrubbing at small industrial plants.

4.5.5 Magnesia Chemical Feedstock

Magnesium Chloride Beneficiated FGD magnesium hydroxide will react with hydrochloric acid (HCI) to produce magnesium chloride. There are two commercial products: a 30% solution as $MgCl_2 \cdot 2H_2O$ which sells for approximately \$90 to \$100 per ton of solution, and a solid flake-like product as $MgCl_2 \cdot 6H_2O$ which sells for \$290 per ton. The $MgCl_2 \cdot 2H_2O$ solution is purchased recently by state highway departments for road ice control. In Pennsylvania, the price is contracted at \$0.52 per gallon. The cost of by-product 25% HCI, although more dilute than virgin 36% HCI is still \$60 per ton. Reacting it with pure $Mg(OH)_2$ would make a 27% $MgCl_2 \cdot 2H_2O$. To make the flake product would require evaporating 6 pounds of water for every 10 pounds of flakes. With a value of \$200 per ton of $Mg(OH)_2$: the cost of raw materials calculates to about \$90 which is close to the \$100 per ton for $MgCl_2 \cdot 2H_2O$. Thus, this process to make the 30% solution would not be economical and could not compete with that made in the U.S. Southwest desert by solar evaporation from brine.

Magnesium sulfate crystals ($MgSO_4 \cdot 7H_2O$) may be a viable commercial opportunity because its production is currently made by reacting with sulfuric acid (H_2SO_4). Smelter grade H_2SO_4 @ \$48 per ton and $Mg(OH)_2$ @ \$200 per ton that is reacted on a 1:1 stoichiometric basis would cost only 20% of the $340 per ton value for magnesium sulfate. Also, there is potentially less water to evaporate before the crystalizer process.

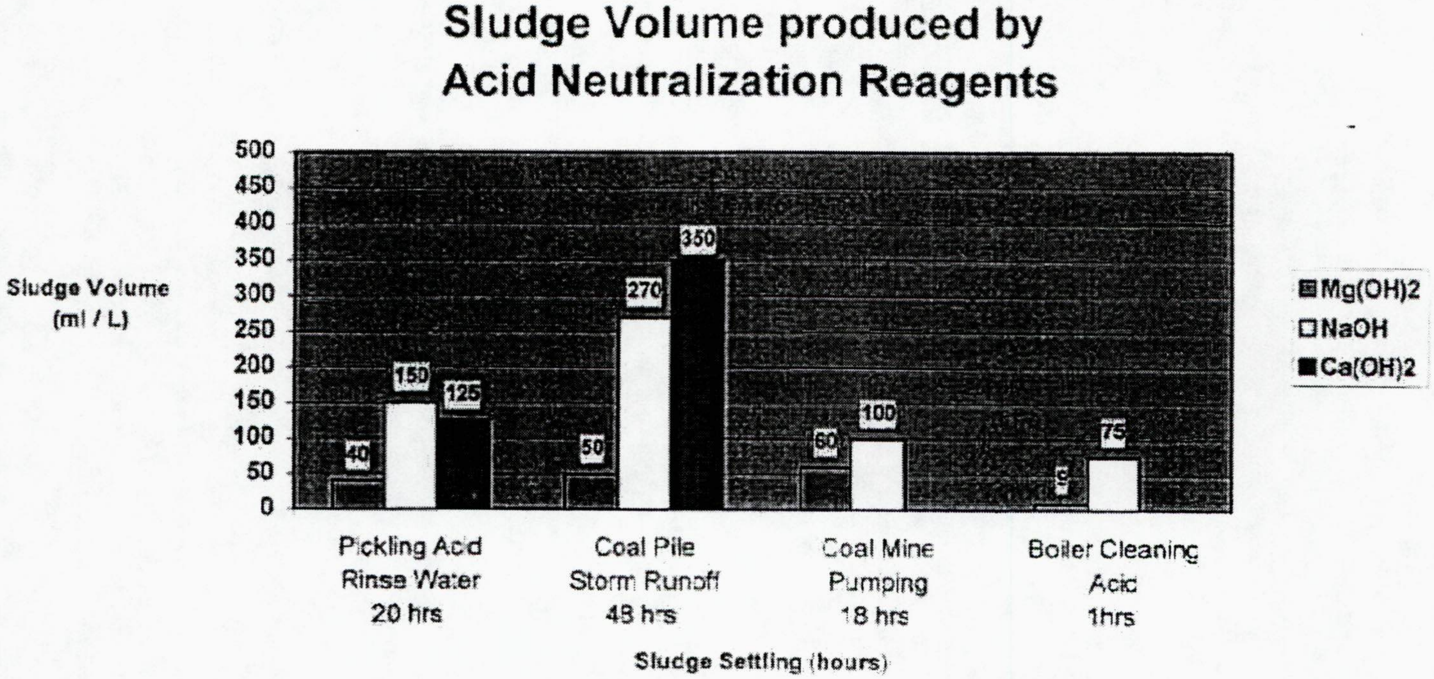


Figure 11

Sludge Volume Produced by Acid Neutralization Reagents

5.0 USE OF FGD BY-PRODUCT GYPSUM ENRICHED WITH MAGNESIUM HYDROXIDE AS SOIL AMENDMENT

5.1 Introduction and Background

Gypsum, classified as sold for "agriculture and miscellaneous" use by the Mineral Industrial Survey of the U. S. Geological Survey is reported recently at 2.4 million tons of uncalcined gypsum. The value is shown at about $17 per ton. (1) The Agricultural Research Service of the U. S. Department of Agriculture (ARS-USDA) began to investigate types or sources of FGD synthetic gypsum as early as 1980. In Ohio the use of dry FGD By-Products, all of which contain some amount of calcium sulfate-gypsum like compounds, was investigated for use on agricultural soil and mine land reclamation soil / spoil starting in 1990 by The Ohio State University under contract with The Ohio Coal Development Office, The U. S. Department of Energy, the Dravo Lime Company and others. The Executive Summary and three in depth reports are found at OCDO as Project CDO/D-89.35. (2)

This research herein was conducted by the same team from The Ohio State University (OSU) and School of Natural Resources. Professor Jerry Bigham was the principal investigator of this project dealing with FGD synthetic gypsum.

