

# A Review of Literature Related to the Use of Spray Dryer Absorber Material

Production, Characterization, Utilization Applications, Barriers, and Recommendations

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## A Review of Literature Related to the Use of Spray Dryer Absorber Material

Production, Characterization, Utilization Applications, Barriers, and Recommendations

### 1014915

Technical Report, September 2007

Cosponsor

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This report was prepared by

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This report describes research sponsored by the Electric Power Research Institute (EPRI) and the University of North Dakota (UND) Energy & Environmental Research Center (EERC) Coal Ash Resources Research Consortium (CARRC).

The report is a corporate document that should be cited in the literature in the following manner:

A Review of Literature Related to the Use of Spray Dryer Absorber Material: Production, Characterization, Utilization Applications, Barriers, and Recommendations. EPRI, Palo Alto, CA and UND EERC CARRC, Grand Forks, ND: 2007. 1014915.

### **REPORT SUMMARY**

This report is a compilation of an extensive literature review focused on spray dryer absorber (SDA) systems and their by-products. It includes background information on the current SDA production and use statistics, characterization data on SDA material reported in the literature, an overview of the current commercial and potential uses of SDA material reported in the literature, identification of barriers to the increased use of SDA material, and the authors' conclusions and recommendations based on the literature reviewed. This report is intended to assist utility ash managers, ash marketers, regulators, and researchers in understanding the issues surrounding SDA material utilization so that they can move from disposal to utilization.

#### Background

SDA systems are a semi-dry SO<sub>2</sub> control technology that currently make up about 12% of the flue gas desulfurization (FGD) systems at U.S. power plants. SDA systems have typically been employed on small-to-moderate size units that burn low-sulfur coal in the western United States, where water supply is limited. The material produced by SDA systems primarily consists of calcium sulfite commingled with varying amounts of fly ash and unspent lime. Because most units in the United States do not pre-collect fly ash, the SDA material often contains a high percentage of it. SDA material presents a unique challenge for use applications, and as a result most coal-fired power plants currently dispose of SDA material. The use of SDA systems is expected to grow along with wet FGD systems over the next 10 years as a result of increased requirements for SO<sub>2</sub> control, heightening the need for increased utilization options.

#### **Objectives**

- To summarize current information in the literature relative to SDA material production, characteristics, and uses
- To rank the potential of different uses for SDA material
- To provide recommendations for maintaining/increasing the use of SDA material in the future

#### Approach

The authors performed a detailed survey of the U.S. and European literature on the use of SDA material in a variety of applications. They summarized information on SDA material characteristics, production, and use, with particular emphasis on the benefits and disadvantages of the higher fly ash content of the SDA material in the United States. Based on the review, the authors developed a prioritized list of potential applications to advance the use of SDA material along with a set of recommendations for further research.

### Results

According to American Coal Ash Association (ACAA) statistics, in 2006 U.S. utilities produced about 1.5 million short tons of SDA material and used only about 0.14 tons, or a little over 9%. Mining applications represented by far the largest type of application, accounting for 85% of the use. Other uses included concrete and concrete products, flowable fill, roadways, waste and soil stabilization, and agriculture. Key attributes of SDA material that must be considered in developing applications are the material's inherent variability, its high sulfur content, and its potential for expansion.

Based on the literature review, the authors ranked the SDA material for use in various applications:

- High potential: cementitious products (such as masonry, flowable fill, and synthetic aggregate) and mining applications
- Moderate potential: cement replacement in concrete, engineering applications, agriculture, soil stabilization, and wet FGD sorbent
- Low potential: binder material, cement manufacture, hazardous waste fixation, marine applications, mineral wool, sulfuric acid production, and wallboard

Barriers inhibiting the use of the material were identified and include the following:

- Inconsistent terminology used to define the material
- Lack of understanding of the material
- Limited data on environmental and health effects
- Inconsistent guidelines on beneficial use
- Economics

#### **EPRI** Perspective

Maintaining and increasing the utilization rate of coal combustion products (CCPs) is a primary strategic goal of EPRI's CCP Use research program. SDA materials currently have a low utilization rate, and their volume is expected to significantly increase over the next several years. Understanding SDA material characteristics and developing increased management options are key components of the overall CCP use research strategy.

#### Keywords

Flue gas desulfurization products Spray dryer absorber material Coal combustion products Utilization

### ABSTRACT

Coal-fired power plants account for the majority of sulfur dioxide  $(SO_2)$  emissions in the United States. Legislative actions in the United States and elsewhere have been responsible for most industrial SO<sub>2</sub> controls, resulting in the installation of flue gas desulfurization (FGD) systems. In the United States, approximately 85% of FGD systems are wet, 12% are spray dryer absorber (SDA) systems, and 3% are dry injection systems. This report is a compilation of an extensive literature review on SDA systems and their byproducts.

Most SDA systems in the United States collect fly ash (40–75%) along with SDA material, producing spherical, glassy fly ash particles coated by and intermixed with fine crystals of calcium/sulfur reaction products. Depending on their source, SDA materials can vary widely in their physical, chemical, and mineralogical properties, and the successful utilization of SDA material is highly dependent on these properties. Characterization data cited in the literature are included in this report.

In the literature reviewed, a number of current commercial and potential uses of SDA material were identified, including agriculture, binders, cement manufacture, cement replacement in concrete, civil engineering, flowable fill, fixating agent for waste, marine applications, masonry, mineral wool, mining applications, soil stabilization, sulfuric acid production, synthetic aggregate, wallboard, and wet FGD sorbent. Many of the commercial uses are being successfully implemented in Europe but are slower to enter the marketplace in the United States. Applications currently commercial in the United States include agriculture, concrete, concrete products, flowable fill, mining applications, soil stabilization, structural fills and embankments, and synthetic aggregate. Potential uses in the research and development stage were rated as high-, moderate-, or low-potential commercial applications. High-potential applications for the U.S. market are estimated to be those that take advantage of the presence of the fly ash component of the SDA material, can tolerate relatively high sulfur content, and either have limited susceptibility to expansion or reduce expansion potential in the production process. These applications fall into two categories: cementitious products and mining applications.

Barriers inhibiting the use of the material were identified and include the following:

- Inconsistent terminology used to define the material
- Lack of understanding of the material
- Limited data on environmental and health effects
- Inconsistent guidelines on beneficial ash use
- Economics

Based on the information obtained in the research, the authors recommend the following to maintain existing commercial markets and develop new ones for SDA materials produced in the United States:

- Work within existing organizations such as ASTM International and the American Coal Ash Association to develop and put into use appropriate terminology and definitions for SDA materials.
- Develop an understanding of the impact of compositional variability on the performance characteristics of SDA materials.
- Develop an understanding of the oxidation profiles of SDA materials, and evaluate the impacts of oxidation on product performance.
- Educate potential users, regulatory representatives, and other stakeholders about SDA materials.
- Address quality, compositional, environmental, and performance criteria in research, development, and demonstration efforts.

