Energy & Environmental Research Center

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

EERC Proposal No. 95-6278

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Submitted to:

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

ABSTRACT

The use of scrubber sludge has traditionally been limited for a variety of reasons; however the chemical and mineralogical composition of these materials show promise for several applications. Two applications identified and focused on in this proposal are agricultural soil amendment and gypsum for gypsum wallboard and other gypsum products.

It is proposed to determine the technical and economic feasibility of producing a lower-quality agricultural soil amendment and, secondarily, a higher-quality gypsum for manufacturing purposes. The scrubber sludge from flue gas desulfurization is produced in high volumes and consists primarily of calcium sulfite in a very wet consistency. The first phase of this proposed work will focus on development of a process to dewater and oxidize the calcium sulfite material to primarily calcium sulfate in a granular or pelleted form that can be used as an agricultural soil amendment to treat the sodic soils that are found in North and South Dakota. If this process is found to be economical, a second phase will be undertaken to develop the oxidation process further to produce a higher-quality gypsum that can be used in manufacturing. Once again, both technical and economic feasibility will need to be evaluated.

PROJECT SUMMARY

The research project detailed in this proposal will investigate the oxidation of North Dakota scrubber sludge to produce two products: an agricultural soil amendment and gypsum. The project is summarized in outline format as follows:

Phase I – Development of an Agricultural Soil Amendment

Task 1 – Sample Collection

Task 2 – Laboratory-Scale Oxidation

A. Literature search and review

B. Characterization of sludge

C. Oxidation experiments

D. Characterization of oxidized scrubber sludge ($CaSO_4$)

Task 3 – Pilot-Scale Demonstration

A. Process and equipment selection

B. Production demonstration

C. Materials handling

D. Product evaluation

Task 4 – Economic evaluation

Task 5 – Reporting

Phase II – Production of Gypsum for Gypsum Products

Task 1 – Determination of Gypsum Quality from Phase I

A. Gypsum specifications

B. Percent conversion

Task 2 – Further Development of Laboratory-Scale Oxidation Process to Meet Gypsum Product Quality Requirements

Task 3 - Pilot-Scale Demonstration

Task 4 - Economic Evaluation

Task 5 - Quality Assurance/Quality Control for Field Production of Gypsum

Task 6 - Phase II and Project Reporting

INTRODUCTION

The use of scrubber sludge has traditionally been limited for a variety of reasons; however the chemical and mineralogical composition of these materials show promise for several applications. Two potential utilization scenarios have been identified for scrubber sludge generated at the Coal Creek Station power plant near Underwood, North Dakota. Coal Creek Station's flue gas desulfurization process uses lime to scrub SO_2 emissions and produces a material that is primarily a calcium sulfite with a wet consistency. Other calcium compounds are also likely present as well as a minor amount of coal fly ash that is carried in the flue gas. The potential for the utilization of this material is based on the calcium-sulfur compounds present and the potential to have the sulfur available as sulfate, which is necessary in most applications. The two applications identified and focused on in this proposal are as an agricultural soil amendment and as gypsum for gypsum wallboard.

BACKGROUND

The result of adding lime (CaO) or portlandite ($Ca[OH]_2$) to scrub SO_2 from the emissions gas in a wet scrubber is the formation of primarily the mineral hannebachite ($CaSO_3 \cdot 0.5H_2O$). The SO_3^{-2} in hannebachite is oxidized to SO_4^{-2} to form the mineral gypsum ($CaSO_4 \cdot 2H_2O$) with time as it is exposed to oxygen in the atmosphere. Gypsum is also a naturally occurring mineral that is mined for use in making wallboard, portland cement, plaster products, and as an agricultural soil amendment.

By-product gypsum is normally a wet powder, while natural gypsum is a dry, rocklike material. Because by-product gypsum is manufactured, its chemical and physical properties are relatively consistent compared to mined, naturally occurring gypsum. By-product gypsum has a high purity, often as high as >95%, while naturally occurring gypsum ranges in purity from 90% to 98%.[1,2]

To produce a consistently pure by-product gypsum, air is sometimes forced into the scrubber slurry, oxidizing the calcium sulfite to calcium sulfate. This forced oxidation has been used in Japan and Europe to make a commercially usable gypsum for wallboard manufacture. An additional cost for dewatering the gypsum is often associated with this method of forced oxidation.

