Oxidation of North Dakota Scrubber Sludge for Soil Amendment and Production of Gypsum

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EXECUTIVE SUMMARY

Cooperative Power's Coal Creek Station (CCS) has successfully marketed its fly ash for commercial use, and Cooperative Power has been an industry proponent of CCB utilization since CCS became operational in 1981. With awareness of the economic and environmental advantages of by-product utilization, the favorable U.S. Environmental Protection Agency (EPA) regulatory determination that CCBs are not hazardous, and the improved understanding of potential local and regional markets, Cooperative Power initiated an investigation on processing and utilization of CCS scrubber sludge. Cooperative Power, the North Dakota Industrial Commission, and the U.S. Department of Energy provided funds for a research project at the Energy & Environmental Research Center. The goals of the project were 1) to determine conditions for the conversion of scrubber sludge to gypsum simulating an ex situ process on the laboratory scale; 2) to determine the feasibility of scaleup of the process; 3) if warranted, to demonstrate the ex situ process for conversion on the pilot scale; and 4) to evaluate the quality and handling characteristics of the gypsum produced on the pilot scale.

The process development and demonstration phases of this project were successfully completed focusing on ex situ oxidation using air at low pH. The potential to produce a high-purity gypsum on a commercial scale is excellent. A relatively extensive evaluation of the pilot-scale flue gas desulfurization (FGD) gypsum product was performed to facilitate the marketing effort for this material in a broad range of applications, including agricultural uses. During the course of this evaluation, it was noted that some trace elements were present in measurable quantities in the FGD gypsum. These elements were mercury, chromium, and chlorine (present as chloride). Although they were present in measurable amounts, it is important to note that the mercury and chromium were present at very low levels, with leachate concentrations less than the primary drinking water standard levels. Air oxidation of scrubber sludge was carried out in laboratory- and pilot-scale operations. Initial experiments to provide information on efficiency of oxidation, most favorable reaction conditions (particularly pH), and other reaction variables such as air flow rates and the effects of iron and manganese catalysts were carried out in a five-necked 500-mL Pyrex reaction flask. The laboratory-scale experiments indicated that the reaction was rapid and complete and thus ideal for scaleup. The pilot-scale oxidation was carried out in a 500-gal stainless steel tank. All reaction conditions were maintained at optimum as determined in the laboratory studies with pH controlled to between 4.5 and 5.0 by adding 20% sulfuric acid as required.

The results of this project demonstrate the feasibility of converting CCS scrubber sludge to gypsum exhibiting characteristics appropriate for agricultural application as soil amendment as well as for use in gypsum wallboard production. Gypsum of a purity of over 98% containing acceptable levels of potentially problematic constituents was produced in the laboratory and in a pilot-scale demonstration.

OXIDATION OF NORTH DAKOTA SCRUBBER SLUDGE
FOR SOIL AMENDMENT AND PRODUCTION OF GYPSUM

INTRODUCTION

The use of scrubber sludge has traditionally been limited for a variety of reasons; however, the chemical and mineralogical composition of these materials shows promise for several applications. This research project evaluated and demonstrated the use of ex situ air oxidation of scrubber sludge from a single North Dakota source to produce calcium sulfate dihydrate (gypsum) for potential use in gypsum wallboard and other gypsum products and for agricultural soil amendment.

The requirements and standards for gypsum vary according to the applications for which it is typically used. The applications of greatest interest to Cooperative Power for regional commercial marketing were wallboard production and agricultural soil amendment. For wallboard use, mineralogy, particle size, and major/minor element concentrations are important. The prime considerations for wallboard applications are suitability for production of material with sufficient strength for wallboard manufacture and appearance. For agricultural soil amendment, the presence of trace elements and unoxidized sulfite is most important because of possible toxicity to plants as well as the potential for accumulation of potentially toxic trace elements in products intended for consumption by animals or humans. In agricultural use, the permissible amounts of potentially problematic constituents can be a variable dependent on what crops will be grown and the rate and/ or frequency of application. Further complicating the use of gypsum in agriculture is the fact that some trace elements, such as boron and selenium, are problematic in both high and low concentrations. Boron is an essential plant nutrient that can also be phytotoxic at high levels, while selenium is an essential nutrient for humans that also possess toxic properties at excessive dose levels. For these and other trace elements, the aspect of toxicity is often a function of concentration or dose rather than identity.

Cooperative Power has a strong commitment to utilization of the lignite by-products generated at Coal Creek Station (CCS) near Underwood, North Dakota, and they initiated an investigation on processing and utilization of CCS scrubber sludge. Cooperative Power, the North Dakota Industrial Commission, and the U.S. Department of Energy (DOE) provided funds for a research project at the Energy & Environmental Research Center (EERC) to perform the required work to evaluate the potential for gypsum production from CCS scrubber sludge. The EERC focused on the development and demonstration of gypsum production through ex situ forced oxidation of the wet flue gas desulfurization (FGD) material, scrubber sludge, produced as a result of sulfur emissions control at the CCS power plant.
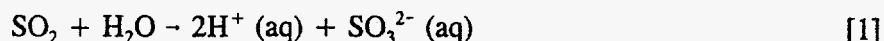
BACKGROUND

Coal Creek Station's FGD process uses hydrated lime to scrub SO_2 emissions and produces a material that is primarily a calcium sulfite slurry. The raw scrubber sludge contains over 80% water. It was decided early on that ex situ oxidation, which requires minimal equipment modification, would be the method of choice for gypsum production. In situ forced oxidation,

which uses air addition to the scrubber to form gypsum directly in the scrubber tower, requires significant equipment modification. Although this method might appear superior for gypsum production in terms of overall simplicity, the implications of trace elements in agricultural applications and the need for high-purity calcium sulfate for wallboard applications make ex situ oxidation an attractive choice. The reasons for this are discussed in detail in the text of this report.

The reactions involved in SO_2 removal in a lime-based scrubber can be summarized as follows:
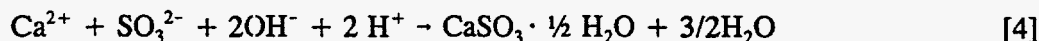
Dissolution of SO_2:

$$SO_2 + H_2O \rightarrow 2H^+ \text{ (aq)} + SO_3^{2-} \text{ (aq)} \tag{1}$$

Hydration of lime:

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{2}$$
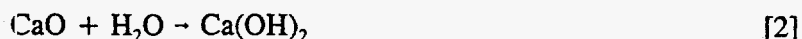
Dissolution of hydrated lime:

$$Ca(OH)_2 \text{ (aq slurry)} \rightarrow Ca^{2+} \text{ (aq)} + 2OH^- \text{ (aq)} \tag{3}$$

Reactions of dissolved SO_2 with dissolved hydrated lime:

$$Ca^{2+} + SO_3^{2-} + 2OH^- + 2 H^+ \rightarrow CaSO_3 \cdot \tfrac{1}{2} H_2O + 3/2H_2O \tag{4}$$

The following reactions also can be expected:

$$Ca^{2+} + 2OH^- + 2HCl \rightarrow Ca^{2+} + 2Cl^- + 2H_2O \tag{5}$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \tag{6}$$

$$Ca^{2+} + 2OH^- + H_2O + CO_2 \rightarrow CaCO_3 + 2H_2O \tag{7}$$
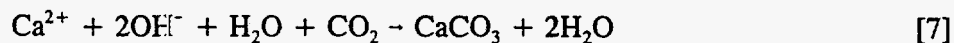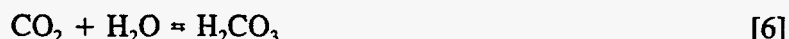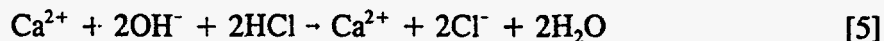
In the case of a scrubber utilizing a strong base such as hydrated lime, the reaction with sulfur dioxide, which is a weak acid anhydride (sulfurous acid, H_2SO_3) is complete and rapid in aqueous solution. The resultant product as shown in Equation 4 above is calcium sulfite hemihydrate (hannebachite). The only additional product of the reaction is water from the neutralization of the calcium hydroxide during the scrubbing process. Since calcium hydroxide is a strong base, it tends to react with any acidic gas or gaseous acid anhydride such as hydrogen chloride (HCl), hydrogen fluoride (HF) or even carbon dioxide, as shown in Equations 5 and 7. Thus chloride incorporated into scrubber sludge from the neutralization of HCl formed during combustion as well as calcium carbonate can be expected to be components of scrubber sludge.

The process development and demonstration phases of this project were successfully completed focusing on ex situ oxidation using air at low pH and demonstrated the potential to produce a high-purity gypsum on a commercial scale. A relatively extensive evaluation of the pilot-

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scale FGD gypsum product was performed to facilitate the marketing effort for this material in a broad range of applications, including agricultural uses. During the course of this evaluation, it was noted that some trace elements were present in measurable quantities in the FGD gypsum. These elements were mercury, chromium, and chlorine (present as chloride), and although they were present in measurable amounts, it is important to note that the mercury and chromium were present at very low levels, with leachate concentrations less than the primary drinking water standard levels. Although it was known from previous analyses that trace elements were present in the wet FGD material, it was anticipated that the oxidation process used would facilitate the removal of "contaminants," especially since the FGD gypsum was washed postproduction. In follow-up work, solid materials, reaction waters, and leachate were all analyzed in an effort to determine the fate of these trace constituents relative to the FGD gypsum produced using the air oxidation process.

GOAL AND OBJECTIVES

The overall project goal was to determine the feasibility of converting CCS scrubber sludge to gypsum for commercial utilization. The supporting objectives were 1) to determine the conditions for conversion of scrubber sludge to gypsum simulating an ex situ process on a laboratory scale; 2) to determine the feasibility of scaleup of the process; 3) if warranted, to demonstrate the ex situ process for conversion on the pilot scale; and 4) to evaluate the quality and handling characteristics of the gypsum produced on the pilot scale. The laboratory- and pilot-scale experiments were developed to provide information to achieve the stated goal and objectives.

EXPERIMENTAL

Air oxidation of scrubber sludge was carried out in laboratory- and pilot-scale operations. Initial experiments to provide information on efficiency of oxidation, most favorable reaction conditions (particularly pH), and other reaction variables such as air flow rates and the effects of iron and manganese catalysts were carried out in a five-necked 500-mL Pyrex reaction flask. The flask was equipped with a constant-velocity stirrer; outfitted for the addition of acid (10% sulfuric acid), the addition of air, and venting of the flask to a stack gas analyzer for the determination of SO_2; and an additional port reserved for removal of samples to determine completeness of conversion of sulfite to sulfate. Oxidation was carried out at between pH 4 and 5. The scrubber sludge provided to us was a relatively pure suspension of calcium sulfite hemihydrate (hannebachite) containing some unreacted calcium hydroxide and some associated calcium carbonate. The mineralogical composition of the scrubber sludge was determined using x-ray diffraction (XRD), while the determination of sulfite content was made using an iodometric titration. The laboratory-scale experiments indicated that the reaction was rapid and complete and thus ideal for scaleup.

