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PROCESSING AND UTILIZATION OF WET FLUE GAS DESULFURIZATION MATERIAL

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BACKGROUND

Flue Gas Desulfurization

Utility emissions of sulfur dioxide are controlled by a variety of methods, including the following systems:

- Wet scrubbers
- Spray dry scrubbers
- Sorbent injection
- Regenerable processes
- Combined SO₂/NOₓ processes

Flue gas desulfurization (FGD) systems may be classified into two broad types: nonregenerable and regenerable. In systems using the nonregenerable process, the SO₂ remains permanently bound with the sorbent to form a new compound. In the systems using the regenerable process, the SO₂ sorbent can be reused following the regeneration step that produces liquid SO₂, sulfuric acid, or elemental sulfur. Figures reported by the American Coal Ash Association (ACAA) indicate that nearly 20 million tons of FGD material was produced in the United States in 1995, but only approximately 7% of this material was utilized.

Wet Scrubbers

Processes that produce wet products are often described as wet scrubbers. These systems commonly use limestone, slaked lime, or a mixture of slaked lime and alkaline fly ash as sorbents. The sorbent is sprayed into the flue gases where it reacts with the SO₂ to form an insoluble calcium compound. The residues from these processes are generally calcium sulfite, or calcium sulfate if forced oxidation has been employed. The wet scrubber materials are generally thixotropic, thus difficult to dewater, and have specific handling and disposal requirements.

Spray Dry Scrubbers

In spray dry scrubbers, a solution or slurry of alkaline material is mixed with the flue gases at air preheater outlet temperatures. The flue gases are humidified by finely dispersed droplets. The water is evaporated, salts are precipitated, and the remaining solids are dried, generally to less than a few percent of free moisture. The precipitated solids and fly ash are entrained in the flue gas and carried away from the spray dryer to a particulate collection device. Slaked lime is commonly used as a sorbent, resulting in an end product consisting of a mixture of calcium sulfite/sulfate and fly ash.

Sorbent Injection

In sorbent injection systems, a dry calcium- or sodium-based sorbent is either added to the coal or injected into the boiler or duct work. Sorbents used include limestone, lime, and trona or nahcolite. Hybrid systems have been developed that use more than one sorbent and/or injection points. Sorbent injection systems produce a dry calcium or sodium sulfite/sulfate waste mixed with the fly ash.
Other Processes

An alternative approach to dry flue gas cleaning involves the use of a circulating fluidized-bed absorber or gas suspension and absorption unit. These systems use a reactor vessel in which a pulverized dry sorbent, such as sodium bicarbonate, limestone, lime, or calcium hydroxide, comes into contact with the SO$_2$-laden flue gases in a fluidized bed or other reactor vessel. A solid-gas separator, located downstream of the reactor, concentrates unused sorbent for recycle and subsequent reuse for additional SO$_2$ capture.

Typical Utilization Scenarios for FGD Material

The residues from wet and dry FGD systems have similar chemical properties. Major constituents are calcium sulfite, calcium sulfate, fly ash, and excess reagent. These properties are significantly different from pulverized coal combustion fly ash and can be best utilized following processing. Calcium sulfite, generally the major component of FGD material, is typically oxidized to calcium sulfate, which with water forms gypsum. This is usually separated and dewatered for utilization. The purity of the FGD gypsum residues from the wet limestone/gypsum systems typically range from 95%-99%. Optimization of the FGD process can ensure a by-product with a consistent quality suitable to substitute for natural gypsum in a variety of applications. Typical utilization applications for FGD gypsum include agricultural applications, a feedstock for cement production, and manufacture of gypsum wallboard. In most cases, the purity of gypsum necessary for these applications requires the removal of fly ash before the scrubbing process to avoid contamination of the gypsum with fly ash.

COOPERATIVE POWER’S COMMITMENT TO ENVIRONMENTALLY SOUND UTILIZATION OF BY-PRODUCTS

Cooperative Power’s Coal Creek Station (CCS) became fully operational in 1981. The two 550-MW units at CCS burn North Dakota lignite. The resulting by-products are fly ash, bottom ash, and wet FGD material. Although disposal of the coal combustion by-products (CCBs) was included in the original site plan at CCS, even early on, consideration was given to utilization of the fly ash as a mineral admixture for concrete and as a partial sorbent replacement for the wet scrubbing system. CCS fly ash has been successfully marketed into North Dakota, Minnesota, and the surrounding region as a construction material that is environmentally benign, highly consistent, and an excellent performer in numerous construction applications.

Attempts to use CCS fly ash as part of the scrubbing medium in the wet scrubbing system at the site were not as successful as first hoped, primarily due to the abrasive nature of the fly ash. Currently, CCS scrubbers use lime as the scrubbing medium for SO$_2$ removal.

CCS’s efforts to market its fly ash have been successful, so with increased awareness of the economic 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 has taken additional steps to investigate the processing and utilization of its wet FGD material.

LABORATORY- AND PILOT-SCALE PROCESSING OF CCS WET FGD MATERIAL

Samples of CCS wet FGD material were collected and evaluated. Typical samples were approximately 15%-20% solids content, exhibited thixotropic behavior, and were primarily calcium sulfite and calcium hydroxide. The pH of the original samples was approximately 7.0–7.5. Samples that were stored at room temperature generated H$_2$S after several weeks, indicating reduction of sulfur under anaerobic conditions.

