Current Status of Spray Dryer Absorber Material Characterization and Utilization

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ABSTRACT

In response to changing sulfur dioxide emission regulations, electric generating companies are considering installing flue gas desulfurization technologies, and it is estimated that spray dryer absorbers (SDA) may be the preferred option for many coal-fired power plants in the western United States. The increased production of SDA material is anticipated to be a challenge to the industry because the current utilization rate for SDA material is 9.7%.

Research to identify use applications for SDA material was initiated by the University of North Dakota Energy & Environmental Research Center through an extensive literature review to assess the current state of the knowledge regarding the characterization and utilization of SDA material. Information was assembled from a wide variety of domestic and international sources. Collected data on physical properties, chemical composition, and mineralogy from the literature review is summarized. A summary of current and potential commercial uses as identified through the literature search and barriers to SDA material utilization are presented.

INTRODUCTION

In an effort to address health and environmental concerns related to sulfur dioxide (SO_2) in ambient air, legislation has been enacted to regulate most industrial SO_2 emissions. In the United States, major regulations include the Clean Air Act Amendments of 1970, 1977, and 1990. The use of flue gas desulfurization (FGD) technologies to reduce SO_2 emissions from flue gases at coal-fired power plants was initiated in the 1980s in the United States. The 1990 Clean Air Act amendment required a permanent 10-million-ton reduction in SO_2 emissions from 1980 levels. On March 10, 2005, the U.S. Environmental Protection Agency (EPA) issued the Clean Air Interstate Rule (CAIR), which will permanently cap emissions of SO_2 and nitrogen oxides (NO_x) in the eastern United States. FGD systems are currently used on approximately 22% of U.S. coal-fired power plants.

Coal-fired power plants are currently evaluating options to comply with U.S. regulations that will require reductions of emissions of air toxics and acid gases. Responses are expected to result in an increase in SO_2 emission controls and a subsequent increase in the volumes of FGD by-products produced in the United States. Spray dryer absorber (SDA) systems, already being used by coal-fired power plants primarily in the western United States, will be one option that power plants may install, especially where water resources are limited. SDA systems are the second most popular FGD technology. SDA systems are used mostly for relatively small to medium capacity boilers (40–500 MW) that burn low- to medium-sulfur coals. Currently, there are 26 SDA units in operation on coal-fired power plants in the United States.

An SDA system captures SO_2 from the flue gas by use of slaked lime slurry, which is sprayed into the flue gas, dried by the heat of the flue gas, and collected in a particulate control device. SDA systems may follow a particulate control device that collects the fly ash or the fly ash may intermingle with the lime slurry and be collected in combination with the SDA material. Recycling of the combined solid may be used to improve sorbent utilization. Alkaline fly ash such as that generated from subbituminous coals and some lignite coals will sorb SO_2 gases. The use of fly ash precollection is widely practiced in Europe, but not in the United States. SDA systems are considered efficient and reliable and have a lower capital cost than wet FGD systems. Operating costs for SDA are higher than wet FGD systems but the water usage is lower.

The advantages of SDA systems over wet scrubbing include:

1. Less costly construction materials typically made of mild steel, thus less costly capital costs.
2. Dry by-products that do not require the use of expensive handling equipment or a wastewater stream.
3. Fewer unit operations requiring less space, making SDA a good choice for retrofit.
4. Flexibility of the feed system allows immediate feed control of sorbent to follow boiler load.
5. High reliability.
6. Less sensitive and simpler process chemistry.[1–4]
7. Elimination of SO_3 from flue gas.

Perhaps the greatest disadvantage of SDA systems is the higher cost of lime sorbents used in relation to limestone used for wet scrubbing.[1–2,4] In addition, SDA systems produce a by-product that is difficult to sell and is oftentimes disposed. SDA material is typically disposed of in a manner similar to fly ash.

The by-product produced from an SDA system is a dry FGD material commonly referred to as SDA material or dry FGD material. Other terms are also used to refer to this material, as noted in Figure 1. This paper uses the term “SDA material” throughout, except where the generic term dry FGD material was used in the review literature.