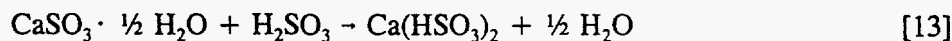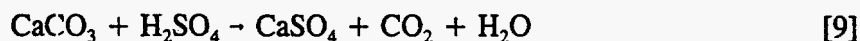### Laboratory-Scale Experiments

500 mL of well-mixed unoxidized scrubber sludge was placed into the reaction assembly described above. Stirring was started, and 10% sulfuric acid was added with a peristaltic pump. Pump speed was adjusted to maintain the desired pH for the experiment currently under way. Most experiments required the addition of between 16 and 20 mL of acid during the course of the air

oxidation experiment. To achieve this addition and maintain pH in the desired range of 4–5, a flow rate of approximately 0.05 mL/min was used. This assured delivery of the required amount of acid over a time frame somewhat less than the 7 to 9 hr required for complete oxidation in the lab experiments. An adjustable-flow peristaltic pump was used to allow addition of acid as necessary to maintain pH at the desired level. pH was constantly monitored and for the lab experiments, manual adjustment of acid flow was used to maintain the desired pH. Air was introduced through a coarse-porosity sintered glass diffuser at a rate of 15–16 standard cubic feet (scf) per hour, which is a nominal 7 L/mm. This was a rather high flow rate for the air but was necessary to keep the frit from plugging and also assured saturation of the solution with air. Samples were removed from the reactor at regular time intervals for determination of sulfite concentration. 1-mL samples were removed at the beginning of the experiment, and sulfite was determined by titrating with standardized iodine to a starch end point. As the amount of iodine required decreased toward the end of the experiment, larger samples were required for meaningful measurement of sulfite. The reaction was deemed to be complete when a 5-mL sample required less than 1 mL of iodine. This indicated a greater than 99% conversion of sulfite to sulfate.

Laboratory-scale experiments focused on the effects of pH on rate of oxidation and sulfur dioxide emission during air oxidation, and the effects of catalysts such as iron and manganese on scrubber sludge oxidation rates. One experiment was also conducted at an elevated temperature.

Air oxidation of calcium sulfite-containing scrubber sludge can be represented by the following equations, which include the reaction of scrubber sludge components with sulfuric acid added for pH control:

$$Ca(OH)_2 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad [8]$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \qquad [9]$$

$$2\,CaSO_3 \cdot \tfrac{1}{2}\,H_2O + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O + Ca(HSO_3)_2 \qquad [10]$$

$$Ca(HSO_3)_2\,(aq) + O_2\,(g) \rightarrow CaSO_4 \cdot 2H_2O + SO_2 \qquad [11]$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad [12]$$

$$CaSO_3 \cdot \tfrac{1}{2}\,H_2O + H_2SO_3 \rightarrow Ca(HSO_3)_2 + \tfrac{1}{2}\,H_2O \qquad [13]$$

Note: Since most of the reactions above occur in aqueous solution, water of hydration is assumed to be contributed from excess water in the overall system and is not included in the equations, which may not appear balanced with respect to water.

Equation 10 is especially important, since this shows the formation of calcium bisulfite. Calcium bisulfite is much more water-soluble than calcium sulfite, which can be thought of as insoluble. It is the formation of calcium bisulfite that facilitates the solution chemistry responsible for the oxidation of scrubber sludge to gypsum. It can also be seen from Equations 12 and 13 how SO_2 in water, forming sulfurous acid, reacts with calcium sulfite to form calcium bisulfite; thus the formation of bisulfite could also be accomplished by allowing additional sulfur dioxide to react with the scrubber sludge. There are advantages to the use of sulfuric acid for bisulfite formation and for

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pH control. These are 1) ease of pH control and 2) complete reaction of any excess calcium hydroxide or calcium carbonate to calcium sulfate. Drawbacks are the added expense of sulfuric acid along with the problems associated with the handling of a strong acid, which can be hazardous. The use of sulfuric acid for pH adjustment is in part responsible for the high purity of the gypsum produced from the ex situ air oxidation of scrubber sludge as carried out in this project. Gypsum produced in this manner contains essentially no unreacted calcium sorbent.

Pilot-Scale Experiments

The pilot-scale oxidation was carried out in a 500-gal stainless-steel tank. All reaction conditions were maintained at the optimum based on laboratory experiments, with pH controlled to between 4.5 and 5.0 by adding 20% sulfuric acid as required. Lab experiments were carried out with pH adjustment using 10% sulfuric acid; however, to keep volumes of material as low as possible, it was decided to use 20% sulfuric acid in the pilot-scale production of oxidized scrubber sludge. It was found in the laboratory-scale oxidation that there was up to several ppm of SO_2 in the excess air vented from the reactor; thus offgas was scrubbed through a dilute solution of sodium bicarbonate before venting. The pilot-scale oxidation of scrubber sludge resulted in the production of over 300 kg of calcium sulfate dihydrate (gypsum) with a purity exceeding 98%. The purity of the final products from pilot- and laboratory-scale experiments was determined using inductively coupled argon plasma (ICAP) spectrometry and XRD, as well as by classical chemical and gravimetric methods for the determination of moisture and residual sulfite content. The gypsum produced in the pilot-scale operation contained <0.1% sulfite and 270 ppm of acid-insoluble material. In addition to bulk characterization of major constituents, the oxidized scrubber sludge was analyzed for trace constituents in the solid and liquid phases. Additionally, the oxidized scrubber sludge was analyzed for major, minor, and trace constituents after dewatering and air drying to the dihydrate. Chemical analyses determined that the material had a nominal composition of approximately 23% calcium and 56% sulfate and contained approximately 20% water, as would be expected for calcium sulfate dihydrate of greater than 98% purity. Pure calcium sulfate dihydrate would have a composition of 23.279% calcium, 55.795% sulfate, and 20.927% water. A complete description of the pilot-scale oxidation is included as Appendix A.

The synthetic gypsum resulting from the pilot-scale experiment was evaluated for its potential to be pelletized. These tests were specifically undertaken to facilitate marketing as an agricultural soil amendment. It was assumed that a soil amendment that could be applied with conventional machinery would be advantageous. It was determined that use of a binder improved the pelletizing process significantly. It was further determined from the limited amount of pellets produced that the pelletized product would allow use with conventional machinery. Results of the pelletizing tests are detailed in Appendix A.

RESULTS AND DISCUSSION

The following sections describe the laboratory-scale experiments used to investigate the various reaction variables of interest.

pH

Since the formation of calcium bisulfite is required for the air oxidation of scrubber sludge, pH adjustment was necessary using dilute sulfuric acid as described above. Experiments were carried out with no pH adjustment, adjustment to pH 4.0–4.1, and adjustment to 5.0–5.1. The initial experiment with no pH adjustment was performed and demonstrated an extremely slow rate of oxidation, as expected. After 2.5 hours of reaction time, there was no measurable amount of reduction of sulfite content, and the experiment was terminated. Additional experiments were carried out at reduced pH. The experiment carried out at pH 4.0–4.1 reached completion in approximately 6.5 hr, while the experiment carried out at pH 5.0–5.1 required 9 hr for complete oxidation of sulfite. The results of the reduced pH experiments are shown in Figure 1.

Use of Iron and Manganese Catalysts

It has been reported that there can be a strong catalytic and even possible inhibiting effects of transition metals such as iron, manganese and cobalt (Karlson et al., 1985). Experiments were carried out using manganese and iron to determine the potential effect of these metals on the ex situ air oxidation of Coal Creek Scrubber Sludge. Cobalt was not studied because of the cost of this material. Manganese at two concentrations, 1.6 and 3.2 millimolar, and iron at one level, 1.6 millimolar, were used in these experiments. pH in all of the catalysis experiments was adjusted to 4.0. An accelerating effect was shown to be exerted by the manganese, especially at higher levels; however, a complete investigation of the use of catalysts was beyond the scope of this work. Experiments on catalysts were not carried out to completion, but were carried out far enough to establish a rate of reaction and to plot a linear regression line over the data to determine rates of reaction and to estimate the time to complete oxidation. Linear regression lines are plotted in
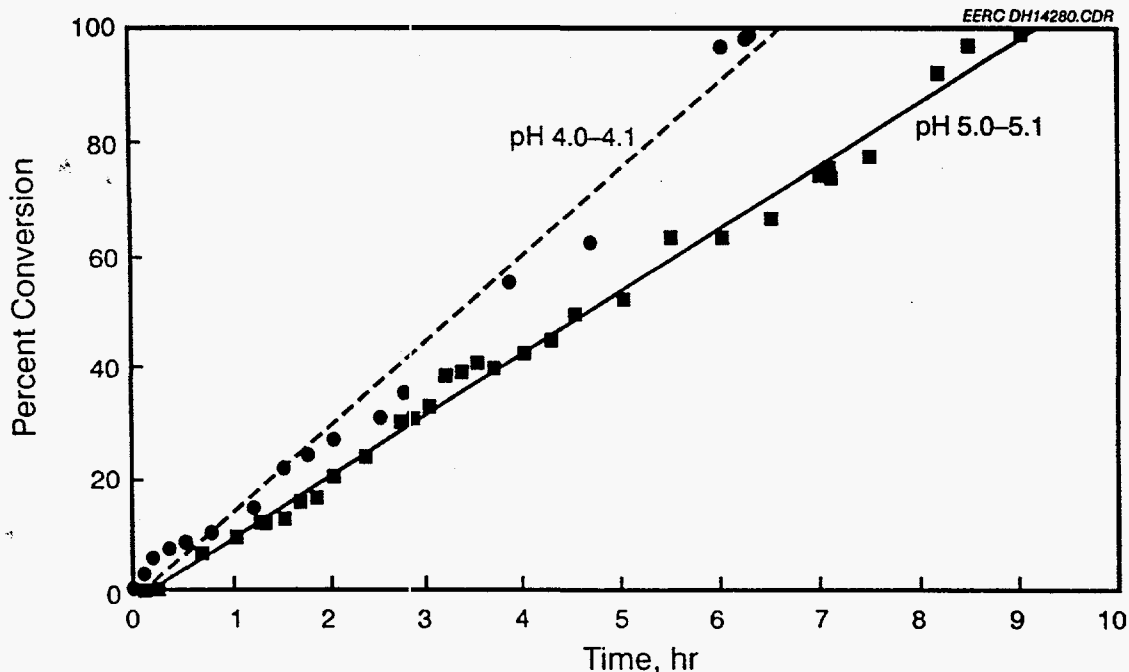
Figure 1. Oxidation of scrubber sludge at two pH levels.