Because this section provides discussion that gives background and insight to the OSU research and thus not found in the Milestone Report or Final Report of Phase 1, some statements will be footnoted to References, Section 5.8.

This project is the first known research in Ohio to study relatively pure synthetic FGD gypsum for treating acidic Ohio soils. The use of natural gypsum for conditioning Ohio soils for all uses on crops, pasture, forest, and mine land reclamation is relatively unknown and practiced very little in contrast to other areas in the United States, such as in the Southeast clay soils and the Western states with saline high sodium soils being irrigated. The Ohio Department of Agriculture does not bother to keep track of tons sold as they do for fertilizers and agricultural limestone.

Although gypsum does not directly neutralize soil acidity, it can generate several reactions that counteract the negative effects of soil acidity on plant growth. The USDA points out the fine particle size and consistent chemical properties of scrubber-produced gypsum may make it more suitable as a soil amendment than mined, pulverized gypsum. (3) Potential benefits include reduced aluminum toxicity in acid soils, increased plant available calcium and sulfur, increased rooting depth and improved utilization of soil water. There is increasing serious interest in the "corn belt" states to use FGD gypsum to raise corn and soybean yields while protecting soil erosion. USDA research is showing that gypsum helps soils hold more water by preventing soil from crusting so more rainwater enters the soil instead of running off the field. Thus, soil with more moisture can help crops survive periods of drought. (4 and 5) Dr. D. Norton of the ARS-USDA states "Using gysiferous by-products would give farmers a low-cost remedy for acid, sodic, and erosion-prone soils." (5)

The use of pure FGD gypsum to improve Appalachian soils for agriculture, including pasture and woodlands was begun to be investigated in 1991. These soils are often acidic with low levels of calcium and magnesium, and high levels of toxic aluminum and manganese. Applied limestone supplies calcium and reduced aluminum and manganese solubility, but incorporation below the surface 15 cm soil layer is impractical. (6)

The interest in some magnesium content in gypsum was noted by the USDA. (3) A Cooperative Research and Development Agreement (CRADA) was formed to work together on this potential benefit. (7) Whenever plants are grown on acid soil amended with high gypsum FGD by-products, consideration needs to be given to potential deficiencies of mineral nutrients, especially magnesium. Magnesium (Mg) deficiencies in soils can be a serious fertility problem and lead to decreases in Mg plant uptake which affects plant growth and influences cattle diseases. Acid soils are already low in Mg, and addition of high Ca materials such as gypsum or high calcium agricultural limestone will accentuate Mg deficiencies. OSU's literature survey reports evidence that supplemental Mg may help to ameliorate aluminum phytotoxicity and the negative effects of high calcium limestone and gypsum application. (8) Thus, there is interest by USDA and OSU agronomists in a FGD gypsum that contains a small amount of $Mg(OH)_2$ because it was likely to be effective in soil / spoil conditioning because it can increase soil pH in addition to providing Mg.

In western Ohio and further west in Indiana and Illinois, gypsum is added for the purpose of reducing the magnesium level of soil. (9) In any case, either way the Ca:Mg imbalance is damaging. For most crops, OSU reports the exchangeable Ca:Mg ratio should ideally not exceed 7:1.

5.2 Potential Gypsum Use in Ohio

All 88 counties have data on aglime usage, which is generated by The Ohio Department of Agriculture. In 1997 there was sold 1.2 million tons of aglime which can range from high calcium limestone (~ 1% MgO) to dolomite (~ 24% MgO) depending on the local available geology and the soil tests which indicate the amount of magnesium deficiency in the soil.

FGD gypsum would be particularly applicable to treating acid soils in Ohio, as shown in Figure 12, that are know to have severe aluminum toxicity problems particularly in acid subsoils that are difficult to neutralize with aglime. (10) These researchers from OSU said this problem may be intensified by heavy applications of acid forming nitrogen fertilizers. It would also be useful for current mineland reclamation efforts and abandoned mineland. Gypsum is not meant to replace aglime in Ohio but could compliment its use particularly acid soils and subsoils containing toxic aluminum.

In agricultural soils this study focuses on assessing the effectiveness of FGD gypsum [with or without $Mg(OH)_2$] in ameliorating aluminum toxicity and subsoil by comparison with conventional agricultural limestone (aglime).

