

FINAL TECHNICAL REPORT
September 1, 1996, through August 31, 1997

Project Title: **MARKETABLE AMMONIUM SULFATE FERTILIZER AND FINE CALCIUM CARBONATE FROM FGD-GYPSUM**

ICCI Project Number: 96-1/3.2A-2
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ABSTRACT

The overall goal of this project is to assess the technical feasibility of a process to produce two marketable products, ammonium sulfate fertilizer and precipitated calcium carbonate (PCC), from wet limestone flue gas desulfurization (FGD) by-product gypsum. The wet FGD process, although effectively removing SO₂ by using limestone, produces a large amount of solid gypsum. Power plants burning high-sulfur coal and using the FGD technologies, in addition to installation and operation expenses, are facing expensive landfill disposal costs for the gypsum. Also, the CAA Amendments of 1990 required SO₂ emissions be further reduced from 2.5 to 1.2 lb/MBtu by the year 2000, which will further decrease the sulfur compounds from air deposition and result in a growing demand for sulfur as a plant nutrient. Our previous study (1994-1995) focused on a process that converted gypsum to ammonium sulfate fertilizer with a by product PCC. The cost estimates suggested that the process is economically feasible when granular size ammonium sulfate crystals are produced, however, the process conditions to produce an acceptable PCC for commercial utilization were not taken into consideration, which is the main objective of this phase of the investigation.

In the current study, various specifications for commercial applications of calcium carbonate, both ground and precipitated, were reviewed. The most significant attributes of carbonate fillers that determine their usefulness in industry are particle size (i.e. fineness), whiteness (brightness), and mineralogical and chemical purity. Reaction conditions are used to control the size and shape of the PCC particles produced, and removal of colored impurities in the gypsum increased the whiteness of the PCC products. The impurities of the gypsum from Abbott power plant were recognized and their removal methods were developed. The results suggested that either limestone with minimum colored impurities should be used during FGD processes, or purification procedures for FGD-gypsum could be used to produce a high whiteness of PCC for higher value commercial applications. The research effort is being continued in modifying reaction conditions and purification procedures for a production of a high quality PCC adequate for paper applications.

EXECUTIVE SUMMARY

Wet flue gas desulfurization (FGD) processes that use limestone as a scrubber for SO₂ and produce gypsum as a by-product have a considerable level of commercial development and demonstrated operational experience. These pollution control technologies will remain preferred choices for Phase-II compliance if successful commercial utilization of FGD by-products is developed to offset the cost of equipment installation, operation, and by-product disposal. A FGD system installed on a 500-MW plant burning 3.5% sulfur coal, with a desulfurization efficiency of 95% and a load factor of 65%, generates about 31 tons of gypsum per hour. From an environmental and economic standpoint, it is desirable to use this by-product as a feed material to produce a salable product. The goal of this project is to assess the technical feasibility for producing the dual commercial products, ammonium sulfate fertilizer and precipitated calcium carbonate, from this gypsum.

Ammonium sulfate is a valuable nutrient source for providing both nitrogen and sulfur to growing plants. There is a growing demand for sulfur in the sulfate form as a plant nutrient because of decreased sulfur compounds in atmospheric deposition. More stringent regulations to reduce sulfur dioxide emissions by the year 2000 (from 2.5 lbs SO₂/10⁶ Btu to 1.2 lbs SO₂/10⁶ Btu) suggest a growing demand for sulfur nutrients in the soil by the first decade of the 21st century. Also, the trend toward using high nitrogen content fertilizers has pressed incidental sulfur compounds out of traditional fertilizer. The current market for ammonium sulfate in the United States is about two million tons per year. It is anticipated that 5 to 10 million tons of new ammonium sulfate production may be required annually in fertilizer markets as a result of the acid-rain control program. The fertilizer industry is seeking a greatly increased source of such product to supply sulfur in nitrogen-phosphorus-potassium (N-P-K) fertilizer blends.

Production of fine calcium carbonate, by either wet-grinding natural high-calcium limestone (GCC) or by chemical precipitation (PCC), is becoming one of the most competitive industrial minerals markets. In traditional acid paper making, wood fiber is used as a filler and titanium dioxide (TiO₂) is used as an additive to enhance the paper's whiteness. In alkaline paper making, PCC (at \$100 to \$300 per ton) can be used as a filler, which costs less than wood fiber (at \$500 to \$600 per ton). Some PCC can also offer such good light scattering quality that it can replace the much more expensive TiO₂ (\$2,000 per ton). Specialty Minerals Inc. has patented technologies to chemically manipulate the morphology of PCC crystals and currently offers its customers 12 different types of PCC. Particle sizes of these products range from 10 μm to 0.01 μm with shapes including spherical, scalenohedral, and rhombohedral. Due to the increasing use of alkaline paper making, PCC sales accounted for about 40% of the Specialty Minerals' \$428 million in sales for 1993, up \$46 million (30%) compared to 1992. Specialty Minerals is currently focusing on the paper industry, but in the future the company hopes to bring its PCC to new markets in the paint and plastic manufacturing industries.