Figure 2. It was observed that in the iron-catalyzed experiment, a brown/tan color developed, likely indicating the formation of an iron compound, which may have been an organic complex. In other experiments, it was observed that anaerobic storage led to rapid growth of microorganisms and the development of an undesirable odor.

Oxidation at Elevated Temperature

One experiment was carried out at an elevated temperature. Oxidation was carried out at 40°C. This experiment was terminated after 7 hr due to difficulties in keeping the frit from clogging. It was determined experimentally that the advantage of heating, which may have caused a slightly faster reaction rate, was not adequately offset by the difficulty of the frit constantly plugging. This particular difficulty, however, might be overcome by proper engineering design on a larger scale. Based on problems encountered in lab-scale experiments, oxidation at elevated temperature is not recommended.

SO_2 Evolution at Varying pH

It can be seen in equations previously presented that the addition of sulfuric acid results in the formation of bisulfite, and as pH is further reduced, free SO_2 is formed from a chemical equilibrium shifted toward the formation of sulfurous acid rather than bisulfite. From this information, it can be inferred that the lowering of pH would result in an increase in SO_2 concentration in gas vented from the reaction vessel. An experiment was conducted to determine SO_2 concentrations in offgas at a constant gas flow rate as pH was reduced by the addition of sulfuric acid. The data generated in these experiments are shown in Figure 3. It can be seen that
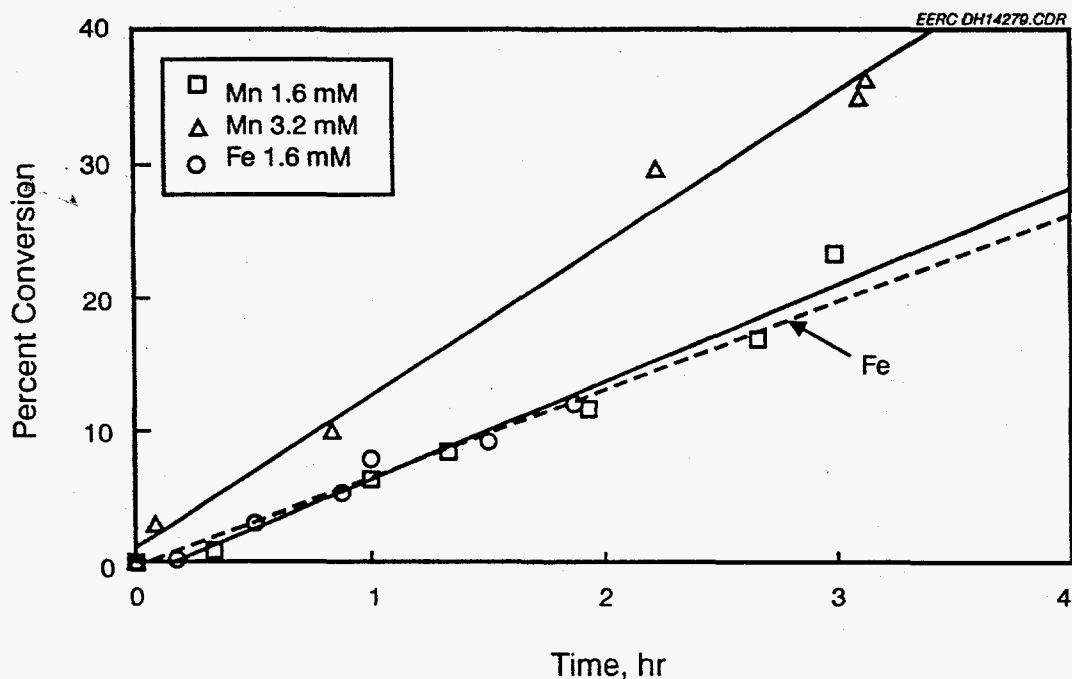
Figure 2. Catalytic oxidation of North Dakota scrubber sludge.

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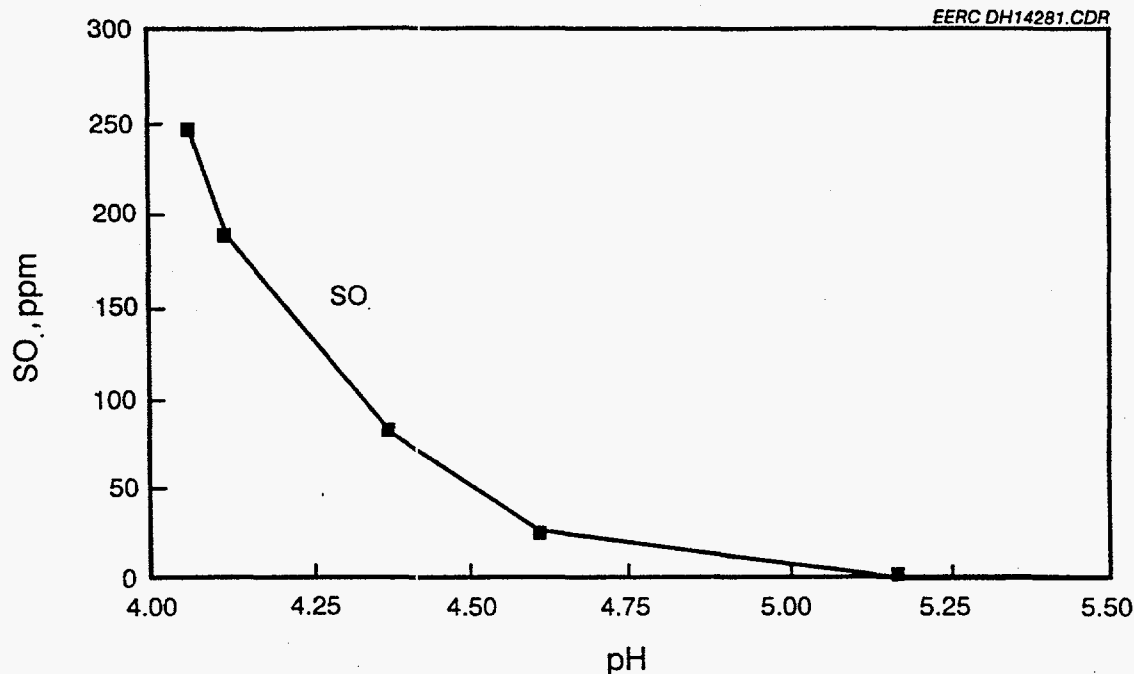
Figure 3. SO_2 evolution versus pH.

SO_2 concentrations increase from 0 to 1 as pH is reduced to 5.0–5.2. SO_2 concentration increased to 1385 ppm at pH 3.2, although this high value is not included on the plot. This plot clearly illustrates the balance that must be maintained between reaction rate and excessive SO_2 offgassing as the pH of the oxidizing solution is reduced. Oxidation of scrubber sludge may necessitate the scrubbing the offgas to remove SO_2.

Trace Element Partitioning

The recent emphasis by the U.S. Environmental Protection Agency (EPA) on evaluation of trace element emissions from coal-fired utilities and the associated potential for regulation of these emissions pose some interesting questions regarding by-products from these facilities. For those coal-fired utilities that have made a commitment to utilization as an economical and environmentally sound by-product management option, it can be beneficial to understand the relationship and interaction between emissions and by-product streams relative to trace elements. It is commonly known that coal and the resulting by-products have varied chemical composition and the composition includes numerous trace elements. Several trace elements commonly found in measurable quantities in coal combustion by-products (CCBs) are also of concern to EPA, as they might be significant in utility emissions. These trace elements include selenium, chlorine, cadmium, and lead. Another significant trace element of great environmental concern is mercury, which is not as commonly found in CCBs because of its unique chemistry and volatility. Mercury in utility emissions has been the focus of several recent EERC research projects (Miller et al., 1996; Laudal et al., 1996; Dunham et al., 1996), but there are many unanswered questions on the partitioning of mercury throughout coal combustion systems. Many of these questions remain to be answered for other trace elements as well, and there are additional questions regarding the impact of SO_x, NO_x, and particulate (often referred to as RO_x) emission control technologies on the fate of trace elements

in the coal conversion processes. These issues are noted here because the evaluation of the fate of trace elements in utility systems should also include postproduction processing such as the demonstrated ex situ oxidation process or other oxidation options.

It is important to note that only very low concentrations of these elements are present in the solid and liquid samples, and the primary concern in evaluating the trace element partitioning was to understand process issues relative to product quality.

The process of forced oxidation of scrubber sludge is a process involving true solution chemistry; thus, in order for complete oxidation of sulfite to sulfate to occur, each particle of calcium sulfite must dissolve and the sulfite must become oxidized to sulfate, with subsequent recrystallization of calcium sulfate as the dihydrate (gypsum). In this process, sulfuric acid is used to adjust pH to approximately 4.5 and residual calcium hydroxide or associated calcium carbonate will be converted to calcium sulfate through a simple chemical conversion involving acid–base reaction. This assures the high purity and high rate of conversion of all alkaline calcium compounds to calcium sulfate in the final product.

Table 1 is a summary of chemical analyses of scrubber sludge water before forced oxidation and chemical analysis of oxidized scrubber sludge and its associated liquid phase after the completed oxidation process. The analytical data given are for the pilot-scale-produced gypsum, which was dewatered and washed prior to air drying. The use of a highly efficient dewatering and washing process would likely result in the production of a material containing lower concentrations of trace elements that partitioned into the liquid phase.

TABLE 1

Chemical Analysis of Scrubber Sludge

Parameter	North Dakota PDWS Limits, ppm	Liquid from Unoxidized Scrubber Sludge	Liquid from Oxidized Scrubber Sludge	Oxidized Scrubber Sludge
Cadmium	0.01	<0.0003 ppm	0.00316 ppm	<0.01 ppm
Chloride			2050 ppm	103 ppm
Chromium	0.05	0.0044 ppm	1.100 ppm	2.6 ppm
Lead	0.05	<0.002 ppm	0.018 ppm	<0.4 ppm
Mercury	0.002	0.0016 ppm	0.0216 ppm	0.20 ppm
Selenium	0.01	<0.008 ppm	0.550 ppm	<0.5 ppm

A sample of scrubber sludge from the pilot-scale oxidation was leached using distilled deionized water at a 20:1 liquid-to-solid ratio using the ASTM D3987 shake extraction procedure. These results are shown in Table 2.

TABLE 2

Results of Leaching

Parameter	North Dakota PDWS Limits, ppm	Leaching of Oxidized Scrubber Sludge, ppm	Calculated Maximum Concentration,[1] ppm	Actually Leached, %
Cadmium	0.01	<0.01	<0.0005	NA[2]
Chromium	0.05	<0.05	0.130	<38
Lead	0.05	<0.002	<0.020	NA
Mercury	0.002	0.0015	0.010	15
Selenium	0.01 (ND)	<0.002	<0.025	NA

[1] Calculated on the basis of bulk chemical analysis and a 20:1 liquid-to-solid ratio used for the leaching procedure.