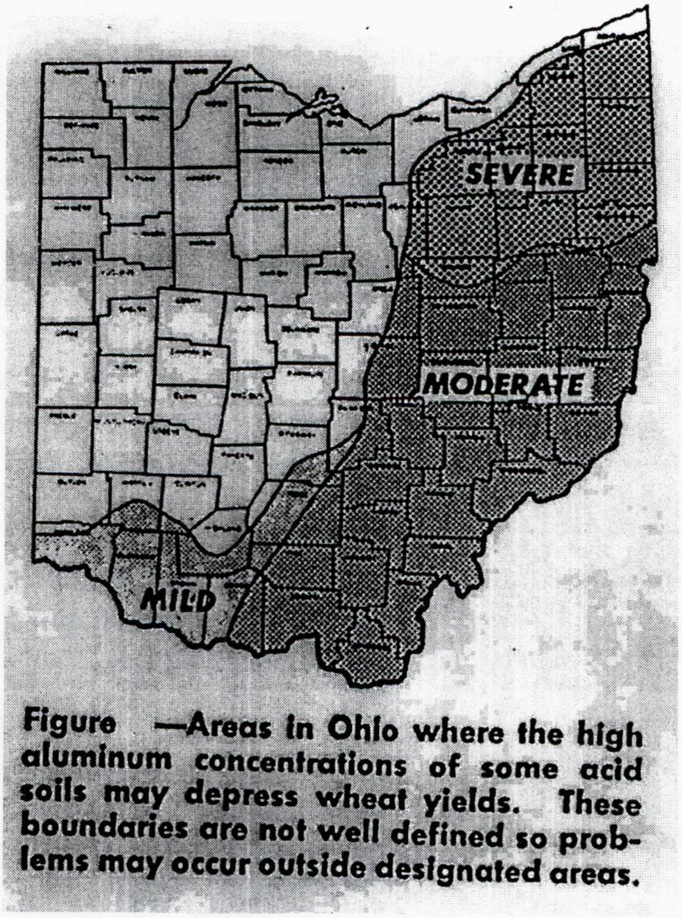


Figure —Areas in Ohio where the high aluminum concentrations of some acid soils may depress wheat yields. These boundaries are not well defined so problems may occur outside designated areas.

Figure 12

"Proper Wheat Variety
Selection For Production on
Acid Soils"
November – December 1976,
Page 92
Reference: Ohio Report

The United States Department of Agriculture reports in the enclosed report by Ritchey et.al. that in the northeastern United States about 24% of the soils have acid sub-soils, i.e. toxic levels of soluble aluminum. (6) They report that "surface applications of gypsum containing products have been shown to reduce detrimental effects of subsoil Al, increase root penetration, and improve soil physical properties". In the past it was reasonable to project that the market potential for gypsum to treat agricultural soils is far less than aglime and it would have to include the "dry FGD" sources. This places the tonnage of pure FGD gypsum potentially less than 250,000 tons per year. The Zimmer Station plant alone is to produce about 700,000 tons per year for wallboard.

Improved crop yields have been recently credited to gypsum applications. (5, 11, 12, 13,) The U.S. DOE recently sponsored a study that looks at soils in the U.S. Southeast and is co-sponsored by the Southern Company, Radian, and performed by the University of Georgia. (11) According to their report the Southeast is a productive region in agriculture, but most soils in the region represent a major limiting factor to increasing productivity and cultivated acreage. Over many years, soil erosion has removed much of the topsoil, bringing acidic subsoils closer to plant rooting zones and resulting in shallow rooting and greatly reduced yields. They state the use of gypsum shows great potential, since its soluble nature allows it to be surface applied rather than mechanically tilled into the soil. It has been successful in reducing soil acidity, improving physical properties through clay flocculation and increased rooting. Researchers at the University of Georgia believe that both perennial and annual crops may benefit from gypsum addition.

As stated above, gypsum use to prevent soil crusting or sealing is probably applicable to much of Ohio and is attracting more interest. Application rates are generally between 2 to 5 tons per acre. Recently agricultural and farm service /

management companies are seeking sources of FGD gypsum in Ohio. One company is crushing scrap wallboard for farmland application. They report tonnage near 100,000 tons per year and growing. A new OSU study is being planned for these "food and feed" crops to prove also they are safe for the environment.

OCDO and the DOE consortium are supporting a new study with OSU that specifically looks at the need for sulfur and trace elements in soils that are available from FGD type coal combustion products. Professor W. A. Dick is the principal investigator.

In summary, pure gypsum is used for reasons in Ohio that have nothing to do with acid soils. Whereas this project promoted the attribute of also being able to add some magnesium hydroxide in Appalachian soils, gypsum with very little or no magnesium is specified and sold in northwest Ohio and regions further west to remove excess levels of magnesium in the soil by ion exchange similar to using gypsum to remove sodium by ion exchange in saline soils in the far west of the United States.

5.3 Gypsum Pellets / Granules

The technical feasibility to agglomerate or pelletize FGD gypsum is very important. One company in Ohio is pelletizing natural gypsum for use as a soil amendment. The pellets use a water-soluble binder. In the fertilizer industry pelletizing is more often referred to as granulating i.e. fertilizer granules. Fertilizers are pelletized and gypsum can be spread with it if it is about the same size gradation. However, for bulk large-scale application the non-pelletized gypsum can be spread if the moisture is low enough, i.e. less than 8%, so it will flow in the spreader box of the spreader truck or trailer. FGD gypsum does not have to be pulverized to be pelletized.

Pelletizing makes it "user-friendly". You will find in the lawn and garden store 40 pound bags of pelletized gypsum and bags of pelletized lime (agricultural limestone). Both rotor type lawn spreaders and drop type spreaders are "conventional". The Ohio State University used a drop type to insure accuracy and equal distribution.

By making it user-friendly, pelletizing adds value to gypsum. It is sold pelletized at about $50 to $55 per ton bulk and $75 per ton in 40 pound bags.

5.4 Project Objectives: Gypsum as Soil Amendment

This report describes the primary objective and results of a greenhouse study designed to evaluate conventional FGD by-product gypsum and magnesium enhanced gypsum from the Zimmer Station pilot plant as amendments for improving the quality of agricultural soils and mine spoils that are currently unproductive because of phytotoxic conditions related to acidity and high levels of toxic dissolved aluminum (Al). The technical literature contains evidence to suggest that gypsum may be more effective than agricultural limestone in modifying soil chemical conditions below the immediate zone of application.

Conventional FGD gypsum, whether from lime or limestone scrubbing will have gypsum purity near 97% to 98% and less than 1% $Mg(OH)_2$. Since the Zimmer gypsum is unique in that it can contain significant levels (3% to 6%) of magnesium hydroxide [$Mg(OH)_2$] a second objective was to assess the effectiveness of the magnesium containing FGD by-product in alleviating or preventing soil and plant deficiencies which often result from application of high calcium materials i.e. gypsum or high calcium limestone. Some soils particularly in eastern Ohio and Appalachia in general require some added source of magnesium, which is normally added via a dolomite type of agricultural limestone.