### NOMENCLATURE

ACAA	American Coal Ash Association
AASHTO	American Association of State Highway and Transportation
	Officials
AFBC	atmospheric fluidized-bed combustion
$Ca_{6}Al_{2}(SO_{4})_{3}(OH)_{12} \cdot 26H_{2}O$	ettringite
CaCl	calcium chloride
CAIR	Clean Air Interstate Rule
CaO	calcium oxide, lime
Ca(OH) <sub>2</sub>	calcium hydroxide, hydrated lime, portlandite, unreacted
× 72	lime
CARRC <sup>®</sup>	Coal Ash Resources Research Consortium <sup>®</sup>
$Ca_3Si(CO_3)(SO_4)(OH)_6 \cdot 12H_2O$	thaumasite
CaSO <sub>3</sub>	calcium sulfite
$CaSO_3 \cdot \frac{1}{2} H_2O$	hannebachite, calcium sulfite hemihydrate
CaSO <sub>4</sub>	calcium sulfate, anhydrite
$CaSO_4 \cdot 2 H_2O$	gypsum, calcium sulfate dihydrate
CCP	coal combustion product
CDF	controlled density fill
CHP	combined heat and power
CLSM	controlled low-strength material
DM	Deutsche Mark
DOE	U.S. Department of Energy
DSI	dry sorbent injection
ECOBA	European Coal Combustion Products Association
EERC	Energy & Environmental Research Center
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ERKOM	"Waste Management of Residues from Coal-Fired Power
	Plants and Waste Incineration Plants" (known as ERKOM
	from the German title)
ESP	electrostatic precipitator
EU	European Union
FBC	fluidized-bed combustion
FGD	flue gas desulfurization
FSI	furnace sorbent injection
FSS	fixated scrubber solids
HCl	hydrogen chloride

LIMB	limestone injection multistage burner
LOI	loss-on-ignition
MnDOT	Minnesota Department of Transportation
MW	megawatt
NO <sub>x</sub>	nitrogen oxides
NR	not reported
OSU	Ohio State University
OVwG	Oberverwaltungsgericht: Administrative Court of Appeals
RCRA	Resource Conservation and Recovery Act
SCS	Stearns, Conrad and Schmidt
SDA	spray dryer absorber
SEM	scanning electron microscopy
$SO_2$	sulfur dioxide
SO <sub>3</sub>	sulfur trioxide
TCLP	toxicity characteristic leaching procedure
TGA	thermogravimetric analysis
UND	University of North Dakota
VAW	Vereinigte Aluminium-Werke AG, Lünen

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# **1** INTRODUCTION

The use of flue gas desulfurization (FGD) technologies to reduce sulfur dioxide (SO<sub>2</sub>) emissions from flue gases at coal-fired power plants gained prominence in the 1980s in the United States. FGD systems are currently used on approximately 22% of U.S. coal-fired power plants. A variety of FGD system types are used globally, and the types of FGD systems used in the United States are summarized in a 2003 Energy & Environmental Research Center (EERC) report [1].

The FGD material that is the focus of this report is termed spray dry absorber material or SDA material. The system is referred to as a spray dry absorber (SDA). An SDA system captures SO<sub>2</sub> 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. Recycle 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<sub>2</sub> gases. As noted by Redinger, the use of fly ash precollection is common in Europe but is not common in the United States. SDA systems are considered efficient and reliable and have a lower capital cost than wet FGD systems [2]. Operating costs for SDA systems are higher than wet FGD systems but the water usage is lower. The resulting product currently has a low utilization rate in the United States.

The 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, and a number of these were identified in a previous literature search on the topic of sulfite-rich FGD materials [3]. These terms are noted in Figure 1-1. This report will use the term "SDA material" throughout, except where the generic term "dry FGD material" was used in the review literature. In the United States, SDA material typically contains fly ash, so the authors have elected to note precollection of fly ash or the level of fly ash content when known.

- Spray/spray-dry/dryer/drier absorber/atomization/absorption (SDA, SAV) sludge, ash, material, product, byproduct, by-product, end-product, waste, or residue
- Semidry absorber/atomization/absorption (SDA) sludge, ash, material, product, byproduct, 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/drier ash, material, product, byproduct, by-product, end-product, waste, or residue
- Lime spray dry/dryer/drier (LSD) ash, material, product, byproduct, by-product, end-product, waste, or residue
- Advanced SO<sub>2</sub> control (ASC) ash, material, product, byproduct, by-product, end-product, waste, or residue
- Sulfite-rich flue has 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, endproduct 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 1-1 Terms Used to Refer to SDA Material in the Literature

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<sub>2</sub> emission controls and a subsequent increase in the volumes of FGD products produced in the United States. 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. While all types of FGD material production are likely to increase, the potential increase in production volumes of SDA materials is a subject that raises the issue of materials management because of the current low utilization rate in the United States. With goals of 50% utilization of coal combustion products (CCPs) set by the U.S. Department of Energy (DOE) and the American Coal Ash Association (ACAA) to be achieved

by 2010, 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 CCP utilization in the United States. The first step in determining the best options for utilization of SDA material is to identify current commercial applications and any potential applications that have been investigated or demonstrated.

The goal of the project was to assess the current state of the knowledge regarding the characterization and utilization of SDA material and make recommendations on how to improve the use of the material. The project focused primarily on products produced from SDA systems; however, the report does contain limited information on other FGD processes and products.

This report provides background information on how SDA systems function, descriptions of the variability of SDA materials, and information on the current production and use statistics. This background information provides a framework from which to evaluate the information on utilization applications summarized from the literature.

### Background

#### Development and Status of FGD Systems in the United States

Currently, coal-fired power plants account for the majority of  $SO_2$  emissions in the United States. Health concerns, including breathing difficulty, respiratory illness, and aggravation of existing cardiovascular disease, are associated with exposure to high ambient concentrations of  $SO_2$ . The emission of  $SO_2$  from coal-fired power plants can also lead to acid deposition in the environment.

In an effort to address health and environmental concerns related to  $SO_2$  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 1990 amendment required a permanent 10-million-ton reduction (to almost half the 1980 level) in  $SO_2$ emissions between 1980 and 2010. 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.  $SO_2$  emission regulations have also been proposed in many other industrialized nations. Most members of the European Economic Community are regulated, and Canadian laws are similar to those in the United States.

#### Introduction

Coal-fired power plants generally employ one of two strategies to control  $SO_2$  emissions: 1) burn compliance fuels or 2) install FGD systems. Compliance fuels can be obtained by burning lowsulfur coal (coals with sulfur content below 2% by weight), blending low- and high-sulfur coals, and washing coal. Most modern power plants, particularly plants built after 1978, are required to have an FGD system. A variety of FGD systems are in use and others are in various stages of development. Commercialized FGD processes include wet, semidry, and completely dry processes. Regardless of type, FGD processes typically use a calcium- or sodium-based alkaline sorbent. The sorbent is injected in the flue gas in a spray chamber/vessel or directly into the duct. The  $SO_2$  is adsorbed, neutralized, and/or oxidized by the alkaline sorbent into a solid compound, either calcium or sodium sulfite or sulfate. The solid is removed from the flue gas stream using downstream equipment.

### FGD Systems

For a typical coal-fired power plant, FGD systems will remove ~90% or more of the  $SO_2$  in the flue gas. According to EPA, approximately 85% of the FGD systems installed in the United States are wet, 12% are SDA systems, and 3% are dry injection systems [4]. The following is a brief description of wet and dry FGD systems.

#### Wet Calcium-Based FGD Systems

In a wet FGD system, flue gas is ducted to a spray chamber/vessel (absorber) where an aqueous solution of sorbent is injected into the flue gas. The most popular type of sorbent used is limestone, but lime can also be used. A portion of the water in the solution is evaporated and the waste gas stream becomes saturated with water vapor.  $SO_2$  dissolves into the solution droplets where it reacts with the alkaline particulates. The resulting wet FGD material falls to the bottom of the spray chamber/vessel, where it is collected [4].

Wet FGD systems are the most popular technology to control  $SO_2$  emissions because they use a widely available and inexpensive sorbent (limestone), can produce FGD gypsum (a usable product) when using forced oxidation, are reliable, and can achieve efficiency up to 99% [1]. Several types of wet FGD processes are available and include limestone-forced oxidation, limestone with natural or inhibited oxidation, lime with or without buffers, lime dual alkali, magnesium-promoted lime, a seawater process, a sodium-scrubbing process, and ammonia scrubbing [1, 5].