[2] NA (not applicable) because of the unavailability of analytical data at or above analytical detection limits or lower levels of quantitation.

It can be seen from the results in Table 1 that trace element concentrations in liquid from oxidized scrubber sludge increase significantly from those observed in unoxidized scrubber sludge. There are likely several reasons for this observation, including the release of trace elements present in the solid matrix of the initial material as a result of the recrystallization that occurs during the conversion of calcium sulfite to calcium sulfate. The process of oxidation of scrubber sludge (calcium sulfite) requires that the calcium sulfite first dissolve, since the oxidation reaction occurs in solution, followed by oxidation to sulfate with formation of calcium sulfate crystals. The process is in a sense analogous to the recrystallization method commonly used for the purification of chemical compounds. Recrystallization results in the formation of crystals of a pure chemical compound with trace constituents excluded from the crystal matrix and thus concentrated in the solution from which the crystals formed. Additionally, the reduced pH of the oxidized system, which is a nominal 4.5 as compared to approximately 7.5 for unoxidized scrubber sludge as received from the power plant, would result in the solubilization of heavy metals such as cadmium and lead. These form insoluble carbonates at near neutral pH values and control solution concentrations in aqueous systems. It can be seen in the data from chemical analysis that favorable partitioning of nearly all associated trace elements into the liquid phase of the reaction mixture did occur. The notable exception to this is mercury. Mercury, which can also form insoluble carbonates, would be kept in solution by the formation of a chloride complex that is highly stable as well as soluble. This particular chemical system has sufficient chloride for the formation of a mercuric chloride complex; however, the verification of this by direct measurement was beyond the scope of the project. The high stability of the $HgCl_4^{2-}$ complex $Hg^{2+} + 4Cl^- = HgCl_4^{2-}$, log K^0 14.47 (Lindsay, 1979) along with the high chloride-to-mercury ratio in the chemical system represented precludes most other forms of oxidized mercury; however, the possibility remains that some elemental mercury may also be present.

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This project focused on the use of gypsum produced from scrubber sludge for use in wallboard and for agricultural use, primarily for the remediation of sodic soils, otherwise unsuitable for crops. The primary concern for gypsum wallboard was purity of the primary product and major parameters, while for agricultural uses, trace elements were a primary concern. This study has brought out several important points. First, during the oxidation of this particular scrubber sludge, many of the trace elements partition to the liquid phase because of recrystallization purification as well as lowering of solution pH. Second, of the trace elements remaining in the oxidized scrubber sludge, only a small percentage is leachable. Thus the minimal concentrations remaining are for the most part immobile under water leaching. The implications of included trace elements for agricultural application are not clearly defined at this time, as standards have not been established. It should be kept in mind however, that many trace elements, excluding a limited suite of heavy metals such as lead, cadmium, and mercury are either known to be essential nutrients or have been implicated in essential metabolic pathways. These include boron, chromium, and selenium, trace elements known to accumulate in CCBs and often thought of as potentially toxic trace elements rather than as nutrients. The evaluation of the potential impact of these and other trace elements must be put into the context of area of application and ambient local concentrations as well as release potential and leachability before a determination of category (hazardous or nutrient) can be made. There are numerous areas of the country where there is a deficiency of these and other essential trace elements, and their presence in an additive such as gypsum could be considered beneficial. A much more important aspect of the application of agricultural gypsum is magnesium depletion, which is known to occur with gypsum application.

Wallboard Application

Gypsum wallboard or sheetrock is a standard building material that traditionally used mined gypsum; however, in recent years, wallboard manufacturers have begun to work with utilities to use FGD gypsum. Wallboard manufacturers have specific requirements on quality and consistency as noted in Table 3. There are some modifications required by conventional wallboard manufacturing processes to accommodate FGD gypsum and recycled gypsum, but many companies are making these adjustments. The U.S. annual consumption of gypsum is approximately 26 million tons. It is interesting to note that the production of FGD materials will be about that same amount after the Clean Air Act Amendments are fully implemented in the year 2000. It is also important to note that the use of FGD gypsum can favorably impact air quality because of the potential associated reduction in mining requirements.

Agricultural Uses

Agricultural uses of FGD gypsum and products produced from gypsum and other CCBs are numerous, and there is much literature available on this topic (Electric Power Research Institute, 1995; Forster, 1994; Hatch, 1993; Hemmings, 1995; Ohio State University, 1993; Warren, 1992). Gypsum from oxidized scrubber sludge has a number of standard agricultural uses (Clarke, 1993). These are as follows:

- Conditioning alkaline and saline, or sodic, soils

- Improving soil permeability

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- Supplying nutritional sulfur

- Providing catalytic support to maximize fertilizer absorption

- Enhancing the production of root nodules that promote the conversion of nitrogen to nitrogen compounds (Steffan, and Golden, 1991)

TABLE 3

Specifications for Gypsum Wallboard Use (Mayer, 1993)

Property	Composition Allowed (Westroc Industries Ltd.)	Composition in Coal Creek Gypsum
$CaSO_4 \cdot 2H_2O$	95.0% min.	98%-99%
$CaSO_3$	0.5% max.	<0.1% (.015%)
Free Moisture	10.0% max.	<1%
Fly Ash	1.0% max.	
SiO_2	1.0% max	
Acid Insoluble		0.027% (fly ash + SiO_2)
Ca/$MgCO_3$	5.0% max.	
Fe_2O_3	0.4% max.	
Cl^-	100 ppm max.	103 ppm
Na	100 ppm max.	280 ppm
Mg	75 ppm max.	52 ppm
K	100 ppm max.	38 ppm
Total Soluble Salts	600 ppm max.	
pH	6-8	6.5
Particle Size	20% max. <10μm	27% <9.6 μm
Aspect Ratio	10 max.	

FGD residues may contain sulfite, which can be toxic to plants. There are several strategies that may be effective for overcoming the potential phytotoxicity of sulfite in unoxidized or incompletely oxidized scrubber sludge. Raising soil pH can effectively accelerate the oxidation of sulfite by forming the more soluble bisulfite, which is then air-oxidized to sulfate; alternately, simply allowing sufficient time for oxidation to occur or limiting application rates, depending on sulfite content can also be done. It has been reported that oxidation need not be complete, with 50%-70% being acceptable (Clarke, 1993). This was not a real consideration in this study, since nearly complete oxidation of sulfite (>99%) could be easily accomplished. The application rates for FGD are also highly variable; however, an application rate of 7-7 t/ha has been recommended in a recent report prepared in Europe (Coal Research Establishment, 1992).

Application of gypsum to soil can also result in magnesium deficiency. Magnesium is relatively easy to displace from ion-exchange sites on soil surfaces. In the presence of the high concentrations of calcium encountered with the application of gypsum, magnesium is displaced into the soil solution. In solution, it forms a noncharged ion pair with sulfate, which can be easily leached out of the soil system (Ritchey et al., 1995). When gypsum is used in agricultural applications, magnesium deficiency should be considered and, if needed, magnesium supplement should be used. Additionally, with agricultural use, the accumulation of trace elements should be factored into use, particularly if heavy or repeated applications are anticipated. Constant monitoring of gypsum, soil, and even plant tissue may be necessary with gypsum containing potentially problematic concentrations of trace elements.

General Uses for Gypsum

Tables 4 and 5 are a summary of production and use as well as major uses for FGD. These tables are based on the American Coal Ash Association (ACAA) 1993 survey results. It can be seen from Table 5 that the three top uses for FGD account for 98% of FGD use in the United States.

TABLE 4

Summary of CCB Production and Use in the United States (Blackstock and Tyson, 1995)*

	FGD Products	Fly Ash	Bottom Ash	Boiler Slag
Production*	20.3	47.8	14.2	6.2
Use*	1.1	10.5	4.2	3.4
Percent Use	6%	22%	30%	55%

*Millions of short tons.

TABLE 5

Summary of FGD Use in the United States (Blackstock and Tyson, 1995)

FGD Uses	Tons Used*	Percent
Wallboard	633,526	54.5
Waste Stabilization	299,262	25.7
Road Base/Subbase	206,699	17.8
Structural Fills, Embankments	11,698	1.0
Miscellaneous	11,891	1.0
Total	1,163,076	100.0

*Figures are in short tons.

Other potential uses include the following:

- Manufacture of ammonium sulfate fertilizer
- Cement production (cement clinker)
- Fabrication of unfired brick, cinder block, and masonry
- Industrial plasters
- Dental plaster and medical plaster
- Self-leveling floor mortar
- Oil well cements
- Waste stabilization
- Mining mortar

Since there are an extremely large number of uses for gypsum, either as gypsum ($CaSO_4 \cdot 2H_2O$), plaster of paris ($CaSO_4 \cdot 1/2H_2O$), or chemical calcium sulfate, this list of uses in not intended to be taken as all-inclusive. Major and innovative applications have been selected for presentation in this summary of use potential.

FULL-SCALE GYPSUM PRODUCTION

Based on the successful demonstration of pilot-scale gypsum production, Cooperative Power initiated an evaluation of equipment needs and costs to scale up the ex situ oxidation process at the Coal Creek Station site. Requirements for the full-scale process were: 1) minimum disruption to current desulfurization process and 2) minimum cost for installation. Cooperative Power's plans included construction in 1998 and changes to the scrubbing material to improve SO_2 removal. The equipment requirements and costs and cost of construction is detailed in a bid supplied by Dravo Lime Company and included in Appendix C.

The primary equipment required for the full-scale ex situ oxidation process is an oxidation tower, hydroclones, and belt dryers. Cooperative Power anticipates costs of $1.5M per unit for equipment and construction. The expected products will be gypsum and magnesium hydroxide.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were drawn from the results of the laboratory- and pilot-scale experiments performed for this study.

- The production of high-quality gypsum suitable for agricultural use and production of wallboard, was demonstrated using Coal Creek Station scrubber sludge. The scrubber sludge was relatively easy to oxidize using simple techniques that could be easily automated, so commercial-scale production has a high potential for success.

- Potentially problematic trace elements, including heavy metals and chloride, appear to partition into the liquid phase during the oxidation process, likely because of recrystallization purification of the product as well as pH adjustment to 4.5 necessary for air oxidation.

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- Concentrations of many of the potentially problematic trace elements are not especially high and thus not of concern for normal agricultural application rates. Trace element concentrations are for the most part not a concern in wallboard application prior to disposal, which is inevitable. Recent recommendations for agricultural application of disposed wallboard may impose trace element considerations for this application.

- Potentially toxic trace elements remaining in the oxidized scrubber sludge at measurable or potentially problematic levels exhibited limited mobility either at or below the concentrations for primary drinking water standard limits.