- Spray dry/dryer absorber/atomization/absorption (SDA, SAV) sludge, ash, material, product, byproduct, by-product, end-product, waste, or residue
- Semi-dry absorber/atomization/absorption (SDA) sludge, ash, material, product, byproduct, by-product, end-product, waste, or residue
- Spray absorption process (SAP) sludge, ash, material, product, byproduct, by-product, end-product, waste, or residue
- Spray dryer (SPD) residue
- Spray dryer by-product (SDB)
- Calcium spray dryer ash, material, product, byproduct, by-product, end-product, waste, or residue
- Lime spray dry/dryer ash, material, product, byproduct, by-product, end-product, waste, or residue
- Sulfite-rich flue gas desulfurization sludge, ash, material, product, byproduct, by-product, end-product, waste, or residue
- Sulfite sludge
- Scrubber residue or sludge
- Dry flue gas desulfurization sludge, ash, material, product, byproduct, by-product, end-product, waste, or residue
- Dry scrubber sludge, ash, material, product, byproduct, by-product, end-product, waste, or residue
- Nonoxidized flue gas desulfurization sludge, ash, material, product, byproduct, by-product, end-product waste, or residue
- Flue gas desulfurization sludge, ash, material, product, byproduct, by-product, end-product, waste, or residue (with no reference to the FGD process)
- Spent slurry

Figure 1. Terms used to refer to SDA material in the literature.

While all types of FGD material production is are likely to increase, the potential increase in production volumes of SDA materials is one that raises the issue of materials management because of its current low utilization rate in the United States. With goals of 50% utilization of coal combustion by-products (CCBs) set by industry and government, through the EPA Coal Combustion Products Partnership (C^2P^2) program, to be achieved by 2011, additional high-volume production of one or more materials with limited potential for utilization in the current market threatens to offset the great strides to increase CCB utilization in the United States.

CURRENT SDA MATERIAL PRODUCTION AND USE RATES

The American Coal Ash Association (ACAA) reports the yearly production and use of CCBs in the United States including statistics on FGD by-products from wet and dry systems. SDA material is reported with all other by-products from dry FGD systems, with the exception of fluidized-bed combustion systems. ACAA reported that 1,427,263 short tons of dry FGD material were produced in the United States in 2005[i]. Of that, 159,198 short tons (or 11.15%) were beneficially used.[5] Figure 2 illustrates the major markets for dry FGD material in the United States.

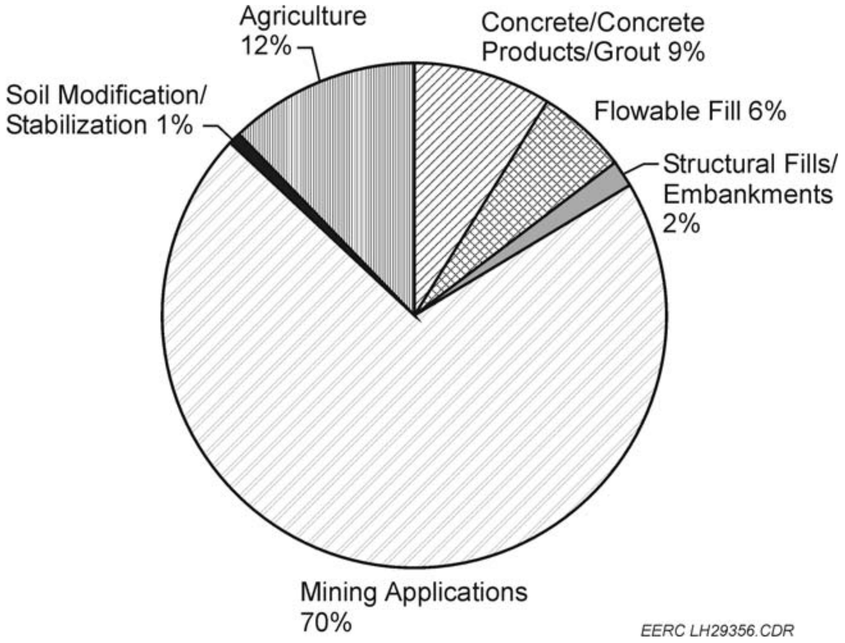

Figure 2. Major Markets of Dry FGD Material in the United States[5]