#### Dry and Semidry FGD Systems

There are four types of dry/semidry FGD systems: 1) SDA (semidry) systems; 2) duct sorbent injection (DSI) (dry); 3) furnace sorbent injection (FSI) or limestone injection multistage burner (LIMB) (dry); and 4) fluidized-bed combustion (FBC) (dry). From 1980 to 1992, 7200 megawatts (MW) of dry FGD systems were installed at electric utilities in the United States and have mainly been applied to units burning low-sulfur coals. Of the 43 electric utility dry FGD system installations in the United States, the majority lie west of the Mississippi River [5, 6]. The technology is also used in western Europe.

Dry FGD systems like DSI, FSI, and LIMB inject powdered sorbent directly into the furnace, economizer, or downstream ductwork. The resulting dry product is removed using particulate control equipment such as an electrostatic precipitator (ESP) or baghouse/fabric filter. The flue gas is generally cooled prior to entering the particulate control device. Water can be injected upstream of the absorber to enhance  $SO_2$  removal [4]. Atmospheric fluidized beds use a sorbent such as limestone or dolomite to capture sulfur released by the combustion of coal. Jets of air suspend the mixture of sorbent and burning coal during combustion, converting the mixture into a suspension of red-hot particles that flow like a fluid [7].

The SDA, or semidry, process consists of four operations: sorbent preparation, the spray dryer absorber (also referred to as a chamber or vessel), particulate collection, and product management. An alkaline sorbent is delivered to the power plant in covered railroad cars, trucks, or river barges and then stored in a suitable container to which is it usually pneumatically conveyed. The most popular sorbent is lime (calcium oxide, CaO precalcined) or calcium hydroxide (hydrated lime, Ca(OH)<sub>2</sub>), but a select number of systems use sodium carbonate. The sorbent is mixed with water, then classified to prevent any large grit particles from going to the spray dryer absorber, where they can cause orifice plugging in the spray nozzles or rotary atomizer. The resulting aqueous slurry is sprayed into the hot flue gas in the spray dryer absorber in a cloud of fine droplets. The residence time is sufficient to allow the SO<sub>2</sub> and other acid gases such as sulfur trioxide (SO<sub>2</sub>) and hydrogen chloride (HCl) to react simultaneously with the sorbent and for the water to evaporate. A diagram of the SDA process is shown in Figure 1-2. In this figure, a fly ash precollection ESP is shown as an option. In Europe, fly ash precollection is common for SDA systems, allowing the fly ash stream to be utilized without being mixed with the SDA material. In the United States, it is not common for the fly ash to be precollected, so the fly ash and SDA sorbent combine and pass into the particulate control device as shown in the figure. It is also typical that a portion of the SDA material is recycled back into the SDA, also indicated in the figure.

The resulting material is a dry powder product, which is a calcium sulfite  $(CaSO_3 \cdot \frac{1}{2} H_2O)$ , or hannebachite) rich material, referred to as SDA material in this report. A small portion of the dry product is collected at the bottom of the absorber, but the bulk of the material is collected in either an ESP or a fabric filter/baghouse. The SDA material may contain up to 75% fly ash by mass, depending on the location of the SDA installation. The distribution of materials collected from the bottom of the absorber and from the particulate control device (ESP or fabric filter/baghouse) in a typical SDA operation is given in Table 1-1 [8]. Since there is a certain amount of unreacted lime in the SDA material, most SDA systems recycle part of their products

(SDA material and fly ash) back into the feed slurry to increase lime utilization and take advantage of the inherent alkalinity of some fly ashes [9, 10, 11].

Introduction

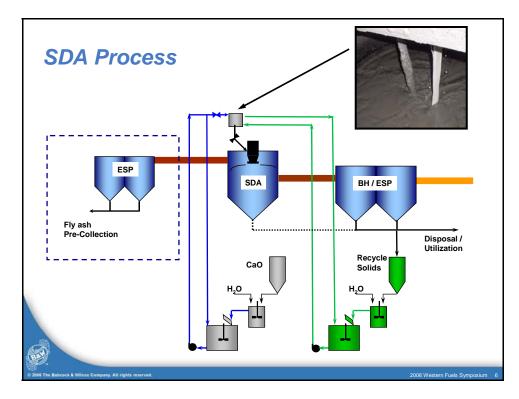


Figure 1-2

Diagram of the SDA Process Showing the Fly Ash Precollection Option and the Solids Recycle [2]

Material	Bottom of Drying Chamber (%)	Particulate Control Device (%)		
Fly Ash	70	72		
Calcium Sulfite	13	15		
Calcium Sulfate	7	9		
Unreacted Lime	5	1		
Water	5	3		

Table 1-1Typical SDA Operation Material Distribution [8]

The advantages of SDA systems over wet scrubbing include:

- 1. Less costly construction materials typically made of mild steel, thus lower capital costs.
- 2. Dry 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, allowing immediate feed control of sorbent to follow boiler load.
- 5. High reliability.
- 6. Less sensitive and simpler process chemistry [5, 9, 12, 13].
- 7. Removal of  $SO_3$  from flue gas.

Perhaps the greatest disadvantage of SDA systems is the higher cost of lime sorbents used in relation to the limestone used for wet scrubbing [9, 12, 13]. In addition, SDA systems produce a product that is difficult to sell and is often disposed of. SDA material is typically disposed of in a manner similar to fly ash.

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. These units are shown in Table 1-2. SDA units in the United States were previously reported by Beidleman and Hilbert [14] and Soud [15]; however, multiple current sources were used to develop this updated table.

#### Table 1-2 SDA Units in the United States<sup>a</sup>

Utility	Plant and Unit with FGD City		State	Сар	Nameplate Capacity (MW)		Design Coal Sulfur (wt%)	Sorbent	Designed SO <sub>2</sub> Removal	Coal Type
	System			By Plant	By FGD Unit	Date	Sullui (wt%)		(% Efficiency)	туре
	Antelope Valley Unit 1	Beulah	ND	900	450	1984	1.20	Lime	Up to 90.0	Lig⁵
Basic Electric Power Cooperative	Antelope Valley Unit 2	Beulah	ND	900	450	1986	1.20	Lime	Up to 90.0	Lig
	Laramie River Station Unit 3	Wheatland	WY	1650	550	1982	0.50	Lime/Alkaline Fly Ash	85.0	Sub⁵
Duke Energy	East Bend Unit 2	Rabbit Hash	KY	669	669	1981	5.20	Lime	99.0	Bit <sup>d</sup>
East Kentucky Power Cooperative, Inc.	H.L. Spurlock Unit 2	Maysville	KY	1118	525	1981	3.60	Lime	90.0	Bit
Grand River Dam Authority	Coal-Fired Complex Unit 2	Chouteau	ОК	1010	520	1986	1.50	Lime/Alkaline Fly Ash	85.0	Sub
Great River Energy	Stanton Station	Stanton	ND	188	188	1982	0.70	Lime	70.0	Lig
Kansas City Power & Light	Hawthorn Station	Kansas City	МО	594	594	2001	0.33	Lime/Alkaline Fly Ash	88.0	Sub
Marquette Board of Light and Power	Shiras 3	Marquette	MI	40	40	1983	0.50	Limestone	80.0	Sub
Otter Tail Power Company	Coyote Station	Beulah	ND	400	400	1981	0.80	Lime/Alkaline Fly Ash	70.0	Lig
PacifiCorp	Wyodak Power Plant	Gillette	WY	365	365	1986	0.80	Lime/Alkaline Fly Ash	75.2	Sub
Platte River Power Authority	Rawhide Energy Station	Wellington	со	294	294	1984	0.30	Lime/Alkaline Fly Ash	80.0	Sub
Sierra Pacific Power CompanySC	Valmy Unit 2	Valmy	NV	521	267	1985	0.50	Lime	70.0	Bit