In 1993, 31 U.S. companies produced 16.5 million tons of gypsum from 58 mines. U.S. markets consumed 25.3 million tons which left about 8 million tons of gypsum to be imported from Canada and Mexico.[1,2]

PROJECT DESCRIPTION

The project for oxidation of North Dakota scrubber sludge will proceed in two phases. Phase I of this project will focus on the production of an agricultural soil amendment. The type of soil amendment to be produced is generally referred to as agricultural gypsum; however, it is more appropriately a mixture of calcium sulfate in several hydration states with a small percentage of calcium hydroxide–carbonate. The actual gypsum content is less important than the oxidation of sulfite in the original material to calcium sulfate. This material must be produced at a cost that allows it to compete in the agriculture market.

Phase II of this project will build on the processes developed and information gained in Phase I. Providing the production of an agricultural soil amendment is economically viable, the actual gypsum production process will be optimized for other markets such as wallboard production. The requirements for gypsum used in wallboard production are much more stringent than for agricultural use, and once again the economic viability of the process will be evaluated. The project description for each phase is detailed below.

Phase I – Development of an Agricultural Soil Amendment

Task 1 – Sample Collection

Cooperative Power will collect a series of scrubber sludge samples (maximum of 10 samples) at regular intervals for a minimum of 2 weeks and submit them to the EERC. Cooperative Power will also collect and submit samples of the lime sorbent used in the scrubber and a representative sample of coal fly ash generated over the scrubber sludge sampling period. The EERC will evaluate the scrubber sludge samples for water content, calcium content, sulfur content, and SO_3/SO_4 ratios as a check on the consistency of the sludge. Preliminary dewatering will likely be required for these samples to be chemically characterized; however, the bulk samples will be retained as received for the dewatering and oxidation experiments. The EERC anticipates making two composite samples from those collected for the laboratory- and pilot-scale oxidation tests. Sorbent and fly ash samples will be retained to facilitate determination of the source of any trace constituents that may be found in the scrubber sludge.

Task 2 – Laboratory-Scale Oxidation

Literature Search and Review

A computer literature search, complemented by a manual literature search, will be used to supplement the current in-house literature database on utilization of scrubber sludges, calcium sulfates as soil amendments, calcium sulfate products, wallboard manufacturing, and oxidation of sulfites. In addition to these topics, the search will also cover commercially available spray drying and wet and dry scrubbing processes that may be useful in developing the equipment for the pilot-scale dewatering and oxidation process. The search will serve to identify equipment available at the EERC and the power plant site that may be used or modified for process demonstration. The literature search may also give indications of new equipment requiring fabrication. A keyword list to be used for the computer literature search will be compiled by the research team. The literature search will be performed by the professional library staff at the EERC and will be reviewed by several members of the research team, and pertinent documents not currently available at the EERC will be noted and obtained. Hard copies of these documents will then be distributed for review and technical evaluation. Each document will be reviewed by the research team and rated for relevance, completeness, and technical merit. As part of this review, bibliographic citations will be checked manually, and any additional pertinent documents will be obtained and submitted for the same review process. Only those documents with a high degree of relevance, completeness, and technical merit, as agreed on by the assembled research team, will be used in developing the philosophical and scientific approach taken for this project and for citation in any reports or articles to be submitted to technical journals.

Characterization of Sludge

The characterization of the two composite scrubber sludge samples will focus primarily on the calcium sulfite and calcium sulfate present. These and other bulk major and minor components will be determined by appropriate analytical techniques, including primarily atomic absorption, plasma emission, and x-ray fluorescence spectrophotometry. Appropriate sample preparation techniques will be selected and employed. As an environmental check, the bulk trace element concentration of several elements of interest will be determined. Those elements will include the RCRA (Resource Conservation and Recovery Act) elements and those detailed by the North Dakota State Department of Health and Consolidated Laboratories. If warranted, because of the presence of potentially problematic trace elements, the composite samples will be leached using appropriate leaching procedures and the leachate concentrations of the identified trace elements will be determined.

The mineralogical characterization of the sludge samples will include a determination of minerals present by x-ray diffraction and characterization by scanning electron microscopy to determine the amounts and sizes of minerals present. These characterization techniques will also be useful in determining the amount of ash included in the final product.

Oxidation Experiments

The key to using the scrubber sludge as a soil amendment is in the ability to oxidize the $CaSO_3$ (calcium sulfite) into the more soluble and less reactive form, $CaSO_4$ (calcium sulfate). There are also concerns that a high amount of $CaSO_3$ may be harmful to microbes and other lower life forms residing in soils that play a major role in breaking down compounds so that they may become usable for plants.