The European Coal Combustion Products Association (ECOBA) reports the production and use of CCBs in Europe. In 2004, 41% of SDA material produced was beneficially used in nonmining applications (general engineering fill, flowable fill, plant nutrition, and other uses). An additional 39% of the SDA material produced was used for mine reclamation and restoration purposes and 20% was disposed.[6]

CHARACTERIZATION OF SDA MATERIALS

SDA materials can vary widely in their physical, chemical, and mineralogical properties depending on their source. The following factors affect both the quantities and characteristics of SDA material:

- Composition of the coal feedstock (ash content, sulfur content, heating value)
- Combustion conditions
- Sorbent type
- SO_2 uptake efficiency (Ca/S ratio)
- Fly ash collection location and efficiency
- Composition and mineralogy of the fly ash

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[i] As submitted based on 54% coal burn.[5]

- Recirculation rate
- Load level
- Stoichiometric (sorbent) ratio

Regardless of the type of process used to scrub the flue gas, all FGD by-products include spent sorbent as sulfites or sulfates plus unreacted sorbent. The quantity of the sorbent used is usually proportional to the sulfur content of the coal burned but is also a result of the percent of SO_x recovery desired and system operating parameters.[7] The calcium sulfite content is dependent on the SO_2 removal efficiency.[8]

Physical Properties

A variety of physical properties of SDA material have been reported. These include particle size, specific surface area, bulk density, specific gravity, optimum moisture content and maximum density, unconfined compressive strength, and permeability. Physical properties of SDA materials are summarized in Table 1.

Table 1. SDA Material Physical Property Ranges Reported in Reviewed Literature

Physical Property	Range Reported in Literature
Particle Size	1–400 µm (2–45 µm mean)
Specific Surface Area	0.2–16 m^2/g
Bulk Density	400–1440 kg/m^3
Specific Gravity	2.09–3.71
Optimum Moisture Content	10%–63%
Maximum Dry Density	790–1870 kg/m^3
Unconfined Compressive Strength	12–3000 psi
Permeability Coefficient	$3.1 \times 10^{-9} – 6.5 \times 10^{-3}$ cm/sec

The particle size distribution of a material is characterized by the proportion of particle sizes within a series of specific size intervals. Particle size distribution is important because many engineering parameters are related to the variation of particle size of a material. Specific surface area ranges are a function of the fly ash content in the SDA material.[8] Density is defined as the mass (or weight) per unit volume of a material. Specific gravity is defined as the ratio of weight in air of a given volume of solids at a stated temperature to the weight in air of an equal volume of distilled water at the same temperature (usually 20°C). Specific gravity is often used as a method of comparison for engineering materials.

The moisture content of a CCB is a measure of the amount of water present in the voids in the CCB and is expressed as a weight percentage of total dry weight. The natural moisture content is a function of the deposition environment of the CCB and must be determined experimentally for each individual CCB. The natural moisture content of a CCB must be known to calculate the quantity of water that must be added or removed to bring the CCB to its optimum moisture content for compaction. The optimum moisture content of a CCB is related to the maximum density obtained by compaction in the laboratory. The values of moisture content versus dry density are plotted to form a compaction curve. As indicated by the curve, density is dependent on moisture content.