# Table 1-2 (continued) SDA Units in the United States<sup>a</sup>

Utility	Plant and Unit with FGD	City	State	Nameplate Capacity (MW)		In-Service Date	Design Coal Sulfur (wt%)	Sorbent	Designed SO₂ Removal	Coal Type
	System			By Plant	By FGD Unit	Dale	Sullur (wt %)		(% Efficiency)	туре
South Carolina Electric & Gas Company	Cope Station	Cope	SC	430	430	1996	1.90	Lime	Up to 98.0	Bit
Tri-State Generation & Transmission Association	Craig Unit 3	Craig	со	1274	446	1984	0.70	Lime	85.0	Sub
Sunflower Electric Power Corporation	Holcomb Unit 1	Holcomb	KS	360	360	1983	1.00	Lime/Alkaline Fly Ash	80.0	Sub
	Springerville Unit 1	Springerville	AZ	1560	380	1985	0.70	Lime/Alkaline Fly Ash	61.3	Sub
Tucson Electric Power Company	Springerville Unit 2	Springerville	AZ	1560	380	1985	0.70	Lime/Alkaline Fly Ash	61.3	Sub
	Springerville Unit 3	Springerville	AZ	1560	400	2006	0.70	Lime/Alkaline Fly Ash	_	Sub
	Cherokee Unit 3	Denver	со	715	151	—	0.40	Lime/Alkaline Fly Ash	70.0	Bit
	Cherokee Unit 4	Denver	со	715	351	2003	0.40	Lime/Alkaline Fly Ash	70.0	Bit
Xcel Energy	Hayden Unit 1	Hayden	со	446	184	1998	0.40	Lime/Alkaline Fly Ash	85.0	Bit
	Hayden Unit 2	Hayden	со	446	262	1999	0.40	Lime/Alkaline Fly Ash	85.0	Bit
	Sherco Unit 3	Becker	MN	2400	900	1987	0.90	Lime/Alkaline Fly Ash	72.3	Sub

<sup>a</sup>Multiple current sources were used to develop this update table. <sup>b</sup>Lignite. <sup>c</sup>Subbituminous. <sup>d</sup>Bituminous

In nine European countries, 49 dry FGD plants were reported [16]. The plants are categorized by country in Table 1-3.

Country	Sites with Dry FGD Plants	Dry FGD Production (approx.) (short tons/year)	Year Reported	% of FGD Units Using SDA Process
Austria	4	50,000	1995	41.7 in 1993
Denmark	2	83,200	1997	37.3 in 1993
Czech Republic	8	140,000	1998	NR <sup>ª</sup>
Finland	4	32,000	1999	NR
Germany	20	378,000	1996	7.0 in 1993
Italy	1	10,000	2000	NR
Poland	5	500,000 - 600,000	2000	NR
Spain	1	5,000	1999	NR
Sweden	4	10,000	1999	100

#### Table 1-3 Dry FGD Plants in Europe [16, 17]

<sup>a</sup>Not reported.

### Projected Future SDA Installations in the United States

The Babcock & Wilcox Company tracks projected future SDA installations in the United States (see Table 1-4) [18]. Details indicating new capacity versus retrofit installations, generating unit size, coal type, geographic location, and reagent system are provided in Table 1-5. The numbers of projected SDA installations shown in Tables 1-4 and 1-5 are planned projects that have been announced, but many factors could change these planned installations. Additionally, installations of circulating dry scrubber-type systems, producing a product expected to be similar to SDA material, are projected to increase.

Table 1-4 U.S. SDA Market Projections [18]

Time Horizon							
1 – 5 Years (2007 – 2012)			5 – 10 Years (2013 – 2017)				
Projected SDA Installations	# Gen. Units	Gen. Capacity (MW)	# Gen. Units	Gen. Capacity (MW)			
New Capacity	14	7,050	3	1,850			
Retrofits	28	11,350	16	7,400			

# Table 1-5Details of U.S. SDA Market Projections [18]

Time Horizon	1 – 5 Years (2007 – 2012)		5 – 10 Years (2013 – 2017)				
	New Capacity	Retrofits	New Capacity	Retrofits			
Generating Unit Size (MW)							
>800	2	3		1			
500 to 800	7	7	3	6			
250 to 500	1	8		8			
100 to 250	2	7		1			
<100	2	3					
Coal Type (sulfur content, %)							
Lignite	1						
Subbituminous	13	18	3	16			
Bituminous – western		3					
Bituminous – eastern		7					
Geographic Location by EPA Region							
1 (ME, NH, VT, MA, RI, CT)		2					
2 (NY, NJ)		3					
3 (PA, WV, VA, MD, DE)		2					
4 (KY, TN, NC, SC, GA, AL, MS, FL)			2				
5 (OH, IN, IL, MI, WI)	1	10		14			
6 (AR, LA, OK, TX, NM)	3	2		1			
7 (IA, MO, KS, NE)	4	2	1				
8 (CO, UT, WY, MT, ND, SD)	4	7					
9 (CA, NV, AZ)	2						
10 (AK, WA, OR, ID)							
Reagent Stream							
Fly ash recycle	11	26	3	16			
Lime only	3	2					

### **Current SDA Material Production and Use Rates**

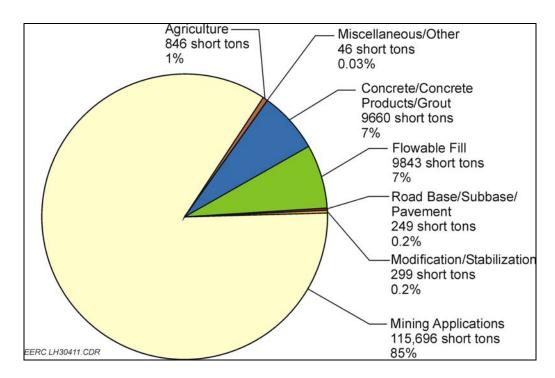
ACAA reports the yearly production and use of CCPs in the United States, including statistics on FGD products from wet and dry systems. SDA material is reported with all other products from dry FGD systems, with the exception of FBC systems, in an FGD dry scrubber material category. The ACAA definitions of dry FGD material and FGD dry scrubber material are included in Figure 1-3 [19].

- Dry FGD material the product that is produced from dry FGD systems and consists primarily of calcium sulfite, fly ash, portlandite (Ca(OH)<sub>2</sub>), and/or calcite. Lime-based sorbent system dry FGD material main constituents are calcium sulfite and dry fly ash, along with minor quantities of calcium sulfate. Sodium-based sorbent system main constituents are sodium sulfite and dry fly ash along with minor quantities of sodium sulfate. Dry FGD material is being used in construction, engineering, and agricultural applications; however, most of the material is stored in landfills.
- FGD material dry scrubbers the dry powdered material from dry scrubbers that is collected in a baghouse along with fly ash and consists of a mixture of sulfites, sulfates, and fly ash.

#### Figure 1-3 ACAA Definitions of Dry FGD Material [19]

The production of dry scrubber FGD material has been reported as a separate category in the annual ACAA CCP Production and Use Survey since the 2002 statistics were released in 2003 [20]. Since then, the reported production has varied from a low of 935,394 short tons in 2002 to a high of 1,829,830 short tons in 2004 [20, 21]. ACAA reported that 1,488,951 short tons of dry FGD material was produced in the United States in 2006. Of that, 136,639 short tons (or 9.18%) was beneficially used, which is the lowest percentage reported by ACAA's survey [22]. Figure 1-4 illustrates the major markets for dry scrubber FGD material in the United States as reported by respondents to the 2006 annual ACAA CCP Production and Use Survey.