5.5 Ohio State University Greenhouse and Laboratory Study – Phase 2

The slipstream by-product recovery plant described earlier at the CINERGY Zimmer Station near Cincinnati produces FGD gypsum by-products that can be formulated to contain varying amounts of magnesium hydroxide [$Mg(OH)_2$]. Such materials should have agricultural value as soil conditioners, liming agents and sources of plant nutrients (Ca, Mg, S).

When the greenhouse study began, Zimmer gypsum was not yet available but the Zimmer $Mg(OH)_2$ was available.

Representative samples of by-product gypsum and $Mg(OH)_2$ from the Zimmer Station were initially characterized. The gypsum was of high chemical purity and consisted of well-formed crystalline, lath-shaped particles of low specific surface area. By contrast, the by-product $Mg(OH)_2$ was a high surface area material (50 m ^{2}/g) that contained 20% $CaSO_4$ material with variable hydration state. Artificial blends of these materials containing 4% and 8% $Mg(OH)_2$ were prepared for comparison with other liming agents in the form of agricultural limestone and gypsum amended with laboratory $Ca(OH)_2$.

Samples from a native agricultural soil (AS), abandoned mine spoil (AML) and a reclaimed mine soil (RML) were used to construct greenhouse columns. All samples had pHs in the range of 3.0 to 5.0 with high exchangeable Al contents. Both topsoil and subsoil / spoil were used to simulate profiles found in the field, and amendments were applied only to the surface layers.

Gypsum alone had no effect on pH of the amended surface layers; however, gypsum with alkalinity in the form of $Mg(OH)_2$ or $Ca(OH)_2$ produced similar, rapid pH increases. Treatments with aglime @ 12 tons per acre were less than a range of gypsum treatments @ 15 to 60 tons per acre. Although the pH response decreased with time (165 days), final soil / spoil reactions were comparable to those achieved using agricultural limestone (aglime). Only the 8% Mg-gypsum produced a significant improvement in the pH of the subsurface layers. All amendments, including pure gypsum, caused a marked reduction in toxic Al in the surface layers. The gypsum-based materials also decreased subsurface exchangeable Al and Fe. By comparison, agricultural limestone had no measurable effect on subsurface chemistry in the AS columns and was less efficient than gypsum-based materials in all other cases. Major increases in subsurface concentrations of exchangeable Ca and Mg with the gypsum by-products suggest that toxic Al is displaced from the soil / spoil column through cation exchange and complexation reactions. These results further suggest that surface applications of Mg-gypsum by-products could improve the chances for successful mine land reclamation by decreasing subsurface Al concentrations and thereby increasing root proliferation within the normally toxic subsurface zone.

All columns were saturated and leached a total of 5 times during the course of the greenhouse study (165 days). Agricultural soil (AS) leachate conductivity (total dissolved salt load) and concentrations of Ca, Mg, S and Al increased over time. By comparison, leachate conductivities and concentrations of dissolved elements peaked with AML and RML columns and then declined with time. This difference in behavior was probably a reflection of more coarse fragments and higher macroporosity in the spoil materials.

All alkaline amendments produced an environment adequate for plant growth. Some early yield reductions were observed at the highest rates of gypsum-based materials due to excessive salts and high pH, but these reductions disappeared over time. No plant response to improvements in subsurface soil / spoil chemistry were observed in these experiments. The columns were always adequately watered and fertilized, and the test crops were able to meet nutritional requirements by exploiting only the amended surface layers.

The success of these greenhouse tests laid the basis for the Phase 3 Field Studies described below.

5.6 Ohio State University Field Studies of FGD Gypsum – Phase 3

The Phase 3 Field Studies described three field studies designed to evaluate FGD by-product gypsum and Mg-gypsum from the Zimmer Station power plant as amendments for improving the quality of mine spoils and agricultural soils that were unproductive because of phytotoxic levels of dissolved aluminum (Al) and low pH. The technical literature suggests that gypsum may be more effective than agricultural limestone for ameliorating Al toxicity below the immediate zone of application. Such considerations are important for deep rooted plant species that attempt to utilize water and nutrients occurring at depth in the spoil / soil.

Bulk samples of FGD gypsum from Owensboro, KY, Municipal Power plant [0% $Mg(OH)_2$] and Zimmer Mg-gypsum [4 and 8% $Mg(OH)_2$] from the Zimmer Station were secured and analyzed for chemical and mineralogical composition. Part of the FGD gypsum was commercially pelletized to evaluate ease of handling; it was found to have excellent spreading characteristics using a standard drop spreader. The FGD gypsum contained significant impurities of both calcite ($CaCO_3$) and dolomite $(Ca,Mg)CO_3$. The Mg-gypsum samples were found to contain somewhat lower quantities of $Mg(OH)_2$ (3 and 6 wt. %) than expected. Chemical analyses showed that trace elements of potential environmental concern were at or below detection limits in the by-products.

Two field experiments were established on abandoned mine land (AML) and previously reclaimed mine land (RML) located on properties of The Ohio State University at the Eastern Ohio Agricultural Research and Development Center (EORDC) – Unit 2 in Noble Co., OH. A third experiment was sited on natural agricultural soil (AS) located on private property in Ashtabula Co., OH.

Characterization studies of samples from these locations confirmed that pHs in the upper 50 cm (20 inch) of the spoil / soil columns were in the range of 3 to 5 and Al toxicities ranged from severe (no plant growth) to moderate (only tolerant species were present). Experimental designs and amendment rates were formulated on the basis of preliminary greenhouse work conducted to mimic field conditions.