- Dewatering of the oxidized scrubber sludge was readily accomplished. The degree of dewatering that can be accomplished will affect concentrations of trace elements in the produced gypsum that are inversely proportional to the efficiency of dewatering. This is due to the partitioning of the trace elements into the liquid phase during the oxidation process.

- There is a relatively high volume of literature available on FGD, gypsum, and related topics. Especially useful are proceedings from the international conferences on FGD and other synthetic gypsum sponsored by Ortech and held every other year in Toronto. A bibliography of selected publications including these proceedings is presented in Appendix B.

The potential markets for agricultural and wallboard-grade gypsum are numerous and as yet untapped in many areas of the country. The primary consideration, especially in the upper Midwest, other than purity and presence of potentially problematic trace constituents, is the problem of transportation of gypsum from generally remote power plants to accessible markets. Using gypsum produced from scrubber sludge for agricultural applications is an easy way to overcome this particular problem, since remotely located power plants are often very near the agricultural markets.

Wallboard applications may necessitate the manufacture of wallboard near the source of the scrubber sludge, providing a higher-value product for transport to both local and remote markets. This requires a reliable, high-volume, and consistent quality source of scrubber sludge for gypsum production.

The EERC makes the following recommendations:

- Ex situ air oxidation is recommended for production of high-purity gypsum at the CCS site based on the laboratory- and pilot-scale demonstrations performed in this study. Many trace elements, especially heavy metals, favorably partitioned into the liquid phase during ex situ air oxidation, resulting in an especially pure form of gypsum. In situ forced oxidation systems would allow trace constituents to be included in the product.

- Past history with ash and analysis of air toxic trace elements at Coal Creek Station would indicate that trace elements are not currently a problem, however quality of any marketed product should be monitored on a regular basis. This is especially important if fuel sources change significantly.

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- Trapping of additional SO_2 to lower the initial pH of Coal Creek Station scrubber sludge could be used as a means to reduce sulfuric acid needed for pH control in the air oxidation process.

- Standards for agricultural gypsum trace element concentrations should be established based on total concentrations as well as plant availability and leaching potential. For scrubber sludge containing potentially problematic concentrations of trace elements, application limits and maximum soil concentrations would need to be established. Since different plant species accumulate and transport trace elements differently, this is an especially complex undertaking. Since accumulation of potentially toxic trace elements is a concern, not only with oxidized scrubber sludge but also with gypsum from natural sources, application should be based on need rather than a blanket amount. Additionally, as with the application of any foreign material on soil on which food will be grown, the accumulation of potentially harmful trace elements must always be kept in mind, especially if repeated application is anticipated or necessary. As was stated in the text of the report, magnesium depletion can be experienced with gypsum application to soils. This may require the addition of magnesium supplements.

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APPENDIX A

DESCRIPTION OF THE PILOT-SCALE DEMONSTRATION

DESCRIPTION OF THE PILOT-SCALE DEMONSTRATION

INTRODUCTION

Following bench-scale testing for proof of concept and basic process development, it was desirable to increase the scale of testing to determine the scalability of process parameters, the quality of the final product, and the potential for granulation/pelletization of the oxidized product. A pilot-scale oxidation process was assembled and operated to convert raw Coal Creek Station scrubber sludge to synthetic gypsum. The synthetic gypsum was subsequently washed, dewatered, and floor-dried prior to final analyses and pelletization/granulation testing.

EQUIPMENT

The pilot-scale oxidation testing was conducted in a 54-in.-diameter, insulated, stainless-steel tank with a 49-in. sidewall depth and a shallow, conical bottom. The nominal capacity of this tank was 500 gal. A 2-in. stainless-steel pipe was connected to the bottom of the tank cone and served as a drain. A single pneumatic mixer with a two-paddle impeller attached to a 55-in.-long shaft was used to maintain complete-mix conditions in the tank and to keep the sludge solids in suspension. Each impeller paddle had a surface area of approximately 0.188 ft^2. The pH of the tank contents was monitored via a Beckman Model 960B pH monitor/controller. Dilute sulfuric acid solution (20% H_2SO_4 [66° Be, technical grade] in deionized water) was added at a rate of approximately 0.1 gal/min with a peristaltic pump when called for by the pH controller. Compressed air from the Energy & Environmental Research Center (EERC) house air system (maintained at approximately 90 psig), in the form of fine bubbles, was supplied to the suspension through two 2-ft-long by 2½-in.-diameter flexible membrane tube diffusers produced under the trade name Sanitare* by the Water Pollution Control Corporation, Milwaukee, Wisconsin. Airflow to each diffuser was measured through rotameters scaled from 40 to 400 scfh. The bulk scrubber solution was transferred from 55-gal barrels to the reaction tank and subsequently back to the barrels via an air-driven diaphragm pump containing 12-in.-diameter diaphragms. Offgases from the oxidizing suspension were pulled from the reaction tank headspace via a 7.5 hp Sutorbilt induced-draft blower through a coarse-bubble diffuser in approximately 45 gal (170 L) of a $NaHCO_3$ scrubber solution and exhausted outside of the building. The blower was operated to pull a vacuum of approximately 24 in. of water.

PROCEDURES

Upon completion of pilot-scale equipment assembly, each of the 55-gal drums of scrubber sludge was placed into a barrel turner and rotated for up to 60 min to completely suspend any solids that had settled during shipment. When it was assured that all solids were resuspended, the contents of each barrel were immediately transferred to the reaction tank, where the raw scrubber sludge solids were maintained in suspension via the pneumatic mixer. When all eight barrels of scrubber sludge had been resuspended and transferred to the reaction tank, a sample of the raw scrubber sludge was taken to determine baseline oxidation conditions; the pH of the suspension was reduced to about 4.6 with 20% H_2SO_4 solution; and compressed air was turned on to the diffusers to start

the oxidation process. Samples of the suspension were taken periodically to determine the percent conversion of sulfite to sulfate. With the exception of the first night of the run, the oxidation procedure was continuous. A portable gas analyzer was used to measure the quality of the offgases in the reaction tank headspace in terms of O_2, CO_2, SO_2, and temperature. The offgases were drawn through a scrubbing solution composed of 1.87 lb (0.85 kg) of $NaHCO_3$ dissolved in approximately 45 gal (170 L) of tap water. When it was determined that the oxidation reactions had gone to completion, i.e., the majority of suspended solids had been converted to $CaSO_4 \cdot 2H_2O$, airflow to the diffusers was shut off and the oxidized suspension was transferred back to 55-gal drums for settling and decanting.

The oxidized solids were allowed to settle, and the supernatant wastewater was decanted from each barrel and pumped back to the 500-gal reaction tank. The settled solids were then triple-washed with deionized water to remove the majority of included contaminants. After each washing operation, the oxidized product was allowed to settle and the supernatant was decanted and combined with the initial wastewater volume. The final volume of wastewater, approximately 315 gal (1192 L), was neutralized with NaOH and discharged to the municipal sanitary sewer system.

Following the solids-washing operations, the wet solids were dewatered via vacuum filtration and transferred to 6-ft^3 totes for ease of transport. The dewatered solids were subsequently weighed and placed into windrows for floor drying. Electric fans were used to maintain air circulation over the windrows to promote drying of the synthetic gypsum product. When the product was dry to the touch and no longer wetted the concrete beneath the windrows, the material was recovered and placed into lined polyethylene 55-gal drums for storage. The floor-dried synthetic gypsum product was subsequently shipped to MMC Mars Mineral, Mars, Pennsylvania, for pelletizing tests. A small amount of the product was initially used to determine the unit operations and binding agent appropriate to produce satisfactory pellets. The remainder of the bulk sample was then processed into pellets and returned to the EERC.

RESULTS AND DISCUSSION

The eight drums of raw scrubber sludge received from Coal Creek Station contained a total net weight of about 4040 lb (1834 kg), with an initial solids content of 10%–12% and a bulk density of 69.5 lb/ft^3 (1.12 kg/L). After the material was resuspended and transferred from the drums to the reaction vessel, the pH of the suspension was adjusted down from the initial level of 7.7 to about 4.7 using 44 lb (20 kg) of 20% H_2SO_4 solution. The scrubber sludge was oxidized over a period of 80 hr, at which point nearly 98% of the calcium sulfite solids in the raw sludge suspension had been converted to gypsum. Figure 1 is a graph of percent conversion of scrubber sludge versus time. Two additional lines are shown on this chart. These represent linear regression lines plotted against select data. It was observed that the rate of oxidation during the first day was considerably faster than for the remainder of the run. Line 1 is a line thorough the origin and the first Data point recorded at 1 hr, at which time 5.47% of the sulfite had been converted to sulfate. Line 2 includes a data point at 4 hr, at which time 9.58% of the sulfite had been oxidized. These regression lines do not include sufficient data to be accurate; however, they can be used to demonstrate that it may have been possible to achieve complete conversion in a much shorter time than was experienced. It is interesting to note that the titration conducted on the first two grab
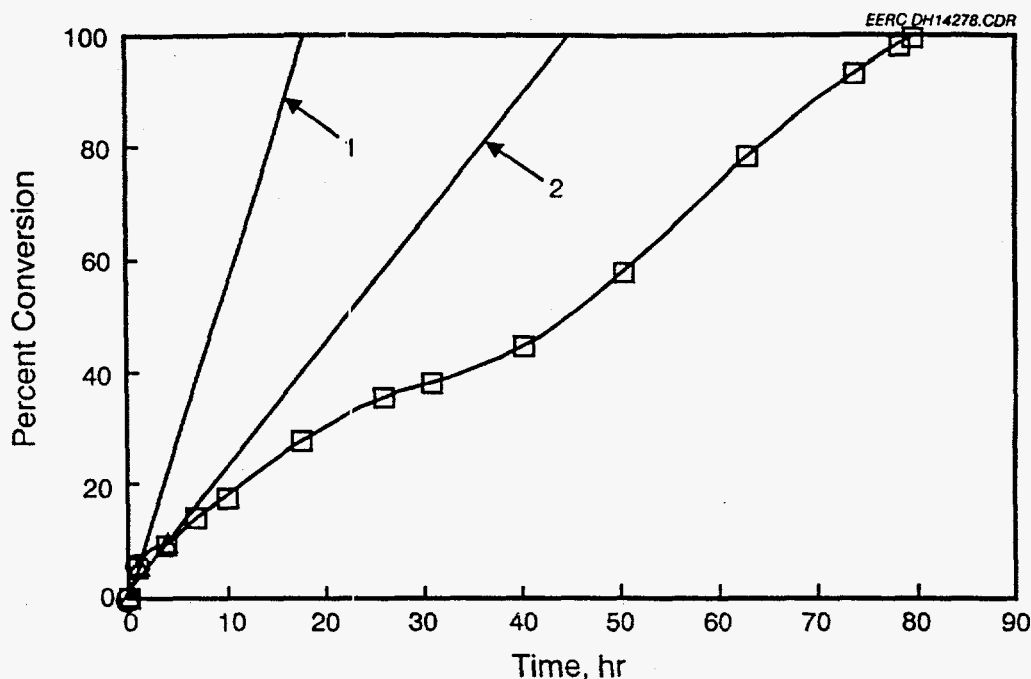
Figure 1. Percent conversion versus time for the pilot plant oxidation
of North Dakota Scrubber Sludge

samples taken, one from each of the first 2 hr of operation, indicated that the reaction was
proceeding at between 2.4% and 4.5%/hr. At this range of oxidation, it was estimated that the
suspended solids would be completely oxidized in from 20 to 40 hr. However, aeration to the
suspension was discontinued for 15.5 hr, from 1715 hr on Day 1 of the test, to 0845 hr on Day 2,
so that close inspection of the oxidation procedure could be maintained. Following resumption of
aeration on Day 2, the instantaneous oxidation rate never climbed above 1.6%/hr. The reason for
this decline in oxidation rate is unclear. It is possible that the suspended scrubber solids underwent
some type of chemical alteration during the 15.5-hr period of nonaeration due to the sulfuric acid
added to reduce the pH of the suspension. In laboratory experiments, it was observed that a tan,
very finely divided material tended to form with time. This material has not been characterized, but
may have coated scrubber sludge particles or in other ways interfered with the oxidation process.