The use application categories reported for dry scrubber FGD material in the ACAA annual survey since 2002 statistics have included concrete/concrete products/grout, cement/raw feed for clinker, flowable fill, structural fills/embankments, road base/subbase/pavement, soil modification/stabilization, mineral filler in asphalt, mining applications, waste stabilization/solidification, agriculture, aggregate, and miscellaneous/other. However, the categories vary annually because of variations in respondents to the annual ACAA survey and added SDA units or unit closures (e.g., Xcel Energy's Riverside Unit 7 went out of service in 2004). ACAA typically notes a utility response rate of 54%–60% for its annual Production and Use Survey.





SDA material production and use figures are incorporated into the overall reporting category of dry FGD material by ACAA, and quantities of SDA material produced and used have never been reported separately by ACAA. Using the 2004 and 2005 production figures for dry FGD material, and an estimate of sodium-based dry FGD material production based on sodium-based sorbent use predictions for 2007, and taking into consideration the ACAA response rate, the authors estimated SDA annual production of approximately 3.6 million tons. Using the data in Table 1-2 and production figures provided by several industrial power plants, it was estimated that 350–400 tons of SDA material is produced for each MW of capacity. Using the approximation of 350–400 tons of SDA material produced per MW unit size multiplied by 9556 MW of existing SDA units indicated that ~3.3–3.8 million tons of SDA material is likely produced annually in the United States. The authors estimate is significantly higher than the ACAA production figures indicate; however, the ACAA statistics are expected to reflect the use profits for dry FGD materials even though not all utilities are responding.

The European Coal Combustion Products Association (ECOBA) reports the production and use of CCPs in Europe (EU 15). EU 15 refers to the fifteen countries that formed the European Union until the end of April 2004. These countries include the United Kingdom, France, Belgium, Luxembourg, the Netherlands, Germany, Italy, the Irish Republic, Denmark, Greece, Portugal, Spain, Sweden, Finland, and Austria. Production of SDA material in 2004 was 463,000 short tons, down from 540,000 in 2003 [23]. Of this, 41% of SDA material produced in 2004 was beneficially used in nonmining applications, which are broken down into general

#### Introduction

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, for a total of 80% SDA product utilization. Therefore, 20% was disposed of [23]. The beneficial use and mine reclamation and restoration applications are compiled in Figure 1-5.

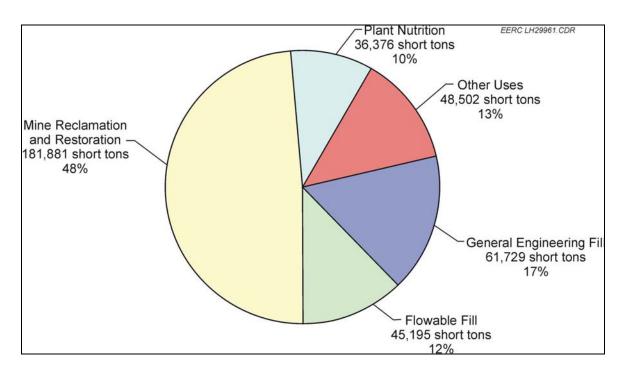


Figure 1-5 Spray Dry Absorption Product Use in Europe (EU 15) in 2004. Of 466,278 Short Tons Produced, 373,684 Short Tons (80.1%) Was Beneficially Used [23]

ECOBA lists several specific current uses for SDA material in Europe [24, 25, 26]:

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

In May 2004, ten Accession Countries joined the existing EU 15, resulting in an EU comprising 25 member states. The Accession Countries were Cyprus, the Czech Republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Slovakia, and Slovenia. SDA material is produced in anthracite and lignite coal-fired plants in Poland. From anthracite, 93,304 thousand short tons of SDA material was produced, with 98% utilized in mining and beneficial landfill/land reclamation in 2000. In addition, 1,134,240 thousand short tons of fly ash + SDA material was produced, with a 100% utilization rate. Applications included building materials, bricks and ceramics, roads, and mining. From lignite, 424,389 thousand short tons of fly ash + SDA material was produced, with 100% utilization in beneficial landfill/land reclamation [27].

#### **Projected Future SDA Production in the United States**

Based on the current production figures, estimated production rate, and MW of SDA scrubbed units in the United States, it is estimated that up to 7 million tons of additional SDA material could be produced from SDA units installed in the next 5 years, making the total annual production as high as 10 million tons, nearly 300% of the current total, by 2012. With an estimated potential additional 9250 MW of SDA scrubbing added between 2012 and 2017, it is estimated that up to an additional 3.5 million tons of SDA material could be generated annually in that time period. If all the projected SDA units are installed as noted in Tables 1-4 and 1-5, and no existing units are taken off line, the total SDA material production could reach 13–14 million tons annually in 10 years. This estimate reflects an increase of 400%–500%.

# **2** RESULTS AND DISCUSSION OF THE LITERATURE REVIEW

Technical reports, journal articles, patents, conference proceedings, book chapters, and news articles were assembled and reviewed to prepare this report. A multitiered search approach was used to obtain literature including sources that were the most readily available and those that required a more in-depth search. The search resulted in a significant number of documents containing references to dry FGD materials including SDA materials. A tiered approach was also used for the review of the literature obtained. Researchers used knowledge about these materials to choose the documents for review. The literature reviewed included information on the characteristics of SDA material and commercial and potential utilization applications for SDA material. An effort is under way to add all of the gathered references to the EERC FIRST SEARCH online database located at www.undeerc.org/carrc/firstsearch/.

# **Definitions of SDA Material**

ASTM International [28] and ACAA [19] have developed and published terminology and definitions related to CCPs including FGD materials. These terms and definitions do not currently include SDA system or material definitions; however, the definition of dry FGD material provided by both organizations is inclusive of SDA material that contains fly ash. The ACAA definition of dry FGD material (see Figure 1-3) includes materials that would be produced in dry FGD systems utilizing sodium-based sorbents, but the ASTM International definition (see Figure 2-1) includes only calcium-based materials. SDA systems utilize lime slurry, so these materials are calcium-based materials. Strictly applying the ASTM International and ACAA definitions for dry FGD material (which includes fly ash as a component of the material), material from an SDA system using fly ash precollection would not be defined as a dry FGD material; however, the term SDA material is used here to refer to materials that do and do not contain a fly ash component to be consistent with the literature reviewed.

- Dry FGD material the product that is produced from dry FGD systems and consists primarily of calcium sulfite, fly ash, portlandite (Ca(OH)<sub>2</sub>), and/or calcite. ASTM equivalent terms are *dry FGD ash* and *lime spray drier ash*.
- FGD material dry scrubbers the dry powdered material from dry scrubbers that is collected in a baghouse along with fly ash and consists of a mixture of sulfites, sulfates, and fly ash.

# **Characterization of SDA Material**

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<sub>2</sub> uptake efficiency (Ca/S ratio)
- Fly ash collection location and efficiency
- Composition and mineralogy of the fly ash
- Recirculation rate
- Load level
- Stoichiometric (sorbent) ratio

Regardless of the type of process used to scrub the flue gas, all FGD 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 [29]. The calcium sulfite content is dependent on the SO<sub>2</sub> removal efficiency [17].