In our previous study (1994-1995) on the current process to make ammonium sulfate from FGD-gypsum, the potential commercial applications for the by-product precipitated calcium carbonate (PCC) was not taken into consideration. The results from previous cost estimates,

without considering the sale of the PCC produced, indicated that there was a healthy profit margin for converting FGD-gypsum to ammonium sulfate if a granule size of 1.2 to 3.3 millimeters could be produced. The results suggested that considering the potential markets of the PCC produced by the process would further improve the economics. Also, the average sale price of ammonium sulfate has been increasing. For example, for the years 1993, 1994, and 1995, the average price per ton was \$129, \$138, and \$146, respectively. With the sale of ammonium sulfate at these prices, plus the possible sale of PCC by-product, the conversion of FGD-gypsum to ammonium sulfate and PCC becomes an attractive process that could improve the economics of FGD systems in Illinois.

The overall goal of this project is to assess the technical feasibility for producing the dual commercial products, ammonium sulfate fertilizer and PCC, from FGD-gypsum. Specific objectives of this phase of study were:

- I. Assess knowledge on the current uses of fine calcium carbonate and their specifications for various commercial applications
- II. Obtain and analyze a FGD-gypsum sample from an Illinois power plant for the work proposed in the project.
- III. Refine the process engineering data, process conditions, and/or the process flow diagram which are required for process scale-up and technical and economical feasibility studies.
- IV. Determine the influence of the properties of the FGD-gypsum and process conditions, if any, on the quality of the ammonium sulfate and calcium carbonate produced.
- V. Evaluate the market potential of the by-product PCC made from conversion of FGD-gypsum to ammonium sulfate fertilizer.
- VI. Prepare progress and final reports, presentations, and publications of the results.

A survey of literature to determine the current application, specification, and price of fine calcium carbonate and to define possible process limitations that need further examination was conducted. The most significant attributes of carbonate fillers, that help determine their usefulness in industry application, are particle size (i.e. fineness) and shape, whiteness (brightness), and mineralogical and chemical purity.

The particle size of commercial grades of carbonate fillers covers the range from 149 microns (100 mesh) to less than 5 microns. Some producers offer as many as twenty products each with a different particle size distribution. In many instances the products were designed to meet the special requirements of a certain application. Such specifications are normally the result of development work, which identifies superior performance characteristics for such "non standard" products. Changes in particle size distribution can cause a measurable change in product performance in some applications. The oil absorption or water demand of a filler is a function of its surface area. Packing density of the particles affects oil absorption, resin or water demand, and also the viscosity of aqueous and organic

systems. Particle size is therefore rigidly controlled at all times during production.

A ground calcium carbonate normally has a rhombic morphology, since this is the natural shape of calcite fragments. With PCC the possibilities are more varied. The most popular PCC filler has the scalenohedral morphology, which very easily combines a suitable specific surface with any particle size wanted. Rhombohedral PCC plays a role in paper filler but is of more interest as a coating PCC. The aragonite is used for special purposes where more exotic properties of the paper are sought. The pseudo-amorphous PCC is really agglomerates of very fine calcite crystals. No practical use for these products is known, but they are of interest to the PCC producer since they tend to show up if control over the process is lost.

Whiteness of a carbonate filler is an important property of PCC for applications in paint, plastics, and paper industries. Other applications are less demanding, allowing the use of off-white to gray products. The use of off-white carbonate fillers for asphaltic roofing, asphaltic sealers, carpet backing, jointing and caulking compounds as well as some plastic applications are dependent upon filler properties such as particle size, freedom from abrasive components, and other performance related characteristics (oil absorption, bulk density, etc.).

Research, by PCC producers and users, continues to develop new products and applications for carbonate fillers. Finer products, and coated or surface modified products, have been introduced in recent years for special uses. In the past 12 years, there have been a period of dynamic growth in the use of calcium carbonate fillers. New applications, particularly in the plastics and paper industry, have necessitated expansion and upgrading of existing plants and the development of new facilities. This trend is expected to continue.

