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TECHNICAL REPORT
September 1 through November 30, 1994

Project Title: **MANUFACTURE OF AMMONIUM SULFATE FERTILIZER FROM FGD-GYPSUM**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)
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ABSTRACT

The overall goal of this project is to assess the technical and economic feasibility for producing commercial-grade ammonium sulfate fertilizer from gypsum produced as part of limestone flue gas desulfurization (FGD) processes. This is a cooperative effort among the ISGS, the UIUC, AlliedSignal, SE-ME, Henry Fertilizer, Illinois Power Co. (IP), and Central Illinois Public Services (CIPS). Bench-scale experiments will be conducted to obtain process engineering data for manufacture of ammonium sulfate from FGD-gypsum and to help evaluate technical and economical feasibility of the process. Controlled greenhouse experiments will be conducted at UIUC to evaluate the chemical impact of the produced ammonium sulfate on soil properties. A process flow sheet will be proposed and market demand for the products will be established. An engineering team at IP will provide an independent review of the economics of the process. AlliedSignal will be involved in testing and quality evaluation of ammonium sulfate samples and is interested in an agreement to market the finished product. CIPS will provide technical assistance and samples of FGD-gypsum for the project.

In this quarter, a literature study that should give detailed insight into the chemistry, process schemes, and costs of producing ammonium sulfate from gypsum is in progress at the ISGS. Acquisition of a high quality FGD-gypsum sample was completed. Collecting of the other lower grade sample was scheduled to be conducted in December. Characterization of these feed materials is in progress.

EXECUTIVE SUMMARY

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 operating 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 made economically favored by many utilities if successful commercial uses are 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.

In this study, the FGD-gypsum will be tested for conversion to calcium carbonate and ammonium sulfate by reacting it with CO_2 and ammonia or by reacting it with ammonium carbonate. This process could provide electric utilities a means to convert the CO_2 and SO_2 in their exhaust gases to useful commercial products. The fertilizer industry would also be provided with a large source of ammonium sulfate to supply sulfur nutrient in NPK fertilizer blends. Five to 10 million tons of new ammonium sulfate production may be required in the fertilizer market annually and there will be opportunities in the fertilizer industry for a greatly increased source of such a product.

Goals and Objectives

The overall goal of this project is to assess the technical and economic feasibility for producing commercial-grade ammonium sulfate fertilizer from FGD-gypsum. The project focuses on developing process engineering data, costs for the production of the fertilizer, and market demand for the product in the agricultural community. If successful, the results of this project could lead to a solution, from both environmental and economic standpoints, to the problem of disposing large quantities of by-products from FGD processes.

Specific objectives of this study are

I. Assess current knowledge on the chemistry, process schemes, and production costs of ammonium sulfate from gypsum.

II. Obtain samples of FGD-gypsum from two Illinois power plants for the work proposed in the project.

III. Obtain engineering data required for process scale-up and the technical and economic feasibility studies.

IV. Determine the influence of the properties of the gypsum and process conditions on the quality of the ammonium sulfate produced.

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V. Evaluate the impact of continued use of ammonium sulfate on soil chemical properties.

VI. Establish a process flow sheet for the production of ammonium sulfate from FGD gypsum and evaluate the production costs and the market potential for the product.

This project is a cooperative effort between the ISGS, UIUC, AlliedSignal, SE-ME, Henry Fertilizer, Illinois Power Co. (IP), and Central Illinois Public Services (CIPS).

The project consists of seven tasks. Bench-scale experiments will be conducted to obtain process engineering data for manufacture of ammonium sulfate from FGD-gypsum and to help evaluate technical and economical feasibility of the process. Controlled greenhouse experiments will be conducted at UIUC to evaluate the chemical impact of the produced ammonium sulfate on soil properties. A process flow sheet will be proposed and market demand for the products will be established. IP will provide an independent review of the economics of the process. AlliedSignal will be involved in testing and quality evaluation of ammonium sulfate samples and is interested in an agreement to market the finished product. CIPS will provide technical assistance and samples of FGD-gypsum for the project.