Because fly ash commonly makes up a large proportion of the SDA material (40%–75%), the overall physical properties and morphology of most SDA materials are similar to fly ash; therefore, handling properties are similar to fly ash. Most U.S. systems collect the fly ash and SDA material together in an ESP or baghouse/fabric filter, producing spherical glassy fly ash particles coated by and intermixed with fine crystals of calcium/sulfur reaction products [10, 12]. The fly ash particles provide reaction sites for the removal of sulfur and, consequently, become coated with reaction products. The result is a dry, free-flowing powder with particles smaller and finer than fly ash [10]. However, if the SDA material is collected as a separate product stream, then it will appear as a fine, dusty powder with an off-white color. The major difference between SDA material and conventional fly ash can be attributed to the higher calcium and sulfur content of SDA material. SDA materials are finer and more caustic, have a higher heat of hydration, and produce more alkaline leachate when compared to conventional fly ash [13].

Dry FGD materials from plants that used different types of boilers and burned different types of coal were collected, and it was found that the products had a moderate to wide range of variability in their chemical, physical, and mineralogical properties [30]. The amount of unused sorbent (portlandite,  $Ca(OH)_2$ ) varied the most, by a factor of 14. This variation depended on whether or not the plant recycled its products. This example shows that the physical and chemical properties of dry FGD materials can be highly variable from plant to plant and that an analysis of the material should be conducted prior to beneficial use, particularly when the material has the potential to expand or will contact water.

The following is an analysis of the physical properties, chemical characteristics, and mineralogy of SDA material, based on the literature reviewed. It is important to note that the properties and characteristics of the SDA materials are affected by varying amounts of fly ash present, which was not always reported.

# **Physical Properties**

The physical properties of SDA material are important because they affect storage, handling, disposal, and engineering uses. Uniformity of the material and the ability to pack tightly are especially important for some applications.

SDA materials are generally free-flowing to average-flowing, but higher moisture content can affect flowability and storage problems. Both qualitative and quantitative physical properties can affect transfer and transport. The quantitative physical properties that can affect transfer and transport include particle size, bulk density, specific gravity, and temperature. Disposal is affected by optimum moisture and maximum density, unconfined compressive strength, and permeability [12].

# **Qualitative Physical Properties**

Qualitative physical properties of SDA material include abrasiveness, hygroscopicity, tackiness, corrosivity, and tendency to aerate. The abrasive nature of SDA material has been demonstrated through reported wear on handling equipment. SDA material has also been found to have hygroscopic tendencies due to potential hydration reactions of the lime, calcium sulfate, and calcium sulfite fractions of the material. Evidence of its tacky nature, if it does absorb water, has been demonstrated by solids buildup at the elbows of pneumatic equipment. If wetted, it can stick and build up on mechanical conveyors. When wet, a moderate corrosivity exists. In addition, it has the tendency to aerate and retain air. This makes it easy to convey pneumatically but limits the speed at which it can be conveyed [12, 13].

# Particle Size

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. The fineness of CCPs is also an important characteristic because high-surface-area CCPs are generally more chemically activated which, in turn, may be of importance in evaluating utilization options [31]. The exposed surface area of a given volume will be greater for the smaller CCP particles.

The particle size of SDA material is very fine and tends to be smaller than conventional fly ash. Most SDA materials can be classified as in the silt size range (1/256-1/16 mm, or  $3.9-62.5 \mu$ m). SDA material particle-size distributions are relatively uniform [13]. Particle sizes depend on both combustion and collection system designs [32].

The particle-size distribution and/or mean mass/particle size of SDA materials have been reported in numerous publications. A compilation is shown in Table 2-1. The reported particle-size distribution ranged from 1 to 400  $\mu$ m, with 1–70  $\mu$ m more typical. The reported mean mass/particle size range is 1–45  $\mu$ m.

Particle-Size Distribution	Mean Mass/Particle Size	Source (s)
NR	16–45	[2, 30]
NR	13.5	[33]
20–40	NR	[1]
5–60°	10–15 <sup>°</sup>	[16]
2–74	NR	[29]
1–70	NR	[31,34 <sup>b</sup> ]
NR	4–30	[17]
NR	2–30	[10]
1–400	7.4–18.0°	[35 <sup>b</sup> ]
NR	20–28	[12 <sup>♭</sup> ]
18–60	24–29	[13]
NR	20–25°	[36]

### Table 2-1

Particle-Size Distribution and Mean Mass/Particle Size of SDA Material Reported in Literature Reviewed, μm

<sup>a</sup> Precollection of fly ash; 3%–10% fly ash content.

<sup>b</sup> Literature review reported within source.

<sup>°</sup> Reported as mean diameter.

Conventional fly ash mean mass/particle size has been reported as  $35-55 \mu m$  [10],  $25-40 \mu m$  [36], and a mean of 45  $\mu m$  at one plant [12, 13].

It was reported that 78%-80% of the SDA material was in the fraction finer than 40 µm, while 57%-78% of conventional fly ash was in this finer fraction [12, 13]. Similarly, four SDA material samples tested had greater than 80% of particles by weight finer than 25 µm, indicating very fine particles [37, 38]. Kolar reported that 85%-100% of the SDA material was less than 60 µm, where 60 µm was the maximum particle size observed with precollection of fly ash [17]. It was reported that the SDA material from Basin Electric Power Cooperative pilot plant was a very fine-grain, powdery material, similar in particle size to the fly ash normally produced at a coal-fired power plant [39].

Early work performed for a University of Tennessee thesis was summarized in another report [40]. The SDA samples tested contained a much smaller percentage of particles less that 2.5  $\mu$ m in diameter than conventional fly ash. The particle-size distribution analysis also showed that the highest percentage of particles in the SDA material was found to be in the range of 4–10  $\mu$ m in diameter. The thesis was not available to researchers for review; therefore, the data could not be reviewed in complete context.

# Specific Surface Area

The specific surface area of FGD samples tested by the Ohio State University (OSU) corresponded with particle size, indicating mostly nonporous materials [37, 38]. Specific surface area ranges are a function of the fly ash content in the SDA material [17]. The specific surface area of SDA materials reported in the reviewed literature  $(0.2-16 \text{ m}^2/\text{g})$  is shown in Table 2-2.

Specific Surface Area	Source (s)
1.64 – 7.47	[2, 30]
$9.49 \pm 3.82$	[37]
~9.4	[38]
1.6 – 7.5	[34ª]
0.2 - 3.39	[35 <sup>ª</sup> ]
1.5 – 16	[17]

 Table 2-2

 Specific Surface Area of SDA Material Reported in Literature Reviewed, m²/g

<sup>a</sup> Literature review reported within source.

# **Bulk Density**

Density is defined as the mass (or weight) per unit volume of a material. The reviewed literature had several means of reporting bulk density as compiled in Tables 2-3 and 2-4. Included with bulk density ranges are aerated, poured, packed, and tapped bulk density ranges. Bulk density measurements are used for different purposes, depending on the intended use of the material. Overall, the range of reported bulk density measurements was 400–1760 kg/m<sup>3</sup> (25–110 lb/ft<sup>3</sup>).

The fly ash in dry FGD materials has similar particle size, particle density, and morphology to those of conventional fly ashes, but dry FGD materials have lower bulk densities [30]. The difference in bulk density is due to variations in the chemical and mineralogical characteristics of the reacted and unreacted sorbent. The range in bulk density has been attributed to the fly ash content [17]. Contrary to Dawson et al. [30], Klimek et al. indicated that the bulk density of SDA material is higher than the bulk density of conventional fly ash because SDA material has a larger fine fraction (78%–80% finer than 40  $\mu$ m for SDA material vs. 57%–78% for fly ash) [13].

Results and Discussion of the Literature Review

The bulk density of fly ash has been reported as  $1000 \text{ kg/m}^3$  (62 lb/ft<sup>3</sup>) [41, 42]. The loose, tapped, and compacted bulk densities were similar for fly ash and SDA material containing fly ash ranging from 30–90 lb/ft<sup>3</sup> (480–1440 kg/m<sup>3</sup>) overall for the conventional fly ash [36].