A laboratory-scale oxidation method will be developed that simply exposes the scrubber materials to atmospheric O_2 and a drying process simultaneously by dropping it from a tower. The amount of SO_3 that is oxidized to SO_4 will be measured using an iodometric titration to measure the amount of oxidizable materials in the sample.

The use of air-type conveyors will be investigated as a means to oxidize the material after the sludge has been dried using excess heat generated from the combustion process. Air conveyors can be used to transport the dried material away from the boiler to an area where further processing for use will be carried out.

Another oxidation method is to force air into the sludge as it is transported. This method, which has been used successfully in Japan and Russia,[1] is called forced air oxidation. This differs from the above-mentioned oxidation method in that it oxidizes the SO_3 while it is still in a wet form rather than partially drying the material first and then oxidizing it.

Characterization of Oxidized Scrubber Sludge

Detailed characterization of the various calcium sulfate and sulfite compounds will be performed by various analytical methods. The primary method will be by x-ray diffraction (XRD), which is able to distinguish a wide variety of forms by measuring the distance between atomic layers, which is unique to each mineral phase. Three primary forms of calcium sulfate occur naturally. The difference between these crystals depends on the amount of water held by each phase. The process of scrubbing SO_2 using CaO is capable of producing a wide variety of these compounds that are not normally found in nature. These variations in $CaSO_4$ will be identified and their degree of solubility will be determined.

Task 3 - Pilot-Scale Demonstration

Process and Equipment Selection

Based on the results of the literature search and laboratory-scale oxidation tests, a processing train that represents the most likely candidate for testing will be selected for pilot-scale demonstration. The pilot-scale process will probably consist of three major components: an oxidation operation to convert the sulfite compound to sulfate, a conditioning operation to wet and blend the oxidized material, and a granulation/pelletizing operation to obtain a product that can be easily handled and land-applied with conventional farming equipment. During assembly of the pilot-scale oxidation equipment, a small quantity of the oxidized material from laboratory testing will be submitted to the pelletizing equipment manufacturer to ensure that the material can be granulated as expected and to determine whether both operations described above are needed. If positive results are obtained from the equipment manufacturer, the appropriate pieces of equipment will be procured, and testing will proceed. If the results of granulation testing are negative, other pelletizing processes will be investigated and tested.

Production Demonstration

Following process and equipment selection, a processing train will be assembled and operated at the EERC. Enough material will be processed to define operating variables and conditions, appropriate product size and quality, and process design variables that can be used in future process scaleup efforts. As much as 2 tons of dried scrubber sludge may be needed to complete the proposed pilot-scale demonstration runs. A relatively large amount of granulated product may be needed to investigate the materials-handling issues, as discussed in the next section below.

All pertinent process data will be collected during the production demonstration runs and entered into a spreadsheet-style format for data reduction. Average operating conditions and material balance calculations will be included in the final deliverables package.

Materials Handling

Material stability is of primary interest in the development of a granulated $CaSO_4$ product for use as a soil amendment. Therefore, the granulated product from the production demonstration runs will be subjected to at least two stability-testing methods to determine friability and susceptibility to dusting. The first planned testing method is a drop–shatter test that consists of dropping a sample of the material in question through a 6-inch PVC pipe, 6 feet in length. At the bottom of the pipe, a collection vessel constructed of stainless steel receives the falling material. The test material is then emptied from the vessel, and submitted for dry-sieve analysis. Based upon a comparison of weight percentages and specific size factors, a friability index is generated to indicate the amount of breakage that occurred from the 6-foot drop. Multiple drops will be performed to simulate breakage during transfer and unloading.

The second testing method will make use of a test loop available at the EERC to more accurately simulate actual handling operations. Pilot-scale stability performance testing will be completed using a test loop consisting of various grain-style augers. The main equipment involved in the test setup will be four augers and a 76.2-cm-diameter vibrating screen. The speed of the augers can be adjusted to create an average loop time of about 30 seconds. The loop features a drop area to simulate loadout stations and transfer areas. Attached to the drop receiving tank is a real-time dust concentration analyzer to measure the level of fugitive or nuisance dust that occurs from dropping the material sample 1.5 m. A vibrating screen, used to remove −20-mesh material, is located directly after the drop area. This screening step inhibits the loss of additional fugitive dust and provides a method to contain the fines in one location. The test loop assembly, which employing belt conveyors instead of augers, is depicted in Figure 1.

