ABSTRACT

The overall goal of this project is to assess the technical and economic feasibility for producing dual-marketable products: ammonium sulfate fertilizer and precipitated calcium carbonate (PCC), from wet limestone flue gas desulfurization (FGD) by-product gypsum. Since utilities using FGD are challenged by expensive landfill disposal costs, successful production of fertilizer from FGD-gypsum would economically favor FGD technology. The economics of the conversion process will be improved by an additional revenue from sale of by-product, PCC.

Phase I of this project focused on an economical process to produce ammonium sulfate fertilizer. Phases I and II used gypsum from Abbott Power plant for laboratory process development. Phase II reviewed various specifications for commercial applications of fine calcium carbonate, both ground and precipitated. Also, the quality of PCC produced from Abbott gypsum was evaluated. The results suggested that limestone with low iron and low organic carbon should be used during FGD process, otherwise, purification procedures for FGD-gypsum (front end purification) or for PCC (back end purification) are needed to improve the quality of the PCC by-product for higher value commercial applications, such as papers and paints.

During phase III, a sample of FGD-gypsum was obtained from a different source, City Water Light and Power Co. The objectives of this phase were to evaluate the chemical properties of ammonium sulfate made from this FGD-gypsum; to estimate its effect on soil productivity; to develop or modify the process in order to purify the gypsum; and to determine engineering parameters and a process flow diagram to aid in the design and construction of a pilot plant. The results indicated that the impurities in the ammonium sulfate produced would not impose any practical limitations on its use at application levels employed by farmers. Removal of impurities from the gypsum prior to the conversion reaction resulted in improved whiteness of the PCC. Estimates of the production cost indicated that the economics for fertilizer production improved significantly with increased revenue from PCC sale and decreased disposal costs for the FGD-gypsum.
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 both environmental and economical standpoints, it is desirable to use this by-product as a feed material to produce salable products. The overall goal of this on-going project is to assess the technical and economic feasibility for producing the dual commercial products, ammonium sulfate fertilizer and precipitated calcium carbonate (PCC), from FGD-gypsum.

Ammonium sulfate is a valuable nutrient source for both nitrogen and sulfur for growing plants. There is an increasing 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) 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 more ammonium sulfate production may be required in fertilizer markets as a result of implementing the more stringent 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 as ground calcium carbonate (GCC) or PCC is becoming one of the most competitive industrial minerals markets. In traditional acid papermaking, 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/ton) can be used as a filler, which cost less than wood fiber (at $500 to $600/ton). Some PCC can also offer such good light scattering quality that it can replace the much more expensive TiO₂ ($2,000/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 0.01μm with shapes including spherical, scalenohedral, and rombohedral. 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 addition to Specialty Minerals, four other major industrial and commercial partners have expressed an interest and desire to work with the ISGS on this project. They are AlliedSignal (Hopewell, VA), one of the largest producers of ammonium sulfate in the United States; Agrium US Inc., a fertilizer company at Henry, Illinois; the
The overall goal of this project is to assess the technical and economic feasibility for producing the dual commercial products: ammonium sulfate fertilizer and PCC, from FGD-gypsum. Phase I of this project focused on an economical process to produce ammonium sulfate fertilizer (Chou 1994-1995). The results from cost estimates, without considering the high value commercial applications 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. Phases I and II used gypsum from Abbott Power plant for laboratory process development. Phase II (Chou 1996-1997) reviewed various specifications for commercial applications of fine calcium carbonate, both ground and precipitated. Also, the quality of PCC produced from Abbott gypsum was evaluated. The results from both literature and laboratory studies indicated that the particle size of PCC met the Grade II size classification; therefore, useful in paints. The influence of impurities of gypsum on the quality of the PCC produced was also established. The results suggested that impurities, such as iron and organic carbon in the gypsum need to be removed to improve the whiteness of the PCC produced. Limestone with low iron and low organic carbon should be used during FGD process, otherwise, purification procedures for the starting FGD-gypsum or for the PCC by-product are needed to improve the quality of the PCC by-product for higher value commercial applications.

During phase III of this project, a bulk sample of FGD-gypsum was obtained from another source, City Water Light and Power Co. Purification procedures for front end purification of the FGD-gypsum, ammonium sulfate product evaluation, process modification for effective removal of FGD-gypsum impurities, and engineering evaluation of the process were emphasized. The objectives of the phase III were: to evaluate the chemical properties of ammonium sulfate made from FGD-gypsum; to evaluate its effect on soil productivity; to develop or modify the process in order to purify the gypsum; and to establish an engineering package which could be easily updated as new information becomes available to aid in the design and construction of a pilot plant.

An effective purification procedure for FGD-gypsum to make white PCC was developed. The purified gypsum was used to prepare ammonium sulfate and PCC using the basic processing in solid-liquid phase reaction developed during phase I of the project. The ammonium sulfate product was analyzed for elements which are considered harmful in fertilizers. The data suggested that there would be no problem to use our ammonium sulfate product on soils at normal application rates used by farmers. A preliminary analysis indicated that the whiteness of the PCC made from purified gypsum improved significantly when compared with those made from raw gypsum.

A modification of the basic process was conducted to examine a procedure using liquid phase reaction. The results showed that production of high whiteness of PCC was achievable. However, the modified process is not economically feasible unless the solubility of gypsum in ammonia water can be improved. Literature data indicated that gypsum was soluble in ammonium salts. Further study was made to examine to what extent the
ammonium salts, such as ammonium nitrate, ammonium phosphate, or ammonium chloride, could be used to improve the solubility of gypsum in ammonia water. The results indicated that ammonium chloride could significantly improve the solubility of gypsum and produce high whiteness of PCC products. However, the conversion (maximum yield) using the modified process in liquid phase reaction was not as effective as that using the basic process in solid-liquid phase reaction.

The current engineering study by the Midwest Industrial Design has examined each unit operation, equipment needs, process conditions, engineering parameters, advantages and disadvantages of process variation, process limitation, and the basic process flow diagram. Estimates of the production cost indicated that the economics for fertilizer production improved significantly with increased revenue from PCC sale and decreased disposal costs for the FGD-gypsum. Possible alternatives for the overall improvement of the process were also suggested. A basic engineering package which can be easily updated as new information becomes available is initiated to aid in the design and construction of a pilot plant.

The remainder of this report contains proprietary information and is not available for distribution except to the sponsor(s) of this project.