Chemical composition and particle size distribution of the FGD-gypsum sample collected from the University of Illinois Abbott Plant, Champaign, IL, were analyzed. The results showed that the sample contained 98.60% gypsum with impurities of limestone (CaCO_3) 0.82%, MgCO_3 0.25%, silica 0.40% in SiO_2 , iron 0.04% in Fe_2O_3 , and magnesium 0.12% in MgO . The analysis of the four size-separated fractions showed that the most coarse, >100 mesh, fraction was less than 9 wt % of the total gypsum, but it contained mainly colored particles and this fraction was rejected from any feed application in this investigation. The PCC products from reagent grade gypsum, or purified FGD-gypsum, have a whiteness greater than 97% which is good for any application. However, the particle size of the PCC products is good for some applications. The results of this study suggested that in order to decrease the colored impurities such as iron and organic carbon in the gypsum, to produce a high whiteness PCC, limestone with minimum colored impurities should be used during the FGD process, or purification procedures for FGD-gypsum are needed to produce a high whiteness of PCC for high value commercial applications. Further improvement of the overall qualities of the PCC products should lead to a product that is adequate for any application.

OBJECTIVES

The overall goal of this project is to assess the technical feasibility for producing commercial-grade ammonium sulfate fertilizer and fine calcium carbonate from FGD-gypsum. This project focuses on optimizing the process conditions, providing process engineering data, and investigating the market demand for the by-product calcium carbonate.

Specific objectives of this phase study were:

- I. Assess knowledge on the current uses of fine calcium carbonate and their specifications for various commercial applications
- II. Obtain and analyze a FGD-gypsum sample from an Illinois power plant for the work proposed in the project.
- III. Refine the process engineering data, process conditions, and/or the process flow diagram which are required for process scale-up and technical and economical feasibility studies.
- IV. Determine the influence of the properties of the FGD-gypsum and process conditions, if any, on the quality of the ammonium sulfate and calcium carbonate produced.
- V. Evaluate the market potential of the by-product PCC made from conversion of FGD-gypsum to ammonium sulfate fertilizer.
- VI. Prepare progress and final reports, presentations, and publications of the results.

INTRODUCTION AND BACKGROUND

The United States Department of Energy's Clean Coal Technology program and the 1990 amendments to the Clean Air Act, mandating a 2-stage 10-million ton reduction in sulfur dioxide emissions in the United States, have especially encouraged the use of FGD technologies. In addition to installation and operational expenses, plants burning high sulfur coal and using FGD technologies must also bear increasingly expensive landfill disposal costs for the solid waste produced. The FGD technologies would be economically favored by many utilities if successful, commercial uses were developed for the gypsum-rich by-products of the wet limestone FGD process. Such developments would encourage the continued use of high-sulfur Illinois coals by electric utilities.

EXPERIMENTAL PROCEDURES

Six tasks were included to meet the objectives.

Task 1. Conduct a literature study (ISGS)

In the previous study, chemistry of the process and process condition for making ammonium sulfate from gypsum have been reviewed. The information obtained was used to set up a reactor system and to conduct preliminary tests. In this study, a further literature survey was conducted to consider any beneficial process variation, calcium carbonate by-product specification, and process limitations that need further examination.

The search by Engineering Index from 1986 to 1996, GeoRef from 1800 to 1996, Carl from 1952 to 1996, Wilson from 1986 to 1996, First Search from 1920 to 1996, Dissertation from 1900 to 1996, and Chemical Abstracts from 1986 to 1996 has given more than 40 useful references.

Task 2. Acquire samples of FGD-gypsum (ISGS, APP, and CWLP)

A new batch of the FGD-gypsum from the University of Illinois Abbott Power Plant in Champaign, IL, was collected during this study. The FGD sample was dried under room air before it was split into 64 bags for storage. Chemical characterization and size fractionation of this sample were completed.

The Abbott Power Plant operates a Chiyoda Thoroughbred 121 (CT 121) FGD-desulfurization system (Maller and Stevens 1990) and produces greater than 1 ton of gypsum (> 98% purity) for every 10 tons of coal burned. The gypsum produced is currently used by farmers to improve land quality.

Task 3. Conduct a bench-scale production of ammonium sulfate and calcium carbonate (ISGS)

A bench-scale reactor system based on the published operating parameters (George and Gopinath, 1963; Blouin et al., 1970; Kenton, 1985) was established in the previous study (Chou, 1995). The system previously used composed of a three neck, 1000 ml round bottom flask with baffles, equipped with a mechanical stirrer, a thermocouple, and a condenser. A heating mantle was used to control the reactor temperature. In the current study, this heating system was modified and replaced by a constant temperature control system to improve the performance. The major reactant ammonium carbonate in solution was prepared by dissolving ammonia in water and bubbling carbon dioxide into the ammonium water or by mixing ammonium bicarbonate with ammonia water. During the major reaction, a gypsum slurry was allowed to combine with the ammonium carbonate in solution to produce ammonium sulfate in solution and calcium carbonate in suspension. After completion, the solution, which contained the ammonium sulfate product, was

separated from the solid by-product, calcium carbonate, by vacuum filtration. The filtrate plus the rinsing were concentrated in a constant temperature water bath and stored for analysis. The calcium carbonate was dried under ambient air before determining the total weight. Detailed analysis were conducted in Task 4 to determine its purity and quality.