In the AML study, agricultural limestone was compared to FGD gypsum and 4% Mg-gypsum with / without added yard-waste compost. Test plots were replicated four times for the AML site as shown in Figure 13. Based on greenhouse results, the FGD gypsum was added at 100 ton/acre and the Mg-gypsum [4% $Mg(OH)_2$] at 110 ton/acre with and without 50 ton/acre of yard compost. Besides an untreated control plot, there was a control plot with 45 ton/acre of agricultural limestone (aglime). The untreated control plots did receive only inorganic fertilizer but did not support plant growth whereas vegetation was quickly established on all plots treated with aglime and FGD by-products. The best early yields were obtained on plots amended with by-product gypsum alone; however, this response did not persist. By the end of the second growing season, dry matter production was highest on plots receiving 4% Mg-gypsum + compost. Final yields from compost treated plots were consistently better than those from corresponding plots receiving only inorganic amendments. In the most severe cases, reduced yields were correlated with elevated concentrations of Al and Fe in plant tissue samples. Exchangeable Al exceeded 400 mg/kg throughout the unamended spoil column. All by-products / amendments lowered exchangeable Al to non-toxic levels within the zone of incorporation and caused some downward leaching of Al. By the end of the experiment, exchangeable Al concentrations in plots treated with gypsum (no compost) were below those of the unamended spoil throughout the 100 cm depth of measurement.

Access Road

101	102	103	104	105	106	107	108
1+C	1	2	2+C	4	4+C	3	3+C

201	202	203	204	205	206	207	208
3	3+C	2+C	2	1+C	1	4	4+C

301	302	303	304	305	306	307	308
4+C	4	1	1+C	3	3+C	2+C	2

401	402	403	404	405	406	407	408
3	3+C	1+C	1	2+C	2	4	4+C

Treatments:

1. Control (no amendment)
2. Ag. Limestone (45 ton/ac)
3. FGD Gypsum (100 ton/ac)
4. FGD Mg-Gypsum [4% $mg(OH)_2$]

(100 ton/ac)

+ C:

Treatment + 50 ton/ac yard waste compost containing 15 pound dry matter

Figure 13

Treatments and Experimental Design for Abandoned Mine Land (AML)
Using 20 x 25 foot plots at EORDC – Unit 2

In the RML study, agricultural limestone was compared to FGD-gypsum and 4% Mg-gypsum applied at two rates (20 and 40 ton/ac) without disturbance of existing vegetation. The results from this experiment were less conclusive than at the AML site because the by-products were not incorporated and the graded spoil was less toxic but more variable in composition. Modifications of mine soil chemistry were limited to the upper 10 cm of the profile regardless of amendment used, and consistent reductions in exchangeable Al were achieved only with 40 ton/ac of gypsum and Mg-gypsum. Throughout the term of the study, FGD-gypsum produced the highest dry matter yields. Concentrations of Al and Fe were also lowest in tissues removed from the gypsum amended plots.

Treatments at the Ashtabula Co. agricultural soil (AS) site consisted of agricultural limestone (12 ton/ac); increasing quantities of 4% Mg-gypsum (15, 30, and 60 ton/ac); and increasing Mg (0, 4, 8, 12%) in FGD gypsum applied at a rate of 60 ton/ac. Alfalfa was used as the test crop. Test plots were replicated four times for the AS site as shown in Figure 14. All treatments produced significant improvements in alfalfa yield compared to the unamended control plots. As shown in Figure 15, increasing the application rates (15 - 30 - 60 ton/acre) of the 4% Mg-gypsum enhanced the yields for the 1997 harvest and the 2 year total. However, increasing the amount of Mg in gypsum had no effect on dry matter production. Plant tissue concentrations of Ca, Mg, and S were similar across all amendments. Concentrations of Al and Fe, on the other hand, were highest in vegetative matter from the control plots. Phytotoxic levels of exchangeable Al were present in the unamended soil, and all amendments produced major decreases in exchangeable Al within the zone of incorporation. By the last harvest, reductions of 50% or more were also observed in the subsoil of those plots treated with high rates (30 and 60 ton/ac) of 4, 8, and 12% Mg-gypsum.

Improved Soil Permeability

Significant improvements in the saturated hydraulic conductivity of the soil at a depth of 30 to 45 cm were also achieved with these treatments. These improvements may reflect better subsoil aggregation due to saturation of the cation exchange capacity and Ca, increased porosity as a consequence of better root distributions in response to less phytotoxic conditions, or both. See Figure 16.

In conclusion: such results suggest that land applications of gypsiferous by-products may produce improved soil chemical and physical properties, even in regions were gypsum has not been traditionally utilized as an agricultural amendment.

101	102	103	104	105	106	107	108
2	8	4	6	7	1	3	5

401	402
6	2

201	202	203	204	205	206	207	208	403	404	405
7	4	6	8	5	1	2	3	4	5	3

301	302	303	304	305	306	307	308	406
5	3	1	8	4	7	6	2	1

407	408
8	7

Treatments:

1. Control (no amendment)
2. Ag. Limeston, 12 ton/ac
3. FGD Gypsum, 60 ton/ac
4. FGD Mg-Gypsum, [4% $Mg(OH)_2$ 15 ton/ac]
5. FGD Mg-Gypsum, [4% $Mg(OH)_2$ 30 ton/ac]
6. FGD Mg-Gypsum, [8% $Mg(OH)_2$ 60 ton/ac]
7. FGD Mg-Gypsum, [12% $Mg(OH)_2$ 60 ton/ac] (prepared by applying one, 50 pound bag of technical grade $Mg(OH)_2$ + 60 ton/ac 8% Mg-gypsum to each plot)

Figure 14

Treatments and Experimental Design for Natural Agricultural Soil (AS)
Using 20 x 25 foot Plots in Ashtabula County