To increase the rate of oxidation, the pH of the suspension was reduced to between 4.5 and
4.7 by adding 20% sulfuric acid. As the reaction proceeded, some of the acid in solution was
consumed and the pH increased slowly. To maintain the solution pH in the proper range, additional
acid was added as needed via a peristaltic pump connected to a pH monitor/controller. A total of
132.5 lb (60.2 kg) of the dilute acid was used throughout the course of the oxidation test to
maintain the desired pH. This reduces to about 3 gal (11.4 L) of concentrated sulfuric acid used to
oxidize the approximately 435 gal (1646.5 L) of raw scrubber sludge. The sulfuric acid
consumption resulted in the release of SO_2 into the headspace of the enclosed reaction tank. The
concentration of SO_2 in the reaction tank headspace averaged 152 ppm for the period of the test
prior to complete oxidation. For this same period of time, the maximum concentration of SO_2 was
332 ppm, while the minimum was 75 ppm. At the point at which the scrubber sludge solids were
completely oxidized, the pH of the suspension dropped from the normal operating level of

approximately 4.6 to near 3.0. This corresponded to a dramatic increase in SO_2 emissions, as the concentration of SO_2 in the reactor headspace increased to over 1200 ppm.

At the conclusion of the oxidation test procedure, the suspension was transferred to eight 55-gal open-top barrels to settle the oxidized solids and decant the supernate back to the reaction tank for final treatment and disposal. The moist settled solids were washed with deionized water at a ratio of about 0.25 gal of water per gal of moist solids three separate times to remove the majority of contaminants present among the gypsum crystals. The moist solids were then dewatered to an average moisture content of 28.5% via vacuum filtration at about 27 in. of Hg. The dewatered solids were floor-dried in two batches, the first batch for approximately 48 hr, and the second batch for over 120 hr, with similar results for both, i.e.; each batch lost the same percentage of moisture. The final moisture content of the material following floor drying indicated that the material was calcium sulfate hemihydrate with a nominal water content of 20 wt%. The total amount of synthetic gypsum produced and collected was 675 lb (306 kg), with an approximate bulk density of 47 lb/ft^3 (753 kg/m^3).

The supernate decanted from the oxidized and settled scrubber solids, along with the water used to wash the moist solids, represents a wastewater that required treatment prior to disposal. The 315 gal (1192 L) of collected wastewater was acidic and therefore was neutralized with NaOH at a rate of about 0.0078 lb/gal (0.935 g/L) to a pH of 7.0. The NaOH addition resulted in the formation of a lightweight yellow precipitate. Following neutralization, the wastewater was analyzed for chemical oxygen demand (COD), which measured 863 mg/L, filtered, and discharged to the municipal sanitary sewer. The use of COD must be approached with caution, since the presence of any unreacted sulfite as SO_2 could appear as COD. It is likely that the actual COD of this solution (minus the sulfite present) was considerably lower than the test results indicated. The precipitate that was filtered from the neutralized wastewater totaled about 80 lb (36 kg) at a moisture content of about 30%. The offgas scrubber solution had a final pH of 7.5 and a COD of 30 mg/L and was discharged without additional treatment.

The majority of the floor-dried gypsum product was shipped to MMC Mars Mineral for pelletization testing. MMC Mars Mineral performed three preliminary bench-scale tests on a small portion of the total sample to define the optimum processing operations to produce a quality pelletized product within the size range requested (6×20 mesh).

The first preliminary test was run using the synthetic gypsum and 3% plaster of paris ($CaSO_4 \cdot \frac{1}{2}H_2O$) by weight as the binding agent. The gypsum and binder were fed into a pin mixer with moisture addition, but at all operational settings attempted, satisfactory pelletization could not be achieved. This test produced a granular type of pellet (similar to a grain of salt), with only 20% of the final product in the required 6×20-mesh size range, 46.6% between 20 and 80 mesh, and the remaining 33.4% smaller than 80 mesh.

The second test was performed using the synthetic gypsum and a lignosulfonate (Norlig-H) as the binding agent. The Norlig-H was mixed with water at a concentration of 50% by weight and introduced into the pin mixer through spray nozzles. This test was more successful in producing a larger pellet with less overall fines. The particle-size distribution for the final product of the second test was as follows: 51.1% of the pellets fell in the 6×20-mesh size range; 33.5% were less than 20 mesh, of which 4.6% was less than 80 mesh and considered powder; and 15.4% were larger

than 6 mesh. Some of the larger pellets were due to lumps in the as-received raw material (synthetic gypsum).

The third test was essentially a repeat of the second test, except that the product from the pin mixer was then run through a disc pelletizer as a finishing step. In this application, the pin mixer was used to partially pelletize and condition the material. The conditioned material was passed through a 6-mesh screen to remove lumps that were not broken up in the pin mixer. This screened material was then run through the disc pelletizer with small amounts of binder added at the disc to complete the pelletization and help control final pellet sizing. With this series of operations, it was possible to produce 90.2% on-spec pellets, with only 0.7% smaller than 20 mesh.

Tests in addition to the sieve analyses mentioned above were performed on the raw material fed to the pelletization process as well as on the pelletized products. The results of these tests are shown in Tables A-1 through A-3. Since the plaster of paris binding agent was added directly to the synthetic gypsum prior to feeding to the pin mixer, a separate raw material analysis was performed for Test 1, as shown in Table A-1. The raw material was equivalent for Tests 2 and 3, and therefore only one raw material analysis was performed and is shown for these tests.

The remainder of the bulk sample sent to MMC Mars Mineral and not utilized for bench-scale testing was pelletized in an extended run using the same process used in Test 3 discussed above. As during Test 2, 50% Norlig-H lignosulfonate and water by weight was used as the binding agent. The bulk density of the Norlig-H and water mixture was 70.3 lb/ft³ (1.13 kg/L).

The synthetic gypsum was fed by hand into a 3-in. (7.6-cm) open-flight, volumetric feeder. The volumetric feeder delivered the material to a 12D54L pin mixer/pelletizer at a feed rate of 1080 lb/hr (490 kg/hr). The pin mixer was equipped with a 40-hp drive motor, with a variable-speed sheave and adjustable motor base. The rotor speed was set at 900 rpm, with motor current recorded at 24 amps. The moisture–binder mixture was injected into the pin mixer near the inlet side through a No. 4003 Spraying Systems spray nozzle at 26 psi. This is equivalent to a flow rate of 0.24 gpm (0.91 Lpm). The conditioned material exited the pin mixer at a moisture content of 25.4% by weight.

The partially pelletized, conditioned material was fed by hand into a Model P-30 pan pelletizer. The P-30 pan pelletizer is equipped with a 1-hp drive motor, with a variable-speed sheave and adjustable motor base. The pan is 3 ft (0.91 m) in diameter and has an 8-in. (20.3-cm) depth. The pan angle was set 36° from horizontal, and the pan was rotated at 16 rpm. Binder was added through a No. 4001 Spraying Systems spray nozzle and delivered intermittently to the 4 o'clock position at 0.07–0.09 gpm (0.26–0.34 Lpm). The conditioned feed material was delivered to the pan at the 3 o'clock position.

The conditioned material pelletized at a moisture content of 29.6% (by weight). Some difficulty was encountered keeping the product pellets within the target size range, which was 10×30 mesh for the extended test. The product pellets had a tendency to grow too large, with 75.7% larger than 10 mesh. Some of the product material that measured larger than 6 mesh was attributed to excessive buildup of material on the pan scrapers. The product of the extended run was then spread out on cardboard and air-dried for approximately 60 hr prior to repackaging and shipment back to the EERC. Upon receipt of the air-dried pellets at the EERC, the pellets were oven dried at 160°C for approximately 3 hr to complete the process. Tables A-4 and A-5 show the results of analyses performed on the pellets produced during the extended test.

TABLE A-1

Pelletization Testing – Raw Material Sieve Analyses

Mesh, U.S. Std.	Opening Size, in.	Test 1		Tests 2 and 3	
		Retained, %	Cumulative Retained, %	Retained, %	Cumulative Retained, %
10	0.0787	0.7	0.7	1.3	1.3
45	0.0138	1.6	2.3	2.2	3.5
80	0.0070	1.7	4.0	2.6	6.1
120	0.0049	1.5	5.5	2.0	8.1
200	0.0029	3.7	9.2	4.4	12.5
325	0.0017	9.5	18.7	11.9	24.4
Pan	0.0000	81.3	100.0	75.6	100.0

TABLE A-2

Pelletization Testing – Product Analyses

Analysis	Green Pellets	Air-Dried Pellets	Oven-Dried Pellets
Moisture Content, %			
Test 1	29.2	21.5	12.4
Test 2	26.1	20.6	14.3
Test 3	30.5	26.1	16.2
Bulk Density, lb/ft^3			
Test 1	43.4	45.4	53.5
Test 2	44.5	50.5	37.5
Test 3	58.3	55.7	47.3
18-in. Drop Test, average			
Test 1	4.0	2.0	1.0
Test 2	9.1	50+	50+
Test 3	9.8	6.4	50+
Crush Test, lb			
Test 1	0.0	0.0	0.0
Test 2	0.0	1.8	0.2
Test 3	0.0	0.0	3.5
Attrition Test, % loss			
Test 1	50.4	19.8	51.9
Test 2	37.3	2.3	6.0
Test 3	0.1	2.1	1.9