Bulk Density	Source(s)
630 kg/m3 (39 lb/ft3)	[38]
780–1250 kg/m3 (49–78 lb/ft3)	[32]
960–1440 kg/m3 (60–90 lb/ft3)a	[11]
700 kg/m3 (44 lb/ft3)b	[16]
400–1100 kg/m3 (25–69 lb/ft3)	[17]
600 kg/m3 (37 lb/ft3)b, c	[41, 42]

# Table 2-3Bulk Density of SDA Material Reported in Literature Reviewed

<sup>a</sup>Reported as density.

<sup>b</sup>Precollection of fly ash; up to 20% fly ash content. <sup>c</sup>Small portion of fly ash.

# Table 2-4 Bulk Density of SDA Material Specified as Aerated or Poured or Loose; Packed or Compacted; and Tapped or Settled Reported in the Literature Reviewed

Aerated or Poured or Loose Bulk Density	Packed or Compacted Bulk Density	Tapped or Settled Bulk Density	Source(s)
480–960 kg/m <sup>3</sup> (30–60 lb/ft <sup>3</sup> )	NR	784–1250 kg/m <sup>3</sup> (49–78 lb/ft <sup>3</sup> )	[2]
580–960 kg/m <sup>3</sup> (36–60 lb/ft <sup>3</sup> )	NR	720–1250 kg/m <sup>3</sup> (45–78 lb/ft <sup>3</sup> )	[34ª]
585–962 kg/m <sup>3</sup> (37–60 lb/ft <sup>3</sup> )	784–1250 kg/m³ (49–78 lb/ft³)	780–1250 kg/m <sup>3</sup> (49–78 lb/ft <sup>3</sup> )	[30]
580–790 kg/m <sup>3</sup> (37–50 lb/ft <sup>3</sup> )	780–1020 kg/m <sup>3</sup> (49–64 lb/ft <sup>3</sup> ) <sup>b</sup>	NR	[12, 13]
550–680 kg/m <sup>3</sup> (34–42 lb/ft <sup>3</sup> )	710–760 kg/m³ (44–47 lb/ft³)	NR	[13ª]
480–1040 kg/m <sup>3</sup> (30–65 lb/ft <sup>3</sup> )	730–1680 kg/m³ (45.5–105 lb/ft³)	640–1040 kg/m <sup>3</sup> (40–65 lb/ft <sup>3</sup> )	[35ª]
980–1460 kg/m <sup>3</sup> (61–91 lb/ft <sup>3</sup> )	NR	NR	[31]
480–640 kg/m <sup>3</sup> (30–40 lb/ft <sup>3</sup> )	1280–1760 kg/m³ (80–110 lb/ft³)	720–1040 kg/m <sup>3</sup> (45–65 lb/ft <sup>3</sup> )	[36]

<sup>a</sup> Literature review reported within source.

<sup>b</sup> Refers to packed (tapped) bulk density.

# Specific Gravity

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. This differs from bulk density because only the solid fraction of the material is used; the void fraction is not considered.

Specific gravities reported in the reviewed literature as shown in Table 2-5 range from 2.088 to 2.84. A specific gravity range of 1.5 to 3.1 was reported for fly ash in a previous literature review [31].

Specific Gravity	Source(s)		
2.29 - 2.80	[2, 30]		
2.088 - 2.560	[33]		
2.3 - 2.8	[34ª]		
2.29 - 2.80 <sup>b</sup>	[12, 13]		
2.48 - 2.84	[31, 39]		
2.50 – 2.71°	[41]		

# Table 2-5 Specific Gravity of SDA Material Reported in Literature Reviewed

<sup>a</sup>Literature review reported within source.

<sup>b</sup>Used ASTM International D854 (Standard

Test Methods for Specific Gravity of Soil

Solids by Water Pycnometer).

<sup>°</sup>Precollection of fly ash; up to 20% fly ash content.

Early work performed for a University of Tennessee thesis as summarized in another report indicated that average specific gravities of lignite-fired calcium-based SDA material increased as a function of unreacted sorbent content [40]. The specific gravity of compacted fly ash was 2.52 and for compacted SDA material was 3.14–3.71. The thesis was not available to researchers for review; therefore, the inconsistency of the data from other available data could not be evaluated.

# Optimum Moisture Content and Maximum Density

The moisture content of a CCP is a measure of the amount of water present in the voids in the CCP and is expressed as a weight percentage of total dry weight. The natural moisture content is a function of the deposition environment of the CCP and must be determined experimentally for each individual CCP. The natural moisture content of a CCP must be known to calculate the quantity of water that must be added or removed to bring the CCP to its optimum moisture content for compaction.

The optimum moisture content of a CCP 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 [31]. Calculations to determine optimum moisture content do not generally allow for the water that will be consumed by the formation of secondary hydrated phases such as ettringite in the use application. Many of these phases contain up to 50% moisture or even higher. The rate of water addition used by engineers in these calculations can lead to incomplete formation of cementitious phases and later expansion caused by delayed ettringite formation. As shown in Table 2-6, the optimum moisture content range reported in the reviewed literature was 10%–63% and the maximum dry density reported in the reviewed literature ranged from 790 to 1860 kg/m<sup>3</sup> (49–116 lb/ft<sup>3</sup>).

Optimum Moisture Content	Maximum Dry Density	Source(s)
40% - 68% <sup>a</sup>	833 – 1056 kg/m³ (52 – 66 lb/ft³) <sup>b</sup>	[38]
28% - 63%	790 – 1300 kg/m³ (49 – 81 lb/ft³)	[43]
16% - 60%	880 – 1630 kg/m³ (55 – 102 lb/ft³)	[34°]
16% – 38%	1140 – 1670 kg/m³ (71 – 104 lb/ft³)	[13, 30]
10% – 54%	977 – 1860 kg/m³ (61 – 116 lb/ft³)	[35°]
18% – 54%	977 – 1630 kg/m³ (61 – 102 lb/ft³)	[12, 13°]
18% – 54%	NR	[31]
19%	1610 kg/m³ (101 lb/ft³)	[44]
18% – 54%	980 – 1460 kg/m³ (61 – 91 lb/ft³)	[40]
30% - 32% <sup>d</sup>	1240 – 1350 kg/m³ (77 – 84 lb/ft³)⁴	[41]

Table 2-6Optimum Moisture Content and Maximum Dry Density of SDA Material Reported inLiterature Reviewed

<sup>a</sup>Weight of water to weight of solids.

<sup>b</sup>Optimum density instead of maximum density.

<sup>c</sup> Literature review reported within source.

<sup>d</sup> Precollection of fly ash; up to 20% fly ash content.

Observations in the literature reviewed include the following:

- Results indicated that the optimum moisture content of the materials increased and the maximum dry density of the compacted material decreased with an increase in the unreacted lime content of the material [40].
- SDA materials had optimum moisture contents higher than the corresponding fly ashes and increased with increasing sulfur content. In contrast, density values at optimum moisture decreased as the sulfur content increased [10].
- Data show that the maximum density is not particularly sensitive to slight variations in the water content in the vicinity of the optimum. Most FGD products can be considered lightweight materials with compacted densities lower than those of a typical natural soil. Lightweight fills impose smaller loads on the natural soils upon which they are placed, resulting in less settlement in the underlying soils and less likelihood that the soils will fail [38].
- Optimum moisture contents of 18%–54%, with an average of 28%, were reported in a previous literature review. Within that same report, the project samples yielded optimum moisture contents of 16%–38%, with an average of 28.5%. These moisture contents represent the amount of moisture added to the dry material even though common practices base the optimum value on moisture content determinations performed after compaction. Moisture content determinations performed during this study used a drying temperature of 110°C, causing hydrated water to be included in the determination. It requires a temperature of over 205°C to dehydrate calcium sulfate completely [13].