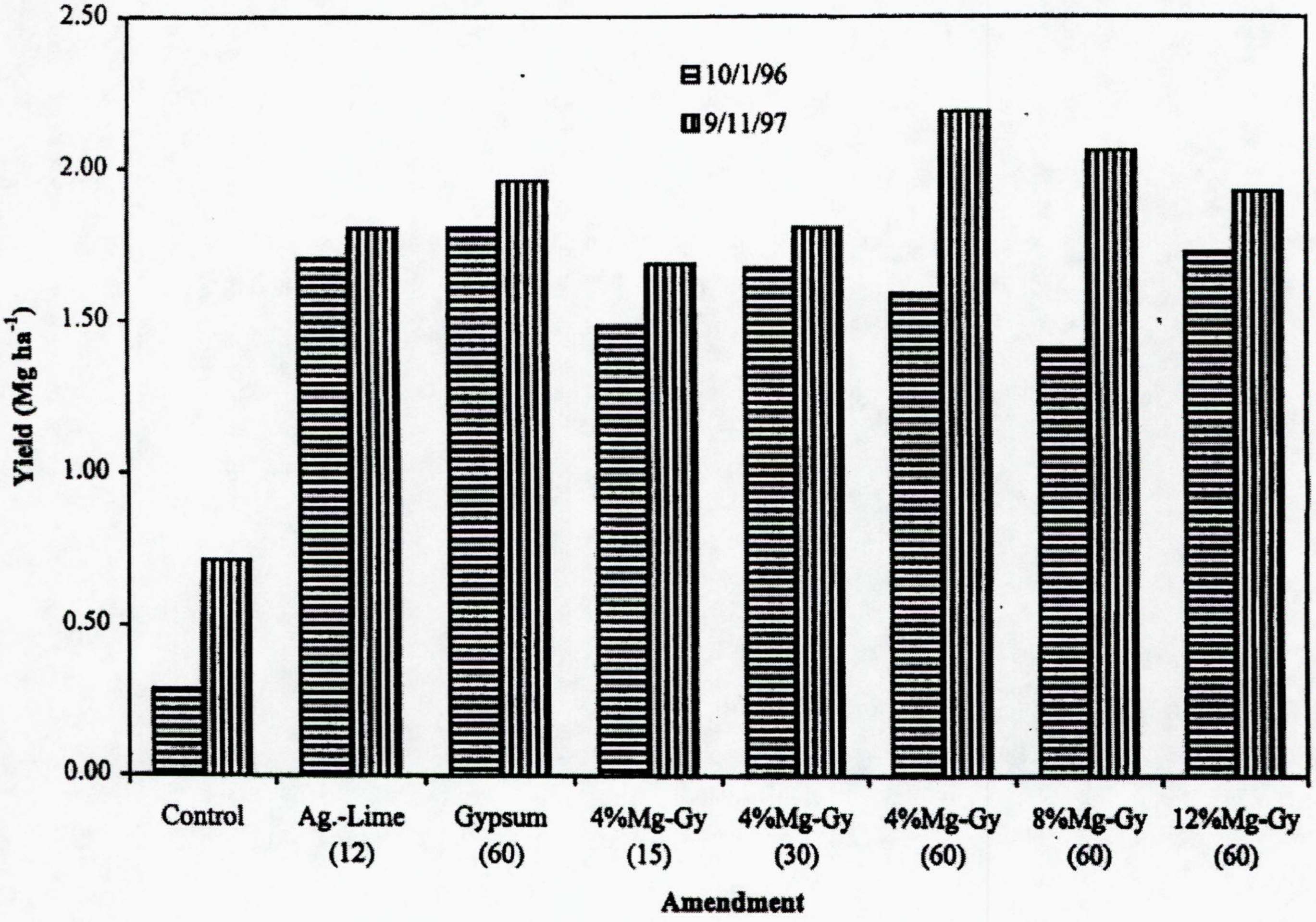


Figure 15

Effects of Amendments and Rates on Plant Yield (Dry Matter Production)
At the AS Field Site
Multiply Yield (Mg ha^{-1}) by 0.45 to obtain ton ac^{-1}