TABLE A-3

Pelletization Testing – Product Sieve Analyses

Mesh, U.S. Std.	Opening Size, in.	Test 1		Test 2		Test 3	
		Retained, %	Cumulative Retained, %	Retained, %	Cumulative Retained, %	Retained, %	Cumulative Retained, %
6	0.1320			15.4	15.4	9.1	9.1
10	0.0787	3.8	3.8	17.5	32.9	65.0	74.1
16	0.0469	8.2	12.0	20.4	53.3	23.1	97.2
20	0.0331	8.0	20.0	13.2	66.5	2.1	99.3
30	0.0232	6.8	26.8	13.0	76.5	0.4	99.7
40	0.0165	8.3	35.1	8.5	85.0		
60	0.0090	19.2	54.3	7.6	92.6		
80	0.0070	12.3	66.6	2.8	95.4		
Pan	0.0000	33.4	100.0	4.6	100.0	0.3	100.0

TABLE A-4

Extended Pelletization Testing – Product Analyses

Analysis	Green Pellets	Air-Dried Pellets
Moisture Content, %	29.6	18.5
Bulk Density, lb/ft^3	57.8	53.5
18-in. Drop Test, average	12.0	50+
Crush Test, lb	0.3	5.6
Attrition Test, % loss	0.2	0.7

TABLE A-5

Extended Pelletization Testing – Product Sieve Analysis

Mesh, U.S. Std.	Opening Size, in.	Retained, %	Cumulative Retained, %
6	0.1320	37.4	37.4
10	0.0787	38.3	75.7
16	0.0469	19.5	95.2
20	0.0331	3.2	98.4
30	0.0232	0.5	98.9
Pan	0.0000	1.1	100.0

APPENDIX B

SELECTED BIBLIOGRAPHY

SELECTED BIBLIOGRAPHY

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APPENDIX C

EQUIPMENT AND COST ESTIMATES
FOR PROCESS SCALE-UP

**DRAVO LIME
COMPANY**

May 30, 1997

Charlie Bullinger
Cooperative Power
Coal Creek Station
P.O. Box 780
Underwood, ND 58576-9759

Subject: Cost Estimate for Gypsum Production at Coal Creek

Dear Charlie:

Using the fuel chemistry and the plant operating data you supplied, I put together the attached mass balance for the oxidation facility. Also attached is a flow diagram and an estimate of the oxidation facility costs.

The estimate is fairly conservative. Some of the assumptions I made were: ·

- The CO_2 content of the solids was set equal to 2%. This is a very high number for a mag-lime scrubber. It is however the only CO_2 result I have from real scrubber solids. The sample was taken during the first week of testing the mag-lime process. The sulfuric acid consumption is directly related to this number. Typical CO_2's for Mg-lime scrubbers are .6 to 1.2. I would expect the acid consumption to be less than this spreadsheet is calculating.

- The oxidation air required for the process calculates to 12,500 scfm based on SO_2 in the inlet gas. The 15,000 scfm compressor was specified to better meet the demands when a sulfur spike is seen due to inconsistent coal quality. The compressor and

BRAVO LIME COMPANY

Charlie Bullinger
May 30, 1997
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oxidation tower may be greatly oversized due to natural oxidation in the scrubber. Microscope pictures of the scrubber solids show crystals with a structure typical of gypsum not calcium sulfite. The samples were submitted to our lab to determine the amount of sulfite oxidation in the crystals. To date, we do not have the results. If natural oxidation is high the size of the tower and compressor can be drastically reduced.

- The belt filter is sized to produce 10% moisture in the product gypsum. If 20% moisture is acceptable the belt filter could be much smaller (approximately 40%). This size reduction would greatly reduce the cost of the most expensive piece of equipment in the process.

- The scrubbers will continue to operate at 15-20% solids. This is necessary for the proper operation of the oxidizer.

It is very important at this time to get representative samples and analyze them for CO_2, S_{tot} and sulfite to nail down the oxidation plant size.

The plant layout would start with a catch basin in the bottom of each scrubber module. These catch basins would collect downcoming low pH scrubbing liquor and deliver it to a pump head tank. This tank would gravity overflow back into the recycle tanks. The oxidizer would be fed by pumping slurry form this head tank to the top of the oxidizer. The oxidizer will operate at a pH of 5.0 —5.6. H_2SO_4 will be added to achieve this. There will be two oxidizers, one for each unit. These oxidizers will be located in or near the scrubber buildings. The oxidized slurries from both units will be pumped to a centralized filter building. The gypsum slurry will be hydrocloned to separate the fines. The HC overflow will go to your existing pond where the fines can settle. The clear pond liquor can be returned as process water. The thickened, (HCUF) gypsum will be fed to a belt filter and dewatered. The filtrate becomes process makeup water and the gypsum is either trucked or conveyed to storage.

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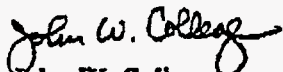
Charlie Bullinger
May 30, 1997
Page 3 of 3

The H_2SO_4 will be held in a storage tank near or in the centralized filter building and delivered to the oxidizers. The H_2SO_4 will need to be diluted with about 5-10 gpm of water before it enters the top of the oxidizer. This is to prevent a localized low pH and provide better acid mixing at the top of the oxidizer.

This plant will produce approximately 210,000 tons of gypsum per year based on a 91% capacity factor and 97% SO_2 removal of the entire gas stream. The bypass is closed to allow for this much gypsum production.

The attached estimate is a first pass and can be improved on once the solid and liquid phase chemistries become stable. The cost factors used are typical for most of the U.S. The North Dakota factor may need to be added for improved insulation or heat tracing. If you have any questions please call Kevin Smith 777-0715 as my last day is May 30th.

Good luck,

John W. College
John W. College
Manager of Technology

Attachments

cc: M. Babu
    R. Forsythe
    R. Todd
    K. Smith
    A. Stewart

Coal Creek Station
Equipment List for Oxidation Plant and Gypsum Filtering

	Quantity	Spares	Design Basis	Size	Material	Cost Per Unit	Total Cost	Const. Cost Index	Installed Cost
Downcomer Surge Tank	2	(one/unit) no spares	> 5 minute residence (always overflowing)	5' = d – 10' = h 1500 gallon	FRP	$5,000	$5,000	2.5	$12,500
Oxidizer Feed Pump	2	(one/unit) no spares	210 gpm 100' tdh	4/3 CAH Warman	Carbon Steel Rubber Lined	$7,500	$15,000	2.5	$37,500
OxidizerTowers	2	(one/unit) no spares	2.5 hr residence time 20% gas expansion 2 ft freeboard	12' = d 50' = h	FRP	$91,800	$183,600	2.5	$459,000
Air Compressor	1	(one/unit) no spares	15,000 SCFM 30 psi	—	—	$430,000	$430,000	2.0	$860,000
Sulfuric Acid Storage Tank	1	no spares	20,000 gallons/wk	25,000 gallons	Carbon Steel	$25,000	$25,000	2.5	$62,500
Oxidizer Acid Pump	2	(one/unit) no spares	1 gpm	Positive Displacement	Stainless Steel	$6,000	$12,000	2.0	$24,000
Oxidizer Product Pump	2	(one/unit) no spares	210 gpm 100' tdh	4/3 CAH Warman	Carbon Steel Rubber Lined	$7,500	$15,000	2.5	$37,500
Hydroclones	4	1 spare	100-130 gpm each 30 psi	6'- Warman	Carbon Steel Rubber Lined	$8,500	$42,500	2.0	$85,000
Belt Filter System	1	no spares	135 lbs/ft²/hr	3 meter x 13 meter Eimco Model 2M31 Extractor	SS	$700,000	$700,000	2.0	$1,400,000
Totals							$1,428,000		$2,978,000

COAL CREEK STATION
MATERIAL BALANCE
BASIS AND ASSUMPTIONS:

		Longview Lime Frac.	Dolomitic Lime Frac.
LIME ANALYSIS %		0.79	0.21
CaO	88.0	96	58
MgO	10.0	2	40
INERTS	2.0	2	2
	100	100	100

MEGAWATTS (Gross)	1100

COAL AS RECEIVED ANALYSIS PERCENT:

CARBON	35.00
HYDROGEN	8.60
OXYGEN	8.82
NITROGEN	0.60
SULFUR	0.70
CHLORINE	0.08
MOISTURE	38.20
ASH	12.00
TOTAL	100.00

HEATING VALUE,BTU/LB	6075
HEAT UP RATE, BTU/KW	9800
GAS INLET TEMP oF	300
GAS OUTLET TEMP oF	145
ESP REMOVAL EFF.,%	99.3
SULFUR OVERHEAD,%	100

DENSITY FORMULA COEFFICIENTS:

SLOPE	1.00737411
INTERCEPT	0.95388354

$$Y = M^X \cdot B$$

EQUIPMENT (operating)

NO. OF SCRUBBERS	4
NO. OF RECYCLE PUMPS	8

OPERATION

LIME SLURRY FEED %	20	
MODULE SOLIDS %	10	) based on
POND SETTLED SOLIDS %	40	) bone dry solids
SO2 REMOVAL EFFICIENCY %	97	
ASSUMED STOICHOMETRY	1.03	
OPERATING L/G	60	
CaO IN LIME FEED,LB/HR	20100	
TOTAL LIME FEED,LB/HR	22835	
OPERATING pH SCRUBBER FEED	8.5	
AVAILABLE Mg %	85.0	

SLUDGE COMPOSITION:

COMPONENT	mol.wt.	mol%	mass%
CaSO3*1/2H2O	129	90	89
CaSO4*1/2H2O	145	10	11

AVERAGE MOLECULAR WEIGHT:
130.6

HUMIDITY OF AIR	0.008 #/# OF AIR
% EXCESS AIR	40

OXIDIZER AIR STOICHS	3
(MOLES O2 USED/ MOLES O2 REQ'D FOR SULFITE OXIDATION)	
OXIDIZER OPERATING TEMP DEGREES F	140
OXIDIZER VAPOR PRESSURE PSI	2.89