The highest point on the compaction curve corresponds to the maximum dry density and optimum moisture content.[9]

Unconfined compressive strength is usually determined using ASTM D2166, Unconfined Compressive Strength of Cohesive Soil, or ASTM D1633, Compressive Strength of Molded Soil-Cement Cylinders. The two procedures are similar except ASTM D6133 assumes there is no deformation of the sample during compression and uses its original dimension to calculate unit compressive strength. Permeability is defined as the rate of flow through a material. Permeability coefficients, typically reported in cm/sec, describe flow through a unit area under a unit hydraulic gradient. Hydraulic gradient correlates the forces causing water to flow and the forces resisting flow. A material is considered permeable if it has interconnected pores, cracks, or other passageways through which water or gas can flow.

Chemical and Mineralogical Properties

Dry FGD materials contain higher concentrations of calcium and sulfur and lower concentrations of silicon, aluminum, and iron than fly ash. The chemical composition of SDA material depends on the sorbent used for desulfurization, the proportion of fly ash collected with the FGD product, coal sulfur content, SO_2 removal, and other factors.

Conventionally, major/minor components of CCBs are reported as oxides. A typical report may include a weight percent value for SiO_2, Al_2O_3, Fe_2O_3, CaO, SO_3, MgO, Na_2O, K_2O, P_2O_5, TiO_2, BaO, MnO_2, SrO, moisture content, and loss-on-ignition (LOI). These data are summarized in Table 2. When reviewing compositional data on CCBs, it is important to understand that reporting of major/minor components as oxides is merely a reporting convention and is not necessarily indicative of the actual chemical forms in the ash. However, the bulk compositional data is useful in evaluating CCPs for various use applications because of the voluminous comparative historical data, empirical evaluations, and comparison with other tests and standards.

The trace metal content of SDA material is as a rule lower than that of fly ash and comparable to that of soil. The highly variable data are summarized in Table 3.

The pH values of SDA materials reported in the reviewed literature ranged from 9 to 13.

Successful engineering applications depend heavily on the mineralogical properties of SDA materials. SDA material has been described as predominantly crystalline and usually finer grained compared to fly ash and as a combination of spherical glassy fly ash particles coated by and intermixed with fine crystals of calcium/sulfur reaction products.

Table 2. Summary of Bulk Chemical Composition, Reported as Oxides, of SDA Material Reported in the Reviewed Literature

Parameter	wt%	Parameter	wt%
SiO_2	1.4–32.4	P_2O_5	0.03–1.2
Al_2O_3	0.8–44	TiO_2	0–1.19
Fe_2O_3	0.4–44	BaO	0.03–0.85
CaO	0.2–60	MnO_2	0–0.12
SO_3	0–32	SrO	0.44–0.46
MgO	0.1–14	Moisture	<0.1–13.2
Na_2O	<0.1–46	LOI or C	0.19–20.5
K_2O	0.1–6.37	Unaccounted	1.7–6.2

Table 3. Summary of Trace Elemental Composition of SDA Material Reported in the Reviewed Literature

Element	Range, ppm	Element	Range, ppm
Aluminum (Al)	<5000–230,000	Manganese (Mn)	24.5–1432
Antimony (Sb)	0.8–29	Mercury (Hg)	<0.001–10
Arsenic (As)	0.4–1200	Molybdenum (Mo)	<0.02–514
Barium (Ba)	0.76–12,000	Nickel (Ni)	1.4–460
Beryllium (Be)	0.7–63	Potassium (K)	1600–9300
Boron (B)	<10–1460	Selenium (Se)	<0.1–760
Cadmium (Cd)	0.01–70	Silver (Ag)	0.04–8
Calcium (Ca)	7100–401,000	Sodium (Na)	710–240,000
Chromium (Cr)	3–1000	Strontium (Sr)	30–13,000
Cobalt (Co)	<0.5–172	Sulfur (S)	3000–230,000
Copper (Cu)	3–655	Thallium (Tl)	0.1–42
Iron (Fe)	6300–367,000	Tin (Sn)	0.01–962
Lead (Pb)	<0.3–800	Vanadium (V)	0.4–950
Magnesium (Mg)	3000–151,000	Zinc (Zn)	<6–9000