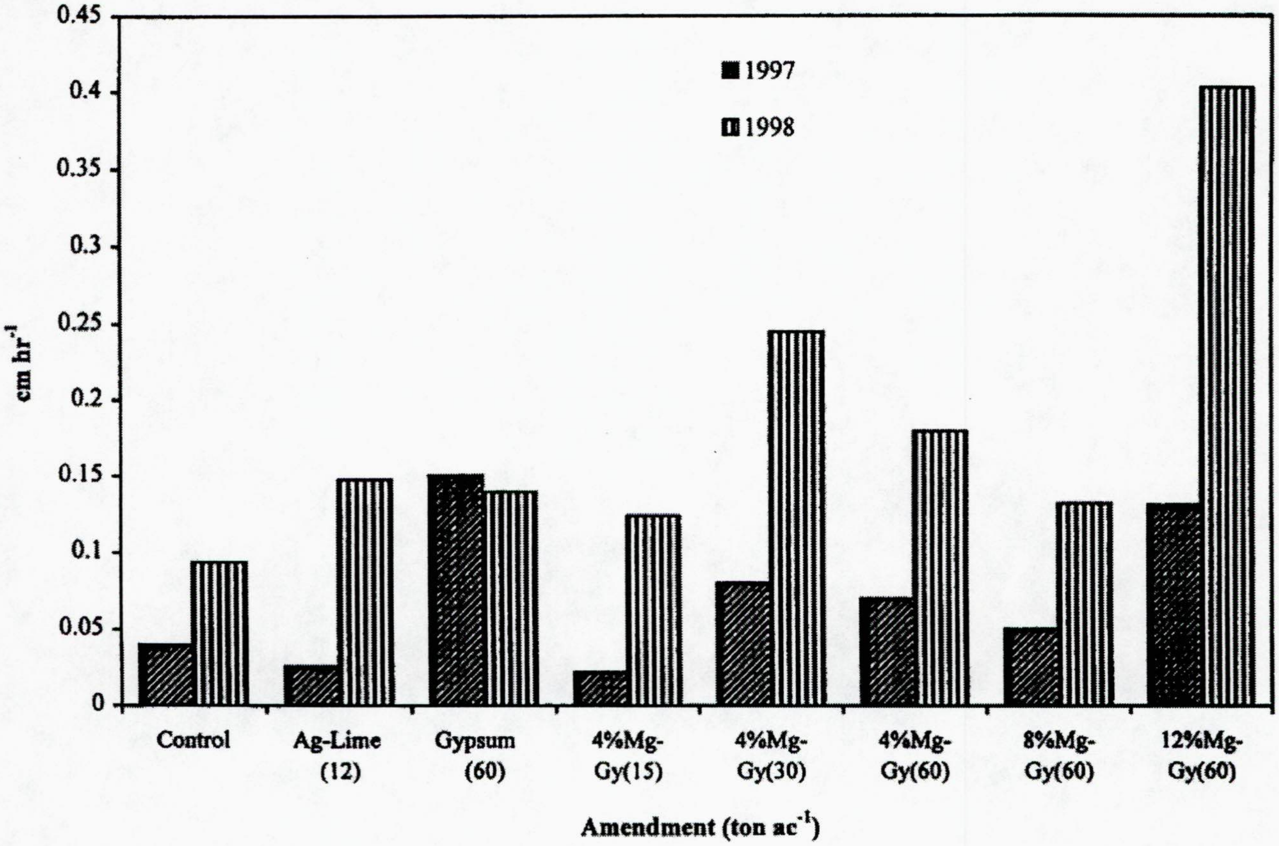


Figure 16

Effects of Amendment and Rates on Saturated Hydraulic Conductivity (K_{sat})

At a Depth of 30 to 45 cm in the Soil at the AS Site

5.7 OSU – Bureau Of Mines Study Using FGD as a Substitute for Borrow Soil

A companion study was conducted at the same AML site and at the same time by the same OSU research group to compare the same FGD materials with and without co-application of sewage sludge and use of a borrow soil as the control plots. Besides the two FGD gypsum materials (Owensboro @ 0% Mg and Zimmer @ 4% Mg) the calcium sulfite-laden FGD filter cake mixed with fly ash and lime was used. This same FGD mixture was used to treat pyrite-laden coal refuse, as discussed later. Test plots were replicated four times. Although constructed by the same OSU group, these test plots were more elaborate in that they were fitted with lysimeters to check ground water quality and collection devices to measure stormwater runoff quality. This project was funded by the U.S. Bureau of Mines, now part of the U.S. Department of Energy.

Results – Reclamation of acidic abandoned minespoils by amendment with by-product materials may provide a low-cost alternative to covering with borrow soil. This three year field study was undertaken to determine if spoil amendment with two types of wet flue gas desulfurization by-products (FGD) and sewage sludge could achieve revegetation of toxic spoils, and to determine the effects these materials have on spoil, water, and vegetation quality. Mixed with the spoil, the calcium sulfite material will eventually oxidize to gypsum. Establishment and growth of vegetative cover on spoil amended with FGD or with sewage sludge was similar to that on spoil covered with borrow soil. Combined amendment with FGD and sewage sludge, however, allowed more rapid establishment and a more vigorously growing stand than was achieved with borrow soil cover. Plant biomass yields over the three years is illustrated in Figure 17. Apparently the combination of slow-release nutrients and organic matter from the sewage sludge and alkalinity, Ca, and Mg from the FGD worked together to enhance growth relative to either material alone. Decreases in subsoil exchangeable Al and Fe, and in vadose water acidity with combined FGD and sewage sludge provided some indication that a combined application of these by-products enhanced the ability of FGD to ameliorate subsoil toxicity. Trace element concentrations in surface runoff and vadose zone water were similar among all treatments except that B was increased by the calcium sulfite – fly ash stabilized type of FGD. The major treatment effects on water quality were that the sewage sludge produced water with lower pH than all other treatments, and all treatments with FGD materials produced water with increased salt loading (primarily Ca and S) relative to the borrow soil treatment. Combined amendment with FGD and sewage sludge was found to be a highly effective method for revegetation of toxic minespoil, with minimal adverse effects on soil, plant, or water quality.