In this quarter, analytical data on FGD-gypsum samples that were generated by various power stations were examined. Based on these examinations, two samples were selected as feed materials for ammonium sulfate production. Acquisition of a high quality FGD-gypsum sample (Task 2) produced from the Abbott power plant in Champaign, IL was completed. Collecting another lower quality sample from CIPS, Newton Power Plant, Jasper, IL, was scheduled to be conducted in December.

A literature study (Task 1) that should give detailed insight into the chemistry, process schemes, and costs of producing ammonium sulfate from gypsum is in progress at the ISGS and will be continue in the next quarter. The results of the literature study will be used to design a batch, bench-scale reactor system. Also, a series of experiments will be conducted to obtain the optimum process conditions for commercial production of ammonium sulfate from FGD-gypsum. The conditions and the engineering data required for evaluating the technical and economic feasibility of the process will be gathered.

GOALS AND OBJECTIVES

The overall goal of this project is to assess the technical and economic feasibility for producing commercial-grade ammonium sulfate fertilizer from FGD-gypsum. This project focuses on providing process engineering data, estimating costs for the fertilizer production, and evaluating marketability of the product in the agricultural community.

Specific objectives of this study are:

I. Assess current knowledge on the chemistry, process schemes, and production costs of ammonium sulfate from gypsum.

II. Obtain samples of FGD-gypsum from two Illinois power plants for the work proposed in the project.

III. Obtain engineering data required for process scale-up and the technical and economic feasibility studies.

IV. Determine the influence of the properties of the gypsum and process conditions on the quality of the ammonium sulfate produced.

V. Evaluate the impact of continued use of ammonium sulfate on soil chemical properties.

VI. Establish a process flow sheet for the production of ammonium sulfate from FGD gypsum and evaluate the production costs and the market potential for the product.

INTRODUCTION AND BACKGROUND

Wet flue gas desulfurization (FGD) process, that use limestone as a scrubber for SO_2 and produce gypsum as a by-product, are advanced pollution control technologies that will remain preferred choices for Phase-II compliance because of their considerable level of commercial development and demonstrated operational experience. A FGD system installed on a 500-MW plant burning 3.5 % sulfur coal, with a desulfurization efficiency of 95%, can generate about 47 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 and economic feasibility for producing commercial-grade ammonium sulfate fertilizer from this gypsum.

Four major industries have expressed interests and desire to work with ISGS on this

project (see letter of cooperation, p.39). AlliedSignal (Hopewell, VA), one of the largest producers of ammonium sulfate in the United States, is interested in developing a process to convert FGD-gypsum to granular ammonium sulfate. They will be involved in testing and quality evaluation of the products. They are also most interested in an agreement to market the finished product. Illinois Power (IP) and Central Illinois Public Services (CIPS), which have long advocated the development of markets for coal by-products, endorse the evaluation of the concepts proposed in this research project. IP will provide an independent review of the economics of the process and CIPS will provide technical assistance and samples of gypsum-sludge for testing. Henry Fertilizer (Henry, Illinois), will provide technical assistance on the project and will allow the use of their commercial facility if the project advances to a scale-up stage.

A more stringent regulation to reduce sulfur dioxide emission in the year 1995 (phase I: 2.5 lbs $SO_2/10^6$ Btu) and the year of 2000 (phase II: 1.2 lbs $SO_2/10^6$ Btu) is mandated by the 1990 Clean Air Act Amendments. Millions of tons of high-quality gypsum may be produced in this decade, the total amounts depending partially on the installment of more FGD systems. This amount of FGD-gypsum by-product may exceed the current demand of the FGD-gypsum industry. The anticipated problems for utilities are increased disposal cost plus limited landfill space. Successful commercial utilization of FGD by-products would economically favor FGD technology.

The degree to which FGD-gypsum is commercially used depends on the quality of the gypsum. Currently, high-quality FGD-gypsum with purity greater than 94% is used mainly to manufacture construction materials, stucco and gypsum-plaster, gypsum wall boards, and cement. Lower quality FGD gypsum is less desirable and unless a market materializes to reuse it, a significant percentage of this by-product will require disposal as a solid waste. Several methods for the use of low quality FGD-gypsum have been proposed and, in many cases, demonstrated. Stabilized FGD material can be used as a liner for a landfill. Some FGD materials are processed to a fixed stabilisate and disposed in abandoned surface coal mines. An alternate approach to utilize both high and low quality FGD-gypsum is to produce ammonium sulfate fertilizer.