Product Evaluation

A portion of the granulated product will be analyzed for particle-size distribution and product quality (in terms of mineral composition). The granulated product will also be applied to a simulated soil and evaluated in terms of solubility and propensity for sodium ion exchange.

Task 4 - Economic Evaluation

Cooperative Power will perform an economic evaluation for the commercial-scale production of agricultural soil amendment at the Coal Creek Station. This evaluation will take into account the processes recommended and information obtained by the EERC in laboratory- and pilot-scale demonstrations of scrubber sludge oxidation. Cooperative Power personnel will work closely with

Figure 1. Test loop assembly.

EERC research staff to facilitate selection of the most cost-effective and practical equipment and materials-handling practices. The economic evaluation will be based on the market price for agricultural soil amendment in the region.

Task 5 - Phase I Reporting

Three months after the initiation of the project, an initial project progress report will be submitted to the NDIC. Results of Phase I will be reported in an interim report to the NDIC within 30 days following completion of Phase I, which is scheduled to continue for 6 months after project initiation. This report will detail the technical findings and the results of the economic evaluation. Based on the technical and economic feasibility of the process developed to produce agricultural soil amendment, a decision will be made as to whether or not to proceed with Phase II of the project. If it is determined that Phase II is not practical based on information gained in Phase I, The interim report will be submitted as a final project report, and the project will be terminated.

Phase II - Production of Gypsum for Gypsum Products

Task 1 - Determination of Gypsum Quality from Phase I

Gypsum Specifications

American Society for Testing and Materials (ASTM) C471, Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products, lists the test methods for gypsum to be used in gypsum products, which includes the manufacture of wallboard. While these test methods mostly deal with chemical properties, there are other physical properties that need to be addressed in order to effectively market by-product gypsum for wallboard manufacture. Since by-product gypsum has a higher degree of purity than mined gypsum, the most important properties are particle size and moisture content.

This task will be primarily concerned with determining the minimum requirements for the physical and chemical properties needed to successfully use by-product gypsum for the manufacture of wallboard and other gypsum products.

Percent Conversion

A very high rate of conversion from SO_3 to SO_4 will be required for the successful conversion of by-product gypsum to wallboard and other gypsum products. Several methods of testing will be evaluated, including XRD, iodometric titration, and additional methods described in ASTM C471.

Task 2 - Further Development of Laboratory-Scale Oxidation Process to Meet Gypsum Product Quality Requirements

Task 1 of Phase II is to identify what the physical and chemical specifications are to be able to successfully use by-product gypsum in wallboard manufacture and other gypsum products. This task will focus on producing a byproduct gypsum capable of meeting those requirements as specified. Methods will be developed to enhance the degree of conversion from SO_3 to SO_4 as well as drying and meeting particle size requirements. It is anticipated that all of these requirements will be met at the plant and the gypsum will be market ready as it leaves the site.

Task 3 - Pilot-Scale Demonstration

The particle-size distribution and purity of the oxidized scrubber sludge will be evaluated in relation to naturally occurring gypsum following pilot-scale oxidation processing. An oxidation process similar to the one selected under Task 3 of Phase I will be used to produce gypsum for further processing into gypsum products. Depending upon the results of testing, additional pilot-scale tests will be conducted to increase the purity of the final product, fine-tune the process, and/or generate design data for scaleup efforts. Should the particle-size distribution fall outside of prescribed industry standards, additional preparation procedures will be undertaken. These procedures may include crushing and pulverizing, and/or screening for the removal of top and/or bottom fractions. The EERC has the capability to process large quantities of dry solids through their coal preparation facility, which includes a Williams roll crusher, two micropulverizers with capacities of 1500 lb/hr and 4000 lb/hr, as well as a 1000-lb/hr CE Raymond air classifier-type pulverizer. Additionally, there are many laboratory-scale crushers and pulverizers on-site which can be used to test the pulverization potential of a given material.

Task 4 - Economic Evaluation

An economic evaluation will also be performed by Cooperative Power personnel on the production of gypsum from Coal Creek Station scrubber sludge to determine the potential for commercialization of the process. Once again, Cooperative Power personnel will work closely with EERC research staff to coordinate the technical information with the economic evaluation.

Task 5 - Quality Assurance/Quality Control for Field Production of Gypsum

A simple quantitative analytical technique will be developed to facilitate the production of a quality-assured gypsum product. This test will be employed in the pilot-scale demonstration as well as recommended for future commercial gypsum producers. A quality assurance/quality control testing schedule will be recommended for commercial scaleup.