The laboratory equipment used for oxidation experiments consisted of a 3-necked, round-bottom flask fitted with a paddle stirrer. Air was introduced into the flask through glass frit at the bottom of the flask, and the pH was controlled through addition of dilute sulfuric acid. Samples were removed and the sulfite content was determined at regular intervals. When the sulfite content was not detectable, the oxidation was considered complete. The sample was then allowed to settle
and was filtered, washed, and air-dried. The oxidized material was then analyzed to determine the mineral composition. It is important to note that as the oxidation approached completion the physical nature of the sample changed from a thixotropic substance to a two-phase (liquid–solid) material, and the solid phase readily settled out of solution. This was an additional visual indication of the oxidation process.

Two laboratory-scale oxidation trials were performed on the FGD material. These were performed at pH 5 and pH 4. The first experiment, at pH 5, required 10 hours to completely oxidize the calcium sulfite to calcium sulfate. The second experiment, at pH 4, achieved complete oxidation in 6 hours. The resulting solid samples of oxidized FGD material were air-dried and evaluated using x-ray diffraction which verified that the material was approximately 98%-99% pure gypsum.

The next phase of the work involved a scaleup to a pilot-scale oxidation process to oxidize four 55-gallon drums of the FGD material. The pilot-scale process was performed at pH 4 in a stainless steel reaction vessel. Automatic pH control was used to maintain the pH of 4 with sulfuric acid. The other laboratory-scale requirements of stirring and introduction of excess air were replicated in the pilot-scale experiment. The pilot-scale experiment proceeded at a slower rate than the laboratory-scale experiment, requiring 80 hours to achieve completion. The final sample was separated and air-dried, yielding 675 pounds of air-dried product. Analysis of the air-dried product indicated that the material was again 98%-99% pure gypsum.

MARKET OPPORTUNITIES FOR FGD GYPSUM

As stated earlier, there are several key utilization applications for FGD gypsum. These include agricultural soil amendment, feedstock for cement manufacture, and production of gypsum wallboard. It has been proposed that the use of FGD gypsum as an agricultural soil amendment may be highly advantageous for treatment of sodic soils. The need to have the soil amendment in the form of gypsum or calcium sulfate is that the calcium sulfate is more soluble than the calcium sulfite in nonoxidized FGD material. As can be determined by the process used to achieve oxidation, the oxidation of calcium sulfite to calcium sulfate is not easily achieved, so it is advantageous for effective soil amendment to oxidize the FGD material before using it in this application. It is also much easier to handle with conventional equipment as gypsum, which can be granulated or pelletized for application, rather than the thixotropic FGD material that is generated in the scrubbing process. One advantage of this market is that the product consistency can usually exhibit greater variability in agricultural applications than in industrial applications. Agricultural soil amendment applications will likely be seasonal, so material storage may be a requirement and needs to be considered. Generally, the agricultural applications for CCBs are high-volume applications, but the market price for these materials is also generally lower than industrial applications.

The use of FGD gypsum in cement and gypsum wallboard manufacturing has become more common in recent years as these industries become more aware of the advantages of recycling and the costs of raw virgin materials. In these applications, the purity and consistency of the FGD gypsum are critical. Another key issue with supplying FGD gypsum to these industries is transportation. If transportation costs from the FGD gypsum production site to the manufacturing site are too great, especially relative to other natural or by-product sources, it will be difficult to market the FGD gypsum into these industries. All of these issues need to be evaluated as part of the marketing and economic evaluation of processing FGD material as a management strategy.

OPTIONS FOR COMMERCIAL-SCALE OXIDATION OF FGD MATERIAL

The oxidation process used for the laboratory- and pilot-scale experiments summarized in this document was performed using an ex situ process. The wet FGD material was removed from the scrubbing system after the \( \text{SO}_2 \) had been reacted with the scrubbing medium. This process can be scaled up to commercial scale as one option; however, there are also options that are generally referred to as in situ oxidation processes. In these processes, the oxidation of the calcium sulfite is forced simultaneously during the scrubbing process. For both the ex situ and in situ processes, there are commercial systems available that can be retrofitted onto existing scrubbers at utility sites. Each system offers advantages either in purity of the FGD gypsum that can be produced or in cost-effectiveness based on the amount of handling and added materials to achieve the oxidation. It is beyond the scope of this paper to evaluate the advantages and disadvantages of all the commercially
available systems; however, it is important for individual companies to perform cost-benefit analyses of the various options, taking into account the FGD gypsum markets of highest interest.

Additional considerations that have been alluded to for commercial-scale oxidation processes include the potential need for granulation, pelletizing, or other postprocessing to facilitate handling, storage, or shipping. Short- and long-term storage considerations must also be evaluated for some utilization applications such as agricultural soil amendment. Quality assurance testing should also be considered as part of the marketing needs, and an alternate plan for management of the FGD material should be considered for cases when specifications may not be met because of process failure or inconsistency.

CONCLUSIONS

FGD material is only one by-product of coal combustion at CCS, but the preliminary work presented here is indicative of some general CCB management issues. CCBs are high-volume materials that can perform well in numerous applications when management plans include the needed options for utilization. A good CCB management plan can benefit from a well-thought-out marketing plan. The laboratory- and pilot-scale work described in this document provided the background information showing that a high-quality FGD gypsum can be produced from CCS FGD material. Cooperative Power continues to evaluate the economics of commercial-scale oxidation of CCS FGD material and the market potential for CCS FGD gypsum.