SUMMARY OF CURRENT AND POTENTIAL USES OF SDA MATERIAL

SDA material is commercially used in a variety of applications. ECOBA lists several specific current uses for SDA material in Europe:

- A component of mining mortar for stabilizing underground cavities
- An addition in the production of sand-lime bricks
- In the production of cement clinker in a special clinker production method (Müller-Kühne Process)
- A sorbent in a wet FGD process in power plants
- As a sulfur fertilizer in agriculture[10–12]

Since ACAA reports all dry FGD material applications in bulk, the commercial applications for SDA material in the United States are not as defined specifically as in Europe but do include mine fill, synthetic aggregate, and agriculture. The SDA material without a fly ash component (as typically produced in Europe) is more consistent in composition even from multiple plants and likely influenced the development of these applications along with more stringent European regulations that encourage utilization of CCBs.

Agriculture

In Europe, SDA material is typically collected separate from fly ash, whereas in the United States, SDA material and fly ash is often intermingled. This difference could be the reason that SDA material is used commercially as a sulfur fertilizer in Germany, Denmark, and Austria, but not in the United States. There are unanswered engineering and environmental questions as well. The potential for SDA material to be used as a liming agent or for soil amendment has received mixed results depending on the pH of the soil, crops planted, amount of SDA material used, and whether the SDA material was blended with any other material.

Binder

SDA material used as a binder for interior plasters was noted in U.S. and German patents. The use of the by-product as a flooring binder is considered promising and other potential applications include use in insulating building materials and raw materials for double floor plates where it may be substituted for cement products. This is a promising low-volume, high-value application.

Cement Manufacture

Although SDA material has been used commercially to manufacture cement in Germany, it has not reached the demonstration phase in the United States. A process has been patented in the United States to use dry FGD material in place of fly ash and gypsum in the production of cement, although it is not anticipated that that process will reach commercialization.

Cement Replacement in Concrete

SDA material should be evaluated for suitability as a cement replacement in concrete, especially as groups like ASTM International and American Association of State Highway and Transportation Officials move toward performance-based specifications as opposed to prescriptive specifications. Research has shown that except for retardation in setting times, concrete, in which cement was partially substituted by SDA material, showed strength and durability performance comparable to or superior to traditional concrete. This application is particularly promising when SDA material and fly ash are collected together, with a high percentage of fly ash.

Civil Engineering Applications

SDA material has been used commercially in Europe and with limited success in the United States. Mixed results have been found in the expansion potential of SDA material used as a road foundation.

Flowable Fill

The basic physical and engineering properties (moisture density, compressive strength development, and permeability) of reactive and low reactivity SDA material indicate that these materials should be able to perform acceptably as flowable fill material. Research conducted to date supports this claim and shows that SDA material can be an economical alternative to conventional materials; however, more research is needed on nonreactive SDA materials. It is recommended that more long-term tests be conducted to test long-term strength, stress-strain behavior, freeze-thaw, swell potential, and corrosivity.

Masonry

Successful aggregate production from SDA material indicates the potential for use in brick and other shaped compacted product production. Although SDA material appears to be an effective material, it may need to be conditioned prior to use and cementitious additives may be required for unreactive to moderately reactive SDA materials.

Mining Applications

SDA material has been used commercially as a mine fill. Additionally, SDA material has been shown to be capable of neutralizing the spoil acidity and reestablishing vegetative cover to stabilize soils and reduce erosion. However, excessive application did cause excessively high pH and cementation.

Synthetic Aggregate

SDA material is already being used to manufacture synthetic aggregate. Other manufacturing processes have been developed to use SDA material to produce synthetic aggregate but have not had commercial success. From a technical standpoint, SDA material can be a very effective raw material for the production of synthetic aggregate; however, the economics of using the material may not be practical in some instances.

Other Potential Uses

Additional uses of SDA material include a fixating agent for hazardous waste sludge, marine applications, mineral wool, sulfuric acid production, a sorbent for the wet FGD process, and a source of gypsum for wallboard production.