Task 6 - Phase II and Project Reporting

The duration of Phase II is anticipated to be 9 months, to begin following completion of Phase I. At the end of Phase II, a brief report summarizing results of Phase II will be submitted 30 days after completion of that phase. Project progress reports will also be submitted every 3 months (quarterly) over the duration of Phase II. A final technical report detailing all results from both phases of the project will be submitted 60 days after the completion of Phase II.

STANDARDS OF SUCCESS

The following milestones will be achieved to measure the success of this project. These milestones are also incorporated into the timetable for the project.

PHASE I

Milestone 1: Determination of technical feasibility of production of agricultural soil amendment

Milestone 2: Pilot-scale production demonstration

Milestone 3: Determination of economic feasibility

PHASE II

Milestone 1: Determination of technical feasibility of production of gypsum for wall board

Milestone 2: Pilot-scale production demonstration

Milestone 3: Determination of economic feasibility

VALUE TO NORTH DAKOTA

This project will be of value to North Dakota from several standpoints:

- It will develop a technology to allow the utilization of a high-volume lignite combustion by-product, thereby reducing the need for disposal. Improved waste management practices facilitate more efficient energy production and protection of the environment.
- This project has the potential to benefit the agricultural community of North Dakota by providing a reasonable-cost agricultural amendment for sodic soils, which are prevalent in North Dakota.
- Additional industry or export of a North Dakota product will potentially develop from the production of manufacturing-grade gypsum.

EXPERIENCE AND QUALIFICATIONS

This project will be accomplished by a team of EERC researchers with cooperation from Cooperative Power personnel. The following EERC researchers will have primary responsibility in performing the proposed project. Resumes of the Project Manager and Principal Investigators are included in Appendix A.

Project Manager

David J. Hassett, Senior Research Advisor

Principal Investigators

David J. Hassett, Senior Research Advisor

Kurt E. Eylands, Research Associate

Tom A. Moe, Research Engineer

Additional Research Staff

Debra F. Pflughoeft-Hassett, Research Manager

Bruce A. Dockter, Research Engineer

Stanley J. Miller, Senior Research Manager

The EERC is one of the world's major energy and environmental research organizations. Since its founding in 1951, the EERC has conducted research, testing, and evaluation of fuels; combustion and gasification technologies; emissions control technologies; ash use and disposal; analytical methods research; groundwater; waste-to-energy systems; and advanced environmental control systems research. Today's energy and environmental research needs typically require the expertise of a total-systems team that can focus on technical details while retaining a broad perspective.

A summary of the EERC's facilities and research programs is included in Appendix B.

MANAGEMENT

The proposed project will be managed by Mr. David J. Hassett. Mr. Hassett will be responsible for budget management, scheduling, and reporting. Technical research tasks will be performed under the direction of the principal investigators with coordination and overall management by Mr. Hassett. Mr. Hassett will be aided in project management tasks by EERC support staff.

TIMETABLE

The proposal project will be performed in 2 phases. The duration of Phase I will be 6 months, and the duration of Phase II will be 9 months. The final project report will be submitted 60 days after project completion.

	Project Months																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Phase I																	
Milestones*			1		2	3											
Phase I																	
Reports			A				B										
Phase II																	
Milestones*									1				2		3		
Reports									A				A			C	D

A = Quarterly progress reports.
B = Phase I interim report.
C= Phase II summary report.
D = Project final report.
* See p. 13 of this proposal.

BUDGET AND MATCHING FUNDS

The cost for this proposed project is $120,000. A budget detailing the costs is included as Appendix C. The industrial matching funds can be broken down as follows: $40K industrial contribution from Cooperative Power, $30K cash contribution and $10K in-kind costs (see Appendix C for letter of commitment). The in-kind cost share from Cooperative Power covers sampling and economic evaluations as indicated in the project description. Funds to match the industrial contribution, $40K, are being requested from the NDIC. Additionally, $40K is being requested from the U.S. Department of Energy through a jointly sponsored research program in place at the EERC.

REFERENCES

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2. Venta, G.J.; Hemmings, R.T. "FGD Gypsum Utilization: Bridging the 'Two Solitudes'," *In* American Coal Ash Association 11th International Symposium on Use and Management of Coal Combustion By-Products (CCBs), Orlando, FL, Jan. 15–19, 1995, Supplemental Proceedings; Tyson, S.S.; Blackstock, T.H.; Hunger, J.M., Eds.; 19 p.