Separated experiments were conducted to determine the rate of the gypsum conversion, and the effect, if any, of the impurity and the reaction conditions on the quality of the PCC produced. A mathematical calculation was also considered to formulate a possible model for the gypsum conversion reaction. The purpose was to compare the data obtained from the laboratory tests with those predicted from the model calculation to give a better direction to process modifications for a controlled reaction. The resulted data were examined in Task 5 for process variations and limitations.

Task 4. Perform characterization studies (ISGS, SM, AS, and HF)

The amounts of free water (released at 45°C) and combined water (released at 230°C) for the whole gypsum sample and the content of calcium oxide (CaO), magnesium oxide (MgO), and carbon dioxide in the sample were analyzed according to ASTM C471 procedures. Based on the analytical results, the composition of these components were then calculated: %CaCO₃, %MgCO₃, %CaSO₃, %CaSO₄.2H₂O, and %(NH₄)₂SO₄ (Table 1).

The typical particle size distribution of the FGD-gypsum of the Abbott plant collected in this study was analyzed by sieve analysis. The sample was separated into four fractions: A) greater than 100 mesh, B) between 100 and 200 mesh, C) between 200 and 400 mesh, and D) less than 400 mesh. The PCC products produced from whole gypsum sample and four fractionated samples were analyzed for its particle size distribution by the Microtract Analyzer at the ISGS. Other ISGS facilities, such as TGA, XRD, XRF, AA, and ICP instrumentation were also used for characterizing the chemical, physical, and mineralogical properties of the feed materials (FGD-gypsum) and the PCC products. These analysis focused on identifying superfine particle size, crystal shape, and impurities of the sample.

Task 5. Evaluate products and the process flow sheet (ISGS, SM, AS, HF, CIPS, and CWLP)

The process engineering data and process parameters obtained from Task 3, and the product properties from Task 4 were examined. Relationships, if any, between the relevant physical and chemical characteristics of the products and the process parameters were examined. Advantages of process variations and limitations of the process were identified. The quality of the calcium carbonate produced were compared with those commercially available. Market potential of the products were estimated. Such results provided a better direction to process modifications for a controlled reaction, and help in determining the technical and economical feasibility for commercial production of ammonium sulfate and calcium carbonate from utility gypsum.

Task 6. Prepare reports, publications, and presentations of results (ISGS)

Three progress reports were submitted to the ICCI. The results of this investigation were presented at the 15th ICCI Contractor's Technical Meeting. After clearance with patent application, the results will be submitted for other publication.

RESULTS AND DISCUSSION

Literature Study (Guillet and Watson, 1983; Roskill Information Service Limited, 1991)

A survey of literature to determine the current application, specification, and price of fine calcium carbonate, and to define possible process limitations that need further examination was conducted. The search by Engineering Index from 1986 to 1996, GeoRef from 1800 to 1996, Carl from 1952 to 1996, Wilson from 1986 to 1996, First Search from 1920 to 1996, Dissertation from 1900 to 1996, and Chemical Abstracts from 1986 to 1996 had resulted more than 40 useful references.

The commercial uses of carbonate fillers cover a wide spectrum of applications, specifications, and prices. The most important properties of carbonate fillers that determine their usefulness in industrial applications are particle size (fineness) and shape, whiteness (brightness), and mineralogical and chemical purity.

Specifications

Particle Size-The particle size of commercial grades of carbonate fillers covers the range from 149 micron (100 mesh) to less than 5 microns. Some producers offer as many as twenty products each with a different particle size distribution. In many instances the products were designed to meet the special requirements of a certain application. Four standard grades are recognized by the American Society for Testing Materials (A. S. T. M.), or are designated by the Pulverized Limestone Association. Within each grade are a number of filler products that fall within the specifications published for these grades. However, consumers of carbonate fillers may request specifications which differ from published standards. Such specifications are normally the result of development work, which identifies superior performance characteristics for such "non standard" products.

Particle size distribution is influenced by the grinding and classification method employed (GCC) as well as by process conditions used (PCC). Changes in particle size distribution can cause a measurable change in product performance in some applications. The oil absorption or water demand of a filler is a function of its surface area. Packing density of the particles affects oil absorption, resin or water demand, and also the viscosity of aqueous

and organic systems. Particle size is therefore rigidly controlled at all times during production.