Ammonium sulfate is a valuable nutrient source for both nitrogen and sulfur to growing plants. There is a growing demand for sulfur as a plant nutrient in the sulfate form because of diminishing sulfur compounds in air deposition and more being taken up by plants because of increased yield. Also, the trend of 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 in fertilizer markets annually as a result of the acid-rain control program. The fertilizer industry is seeking a greatly

increased source of such by-product to supply sulfur in NPK fertilizer blends. Currently, the wholesale price for granular ammonium sulfate ranges from $75 to $130 per ton. At these price levels, converting some of the FGD-gypsum to ammonium sulfate becomes an attractive solution and could improve the economics of FGD systems in Illinois.

An ammonia-based FGD process, which produces ammonium sulfate as by-product, has been developed by General Electric (GE) and tested on a pilot-scale at the Great Plains Synfuel Plant in Beulah, ND. An economic study conducted by GE shows that for coals greater than 3% sulfur, this FGD process is favored over the forced oxidation process when the ammonium sulfate price is greater than $40/ton. The annual levelized cost was shown to decrease with increasing sulfur content when the ammonium sulfate price is greater than $70/ton. There are no published reports on the economics of converting FGD-gypsum to ammonium sulfate.

EXPERIMENTAL PROCEDURES

Seven tasks will be completed to meet the project objectives.

In this quarter, two FGD-gypsum samples, one produced from the Abbott power plant in Champaign, IL and the other from Newton Power Plant, Jasper, IL were selected as feed materials for ammonium sulfate production.

The Abbott power plant operates a Chiyoda Thoroughbred 121 (CT 121) FGD-desulfurization system (Maller and Stevens 1990) and produces 1 ton of gypsum (> 98% purity) for every 10 tons of coal burned. Collection of the gypsum sample, about 100 lb, from Abbott power plant was completed.

Newton Plant operates a wet limestone scrubber system and produces a lower quality of FGD-gypsum sample. Collection of this sample is scheduled on December 5th, 1994.

RESULTS AND DISCUSSIONS

In this quarter, a literature study (Task 1) is being conducted to gain information which will help in designing the bench-scale reaction system for ammonium sulfate production in the second quarter. At that time, a bench-scale reactor to convert FGD-gypsum to calcium carbonate and ammonium sulfate will be constructed at the ISGS. The conversion reactions will be tested by reacting the FGD-gypsum with CO_2 and ammonia or by reacting it with ammonium carbonate.

The chemical compositions data provided by the individual power company were used for sample selection purposes. The chemical compositions of the two selected samples are summarized in Table 1.

Table 1. RESULTS OF GYPSUM BYPRODUCT ANALYSIS

Composition in wt. %, moisture free	Abbott Power Plant	Newton Power Plant
Gypsum	98.70	10.00
$CaSO_3$	0.07	80.00
$CaCO_3$	0.59	7.00
Residue	0.70	3.00
Free Moisture	8.52	20.00

Analytical data were provided by the individual power station.

The Abbott power plant operates a Chiyoda Thoroughbred 121 (CT 121) FGD-desulfurization system (Maller and Stevens 1990) and produces high quality FGD-gypsum (> 98% purity). The gypsum produced is currently used by farmers to improve land quality. Acquisition of this high quality FGD-gypsum sample was completed in this quarter. Chemical and physical characterizations of this sample are in progress. Newton Plant has a wet limestone scrubber system which produces lower quality of FGD-gypsum (about 10% purity). The scrubber system, which will be in operation by December, was not operated during the time when our contact was made. A trip to collect this FGD-gypsum sample from Newton plant is scheduled on December 5th, 1994.

Two meetings were held in Champaign/Urbana to discuss the activity as well as the extension of this project which included a visit by a project manager of Dravo Lime Company.

DISCLAIMER STATEMENT

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