BARRIERS TO SDA MATERIAL UTILIZATION

The European and U.S. production and utilization statistics for SDA material clearly indicate that SDA materials are currently under utilized, especially in the United States. The literature reviewed brought into focus the barriers that exist and limit the use of SDA material in the United States. The barriers identified by the authors are:

- **Inconsistent Terminology Used to Define the Material –** In the literature reviewed, there was a marked discrepancy among the terms used to describe SDA materials. The discrepancies were so broad that in some cases, the Energy & Environmental Research Center (EERC) technical staff performing the review could not determine the specific by-product to which the authors referred. Inconsistent terminology makes it difficult for those in the industry, particularly government entities, to properly define the material and its potential uses. In any area, a well-defined vocabulary is the cornerstone of effective communication and is essential in technical fields. This lack of consistent terminology is a barrier in both the commercialization and in the research and development of SDA material utilization.

- **Lack of Understanding of the Material –** The successful management of SDA material requires a thorough understanding of the engineering and chemical properties of the material. Although a number of references were identified that considered the characterization of the material as it relates to potential uses, the engineering and chemical properties of specific materials need to be investigated further. As with other by-products, it is difficult to generalize the properties of the material because of differences in coal type, combustion system, collection process, and management. As previously noted, SDA materials exhibit a variability that results from the system configuration and the percentage of fly ash present in the final SDA material. Potential uses that apply to one type of material may not be appropriate for others. The natural oxidation of sulfite to sulfate in SDA material is documented, and yet the impact of this oxidation process on product performance is not well-defined and needs to be considered in evaluating utilization applications.

- **Limited Data on Environmental and Health Effects –** Although all SDA materials encountered in this literature review meet regulatory limits for classification as nonhazardous wastes, there are still concerns about surface water and groundwater contamination by runoff, seepage, and leachate during disposal or use applications. Many potential uses for SDA material fall under the general category of land application, which raises questions about the potential for the material to impact the environment and/or human health.

- **Inconsistent Guidelines on Beneficial Ash Use –** Many state rules apply to fly ash, bottom ash, and boiler slag utilization; however, by-products from FGD systems are relatively new in comparison to other by-products and specifications have not been written that deal specifically with SDA material.

- **Economics –** Economic factors are the overriding issue in electric generating company ash management decisions. Currently, the potential to produce revenue from the sale of SDA material is limited; therefore, most electric generating companies find it more economically feasible to dispose of the material rather than dedicate resources (i.e., employees and infrastructure) to utilize it. The prices received for SDA material are simply too low to justify a large financial commitment to SDA material marketing. In some countries in Europe, increasing landfill taxes have driven the development of SDA material applications.

CONCLUSIONS

The literature assembled and reviewed provided a good representative cross section of the technical information available on the utilization of SDA material in the United States and Europe. The following conclusions were developed based on the information assembled from the review:

- SDA materials exhibit a broad variability based on the SDA system configuration, the fly ash content of the SDA material, the composition of the fly ash in the SDA material, and the use of optional sorbent recycle.

- The natural oxidation of sulfite to sulfate, which is relatively unique to SDA materials among CCBs, has the potential to impact the material performance in utilization applications and products.

- European SDA materials, frequently referred to as dry FGD material in the European literature, generally do not incorporate fly ash into the final SDA material, and documented commercial utilization of SDA material in Europe is higher than in the United States.

- U.S. SDA systems typically incorporate fly ash into the final SDA material and are most commonly used in coal-fired units where alkaline ash is produced, allowing the fly ash to act as an SO_2 sorbent.

- U.S. SDA material utilization rates are lower than European utilization rates, likely because of higher variability of the U.S. material and less stringent regulations in Europe that promote industrial resource utilization.

- Numerous utilization applications have high to moderate potential for commercialization in the United States, but technical, environmental, and economic evaluations will likely be needed before these materials can be successfully introduced into the identified markets. New regulations regarding the use of SDA material will also have to be adopted.

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