CO2 CONTENT OF SCRUBBER SOLIDS WGT. %	2
H2SO4 SPECIFIC GRAVITY	1.84

GYPSUM SOLIDS SPLIT OVER FINES HC %	06
WATER SPLIT OVER FINES HC %	70

GYPSUM PRODUCT % SOLIDS	85
GYPSUM WASH WATER RATIO	2

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COAL CREEK STATION                      PAGE 2 OF 4                                      PRINTED:
MATERIAL BALANCE                                                                        13:42
CALCULATIONS:                                                                           5/23/97
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		#MOLES	#/HR	%vol	STACK GAS OUTLET TEMP	VAPOR PRESSURE (PSIA)	Regression Output:	
HEAT INPUT,MM BTU/HR	10099	STOICH O2 REQD.	83150					Constant	-7.405054
FUEL FIRING RATE,LB/HR	1702503	% EXCESS AIR	40					Std Err of Y Est	0.12703
SO2 IN,LB/HR	25006	GROSS O2 REQD.	116410	3725127				R Squared	0.9796907
SO2 OUT,LB/HR	753	NET O2	36368	1162992	5.83	120	1.6927	No. of Observations	13
SO2 REMOVED,LB/HR	24343	NITROGEN	438308	12272632	69.12	122	1.7881	Degrees of Freedom	11
SO2 REMOVED,MOL/HR	380.4	CARBON DIOXIDE	52284	2300494	8.25	124	1.8901		
SO2 Emission,#/MM BTU	0.07	WATER	106130	1910443	10.74	126	1.9959	X Coefficient(s)	0.0743802
		SULFUR DIOXIDE	392	25098	0.08	128	2.1063	Std Err of Coef.	0.003229
		HYDROGEN CHLORIDE	40	1475	0.01	130	2.2230		
		ASH		1508		132	2.3445		
SLUDGE GENERATED(DRY) LB/HR	43398	TOTAL FLUE GAS	634129	17693131	100.00	134	2.4171		
SO2 PICUP BY MG(OH)2 MOL/HR	46.1					136	2.6047		
CaO ACTIVE MOLES/100#LIME	1.6					196	2.7438		
MgO ACTIVE MOLES/100#LIME	0.2		40048.15			140	2.8892		
TOTAL ACTIVE MOLES(CaO+MgO)	1.8					150	3.718		
LIQ. SO4/SO3= RATIO	2.5					160	4.741		

```
pKa VALUE          6.05   Frac. SO3=      0.74                    TEMP SELECTED:      EXIT GAS % SATN (ASSUMED):
pH                 8.5                                                 145                       100

                                                               VAPOR PRESSURE:
                                                                   2.889 PSIA
                                                                   0.197 ATM

                                                             FLUE GAS OXYGEN, PERCENT:
                                                                    5.83
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| | | | | | | | | | PAGE 3 OF 4 | | | | | PRINTED: 13:42 5/23/97 |

COAL CREEK STATION
MATERIAL BALANCE

STREAM NO		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
BASE CASE		LIME FEED	SERVICE WATER	SLAKED LIME	SERVICE WATER	LIME SLURRY	PER MOD. LIME SLURRY	TOTAL FLUE GAS IN	TOTAL FLUE GAS OUT	PER MOD. FLUE GAS IN	PER MOD. FLUE GAS OUT	PER MOD. SCRUB. BLWDWN	RECYCLE RATE PER SCRB.	OXIDIZER FEED	OXIDIZER AIR	OXIDIZER VENT
COMPONENT	MW															
N2	28							12272632	12272831.6	3068158	3058157.912				56483.082	56483
CO2	44							2300494	2300494	575123	575123					
O2	32							1182892	1182892	295748	295748				1501449	10010
SO2	64							26090	753	8274	188					
HCl	36							1476	0	369	0					
H2O(VAP)	18							1910443	2322820	477011	580705				571.98067	10283
WATER	18		68506	81020	51333	112353	28089					48587	31335003	186349		
MgSO3	104											358	240885	1432		
MgSO4	120											1652	1111259	6609		
MgCl2	85											705	474439	2821		
H2SO4																
CaSO3*1/2H2O	129											9045	6487312	38560		
CaSO4*1/2H2O	145											1205	810215	4818		
CaSO4*2H2O	172															
FLY ASH								1508		376		376	253201	1506		
MgO	40	2278		337		337	84					04	56728	337		
CaO	56	20100		1315		1315	329					82	55278	329		
Ca(OH)2	74			24823		24823	6203					58	39129	233		
Mg(OH)2	58			2809		2809	702					0	0	0		
INERTS		457		457		457	114					114	76797	457		
TOTAL(LB/HR)		22835	68506	90761	51333	142094	35523	17694030	18079690	4423059	4519922	60868	40940318	243471	72070	76758
TOTAL GAS								17690131	18079690	4423283	4519022					
TOTAL SOLIDS		22835		29741		29741	7435	1500	0	376	0	11505	7778060	46259		
TOTAL(MOLS/HR) GAS								634089	656618	158522	164155				2518	2000
% SOLIDS		100	0	33	0	21	21					19	19	19		
SP. GR.			0.98	1.25	0.98	1.15	1.15					1.13	1.13	1.13		
LIQUID(GPM)			134	145	104	248	62					106	72379	430		
AVE. MOL. WT.								28	28	28	28				29	28
BULK DENSITY(#/CFT																
TEMP(oF)		80	80		80			300	145	300	145					
PRESS(psia)								15	15	15	15					
GAS FLOW (SCFM@60)								4005328	4147837	1001331	1036900				15907	18320
(ACFM)								5855491	4825287	1463873	1206317					
SO2 (PPM) Dry Gas								743	22	743	22					

COAL CREEK STATION   PAGE 4 OF 4   PRINTED:
MATERIAL BALANCE   13:42   5/21/97

STREAM NO BASE CASE COMPONENT	MW	16 H2SO4 REQUIRED	17 OXIDIZER DISCHARGE SLURRY	18 FINES HC OVERFLOW	19 FINES HC UNDERFLOW	20 GYPSUM FILTER PRODUCT	21 FILTER WASH WATER	22 FILTRATE	23 POND SETTLED SOLIDS	24 POND BLOWDOWN WATER	25 RECOVERED PROCESS WATER	26 SERVICE WATER	27 TOTAL LIQUOR TO SCRUB
N2	28												
CO2	44												
O2	32												
SO2	64												
HCl	36												
H2O(VAP)	18												
WATER	18		176857	123860	52997	8248	16490	61245	8332	117328	61245	428181	489406
MgSO3	104		0	0					0	0	0		0
MgSO4(l)	120		8261	5783	2478			2470	225	5058	2478		2478
MgCl2	95		2821	1975	846			846	90	1879	846		846
H2SO4	98	2061											
CaSO3*1/2H2O	129		0						0	0			
CaSO4*1/2H2O	145		0						0	0			
CaSO4*2H2O	172		57155	2858	54298	54298			2858	0			
FLY ASH			1506	1054	452	452			1054	0			
MgO	40		337	236	101	101			236	0			
CaO	56		329						0	329			
Ca(OH)2	74		233						0	233			233
Mg(OH)2	58		0						0	0			0
INERTS			457	320	137	137			320	0			
TOTAL(LB/HR)		2061	247756	135885	111309	63238	16490	64570	11109	125326	64570	428181	492083
TOTAL GAS													
TOTAL SOLIDS		0	60017	4468	54987	54987	0	0	4468	561	0	0	233
TOTAL(MOLS/HR)													
% SOLIDS			24	3	49	87	0	0	40	0	0	0	0
SP. GR.		1.84	1.10	1.01	1.41	1.86	0.98	0.98	1.32	0.99	0.98	0.98	0.98
LIQUID(GPM)		2	422	270	157	68	34	131	17	254	131	870	1002
AVE.MOL.WT.													
BULK DENSITY(#/CFT)													
TEMP(°F)												80	
PRESS(psia)													
GAS FLOW (SCFM@60) (ACFM)													
PPM Cl-										14984			1717

STREAM NO BASE CASE	FGD RECYCLE LIQUOR		
		lb/hr	mg/l
ION	MW		
Alka. as CaCO3			2579
H2O	18.0	31335093	
Cl	35.5	353739	10681
HSO3	81.1	45033	1478
SO3=	80.1	136473	4113
SO4=	96.1	887382	20745
S2O3=	112.1		0
Mg+2	24.3	402014	12118
Ca+2	40.1		0

Total liquid	lb/hr	33181657
	gpm	69323
	gpm	251058
Total solids	lb/hr	7778660
Total gas	lb/hr	
Total stream	lb/hr	40940318
	gpm	72379
Wt.% solids		19
pH		8.50

CALCULATION OF pH IN ABSORBER TOWER   PRINTED:

BASIS: (PER ABSORBER)   13:42

                                                                        5/23/97

250 = REGEN LIQUOR FLOW TO ABSORBER SUMP, GPM

72379 = RECIRCULATING FLOW IN ABSORBER, GPM

5591 = TOTAL SULFITE CONC. IN REGEN LIQUOR,PPM

6.5 = ABSORBER INLET PH

97 = SO2 REMOVAL ACROSS ABSORBER TOWER,%

743 = PPMV SO2 IN FLUE GAS INLET TO ABSORBER TOWER

1463873 = ACFM FLUE GAS INLET TO ABSORBER

300 = GAS INLET TEMP. TO TOWER, oF

RESULTS:

6274 = LBS/HR SO2 INLET TO ABSORBER

101 = LBS/MIN SO2 ABSORBED IN ABSORBER

4127 = SULFITE (SO3=) CONCENTRATION IN REGEN. LIQUOR, PPM

1464 = BISULFITE (HSO3-) CONC. IN REGEN LIQUOR,PPM

210 = MAKE PER PASS TOTAL SULFITES, PPM

5801 = TOTAL SULFITE CONCENTRATION IN ABSORBER SUMP LIQUOR, PPM

1885 = BISULFITE CONCENTRATION OF ABSORBER SUMP LIQUOR, PPM

3917 = SULFITE (SO3=) CONCENTRATION OF ABSORBER SUMP LIQUOR, PPM

67.51 = PERCENT OF TOTAL SULFITES IN ABSORBER LIQUOR THAT IS SO2=

5.85 = PH OF ABSORBER SUMP LIQUOR (FROM CHART) @pKa=6.06

28.47

WATER AND SO2 BALANCE AROUND SCRUBBER

	LB/HR	GPM
WATER IN	2512202	5024
WATER OUT	2512159	5024
DIFFERENCE	43	0
SO2 IN	26415	
SO2 OUT	26415	
DIFFERENCE	0	

Ca AND Mg BALANCE AROUND SCRUBBER

	LB/HR
Ca IN	13543
Ca OUT	13418
DIFFERENCE	126
Mg IN	2001
Mg OUT	2503
DIFFERENCE	-502

WATER AND SO2 BALANCE AROUND Plant

	LB/HR	GPM
WATER IN	2458443	4917
WATER OUT	2329759	4660
DIFFERENCE	128692	257

SO2 BALANCE AROUND PLANT

	LB/HR
SO2 IN	25098
SO2 OUT	872

Ca AND Mg BALANCE AROUND THE PLANT

	LB/HR
Ca IN	14357
Ca OUT	685
DIFFERENCE	13692
Mg IN	1374
Mg OUT	212
DIFFERENCE	1162

COAL CREEK
PROPOSED GYPSUM
FACILITY

FLUE GAS
IN

HEAD
TANK

TO POND

HYDROCLONE

FILTER

GYPSUM
PRODUCT

OXIDIZER

RETURN LIQUOR

H2SO4
STORAGE

AIR COMPRESSOR

V V V