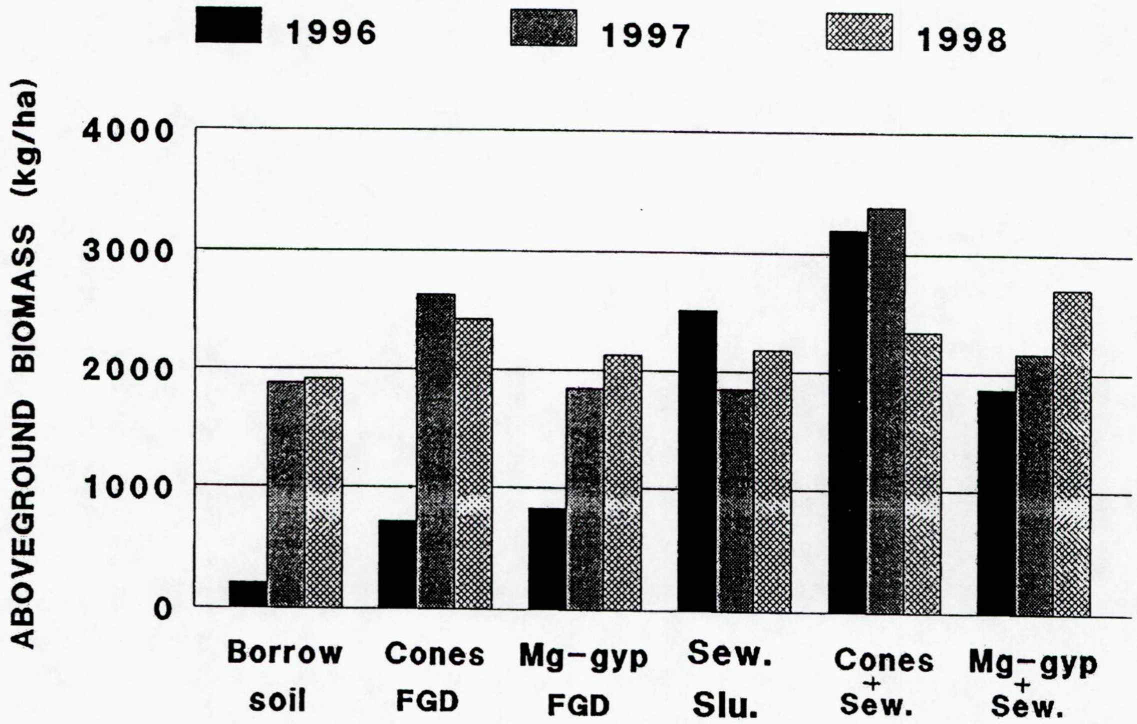


Figure 17

Herbaceous Biomass (Dry Weight) for Soil Amendments by Year of Harvest

5.8 References

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6.0 MINESPOIL TREATMENT BY CALCIUM SULFITE CONTAINING FGD

A study that is a different aspect of land application is included in the Zimmer By-Products Study formally called *"Inhibition of Acid Production in Coal Refuse Amended with Calcium Sulfite and Calcium Sulfite-Containing FGD"*.

The research was conducted by The Ohio State University at the Ohio Agricultural Research and Development Center under the direction of Professor Warren Dick in the School of Natural Resources.

The Zimmer Station produces 1.8 million tons per year of lime and fly ash fixated calcium sulfite FGD material requiring landfill disposal.

Calcium sulfite ($CaSO_3$) contained in flue gas desulfurization (FGD) by-product is a strong reductant, an alkaline material, and a toxicant against pyrite-oxidizing bacteria. These chemical properties of $CaSO_3$ are all useful in inhibiting formation of acid in coal refuse, which is defined below.

The objective of this part of Phase 2 is a laboratory investigation on the effect of calcium sulfite to control pyrite oxidation in order to suppress acid mine drainage formation.

Like FGD, coal refuse is a waste product arising from the reduction of sulfur in coal in order to be used for energy. Coal refuse is the reject material from cleaning (washing) coal and is currently produced and landfilled. There are abandoned waste piles of coal refuse called gob piles that also leach acid mine drainage. Abandoned mineland also has areas concentrated with coal refuse often called minespoil.

Another way to look at the relationship between coal refuse and FGD material is that reduction of sulfur oxide emission in coal combustion is accomplished by both the desulfurization of mined coal prior to coal combustion and also the desulfurization of coal combustion flue gases during and after coal combustion.

Among several "coal washing" methods, gravity separation and froth flotation are used to remove the sulfur containing mineral in high sulfur eastern bituminous coals, called pyrites. Based on differences in density and surface properties, the gravity separation method can cause the pyrite to separate from the coal. It is the main method used and can remove up to 30% of pyrite from coal (IEA Coal Research, 1989). The gravity separation method also removes non-sulfur inorganic compounds such as aluminosilicates and metal oxides to increase the heating value of coal. The sulfur and non-sulfur minerals removed from raw coal are called coal refuse. Abandoned minespoil is concentrated with pyrite.

The American Electric Power Company, which co-owns Zimmer Station, has a coal wash plant that generates coal refuse adjacent to its Conesville Power Plant that also generates FGD containing calcium sulfite. The project chose to study the use of the Conesville FGD to "treat" the Conesville coal refuse from its coal preparation (wash) plant. It contained total sulfur concentrations as high as 10%. Thus, coal refuse comes in contact with air during landfilling, and the pyrite becomes oxidized and in the process produces copious amounts of acid which eventually leaches into streams and groundwater. Modern coal refuse disposal areas leach into a wastewater treatment neutralization system.

Laboratory Test Results

In a lab-scale column (2.5 x 13 cm) leaching experiment, 10 g FGD containing 6.4 g $CaSO_3$, 1 g $CaCO_3$, 0.9 g $CaSO_4$, and 1.7 g fly ash were applied to 50 g ground (<2 mm) fresh coal refuse. Calcium sulfite, $CaCO_3$, and fly ash were also applied individually and in combination to the coal refuse. During 27 weeks of leaching with water, $CaSO_3$ inhibited the onset of acid production in coal refuse. Such inhibition was enhanced by $CaCO_3$ and fly ash and these materials in combination with $CaSO_3$, resulted in the FGD having the strongest inhibitory effect. Up-scaled next in a greenhouse column (30 x 112 cm) leaching experiment, the FGD was incorporated into fresh coarse coal refuse at 5.5%, 11%, and 22% (w/w) in the surface (0 to 15 cm) layer, and FGD was applied at a rate of 1.25%, 2.5%, and 5.0% (w/w) in the middle (50 to 65 cm) layer. The low rate of FGD in the surface layer was matched with the low rate in the middle layer and this experimental design was also used for the other two rates. During 39 weeks of leaching, all FGD treatments significantly decreased leachate acidity and increased leachate pH. This effect increased with increasing FGD rates. See Figure 18.

Ohio State University concludes that application of $CaSO_3$ - based FGD to coal refuse is a potential new method to inhibit acid mine drainage and a field test needs to be conducted.

This successful research led the American Electric Power and OSU to initially propose this research in a full scale demonstration at its Conesville operation in a fashion of intermittent capping or layering of the coal refuse with FGD with the objective of saving FGD landfill capacity while preventing acid mine drainage from its coal refuse disposal area. About 160,000 ton/year of FGD would be beneficially used to prevent acid mine drainage and treatment. A scaled down version of this FGD tonnage and scope has recently been implemented as a demonstration test.