The natural moisture content of SDA material has been reported at 1%-5% [31] and with a range of <0.1%-13.2% in previously reviewed literature [35], while the residual moisture of SDA material has been reported to be about 2% [45]. The values reported for optimum moisture content for compaction indicate that a substantial amount of moisture should be added to SDA materials in order to obtain maximum density [12].

# **Unconfined Compressive Strength**

Unconfined compressive strength is usually determined using ASTM International D2166, Unconfined Compressive Strength of Cohesive Soil, or ASTM International D1633, Compressive Strength of Molded Soil–Cement Cylinders. The two procedures are similar except that ASTM International D6133 assumes there is no deformation of the sample during compression and uses its original dimension to calculate unit compressive strength. Results reported in the reviewed literature are summarized in Table 2-7.

Typically, the samples continued to gain strength between 28 and 56 days of curing. It was hypothesized that the most probable reason for the wide range of strengths is the difference in chemical composition [13].

It was noted that for low-sulfur SDA materials, a false set may occur as a result of the high calcium and low sulfur content, resulting in disruptive expansion reactions [10]. Strengths were found to increase with curing time, with values being higher after 28 days than after 10 days [38]. The lowest unconfined compressive strength values closely resemble low-strength soil– cement mixtures, and the highest values represent low-strength concrete [40].

1-Day	7- Day	21- Day	28- Day	56- Day	Maximum	Source
NR	NR	NR	51 – 88	NR	NR	[38]
60ª	NR	NR	2700	NR	NR	[46]
NR	280 – 4690	NR	20 – 790	140 – 1650	NR	[34]
NR	78 – 1780	NR	NR	NR	NR	[10]
NR	NR	NR	NR	NR	12 – 3000	[13 <sup>⊳</sup> ]
NR	41 – 536	81 – 2250°	50 – 1411	72 – 1775	NR	[40 <sup>b</sup> ]

 Table 2-7

 Unconfined Compressive Strength of SDA Material Reported in Literature Reviewed, psi

<sup>a</sup>Used ASTM International C109 (Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens).

<sup>b</sup>Literature review reported within source.

<sup>c</sup>Separate sample set.

Scanning electron microscopy (SEM) confirmed that the presence of unreacted CaO or  $Ca(OH)_2$  increases the firmness of the SDA materials. The available moisture dissolves some of the calcium compounds, which then recombine in a pozzolanic reaction with aluminosilicates contained in the fly ash, forming high-specific-volume compounds [40].

# Permeability

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. The range of permeability coefficients, or hydraulic conductivities, of fly ash compacted to its maximum dry density is from  $10^{-7}$  to  $10^{-4}$  cm/sec for bituminous fly ashes,  $3 \times 10^{-6}$  to  $1 \times 10^{-5}$  cm/sec for subbituminous ashes, and  $1 \times 10^{-7}$  to  $9 \times 10^{-6}$  cm/sec for lignite ashes [31]. Permeability coefficients for SDA materials from the reviewed literature compiled in Table 2-8 ranged from less than  $9 \times 10^{-10}$  to  $6.5 \times 10^{-3}$  cm/sec.

# Mineralogical and Chemical Composition

Successful engineering applications depend heavily on the mineralogical properties of SDA materials. SDA material has been described as a combination of spherical glassy fly ash particles coated by and intermixed with fine crystals of calcium/sulfur reaction products [13]. Three SDA materials (with up to 20% fly ash) produced in Europe were described as dominated by fine, easily crushed spheres composed of finely aggregated crystals of calcium sulfite hemihydrate [41]. They hypothesized that the spheres were probably formed from the atomized slurry droplets, suggesting rapid water evaporation as the slurry meets the hot  $SO_2$ -laden gases. There was also evidence of calcite, gypsum, clay mineral, and quartz, usually coated with a fine layer of sulfite. An SDA material tested consisted of 46% amorphous glassy material, 26.6% hannebachite, 17% mullite, 5.5% hydrated lime, and 3% quartz [47].

Permeability Coefficient	Source(s)
10 <sup>-9</sup> - 10 <sup>-6</sup>	[34ª]
$9 \times 10^{-10} - 9.7 \times 10^{-5}$	[34]
$3.1 \times 10^{-9} - 2.7 \times 10^{-7}$	[30]
$10^{-7} - 6.5 \times 10^{-3}$	[35]
$3.1 \times 10^{-9} - 6.8 \times 10^{-7}$	[13]
<9 × 10 <sup>-10</sup> – 9.7 × 10 <sup>-5</sup>	[13ª]
10 <sup>-7</sup> - 10 <sup>-6</sup>	[11, 31, 40]

Table 2-8	
Permeability Coefficient of SDA Material Reported in Literature Reviewed, cm/sec	

<sup>a</sup> Literature review reported within source.

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<sub>2</sub> removal, and other factors. Dry FGD materials contain higher concentrations of calcium and sulfur and lower concentrations of silicon, aluminum, and iron than fly ash. The principal reaction product of dry FGD is hannebachite (calcium sulfite hemihydrate):

CaO (lime) + SO<sub>2</sub> (g) + 
$$\frac{1}{2}H_2O = CaSO_3 \cdot \frac{1}{2}H_2O$$
 Eq. 2-1

Under more oxidizing conditions, gypsum (calcium sulfate dihydrate) may also form:

CaO (lime) + SO<sub>2</sub> (g) + 
$$\frac{1}{2}O_2$$
 + 2H<sub>2</sub>O = CaSO<sub>4</sub> · 2H<sub>2</sub>O Eq. 2-2

Results and Discussion of the Literature Review

Sulfite-to-sulfate ratios range from 2:1 to 3:1 [10]. Unreacted sorbent remains as portlandite  $(Ca(OH)_2)$  in the residuals. At ambient temperature and moist conditions, calcium sulfite  $(CaSO_3)$  will slowly oxidize to calcium sulfate  $(CaSO_4)$ , and calcium hydroxide will be converted to  $CaCO_3$  by  $CO_2$  in the air. SDA material from lime-based systems has similar chemical composition to stabilized wet FGD material [10].

The major constituents of Basin Electric Power Cooperative's pilot SDA material were found to contain 14.6% CaSO<sub>3</sub> and 8.9% CaSO<sub>4</sub> [39]. The resulting sulfite/sulfate ratio was 1.64.

Unreacted lime concentrations were 1.6%, and  $CaCO_3$  was 2.1%. Fly ash comprised 71.5% of the material, while the reaction products and unreacted sorbent were the remaining 28.5%.

The weight ratio of fly ash to sorbent-derived material can vary between 0.7 and 8, depending on the composition of the coal [45] and the proportion of the fly ash that is removed before the scrubber. Without precollection, the fly ash proportion will be 70%–85% by weight, producing a spherical grain. When fly ash precollection is utilized, a filter separation efficiency of >80% will produce an SDA material with <30% fly ash, and very good filters (>99%) will produce contents as low as 1%–4% [17]. If fly ash is recovered before the SDA system, then the product consists mainly of irregular clusters of sulfite crystals, forming agglomerates up to 50 µm across [17, 45].

Examples of the composition of SDA material containing fly ash are shown in Table 2-9.

	i	i	i		
Material	From Low- Sulfur Coal	From Low- Sulfur Coal	From High- Sulfur Coal	Five Samples	European Coal
Fly Ash	75	75	40	12–29	20–85
Calcium Sulfite (CaSO <sub>3</sub> $\cdot$ 1/2H <sub>2</sub> O)	16	13	38	28–44	9–47
Calcium Sulfate (CaSO₄)ª	6	6	15	6	1.7–17
Unreacted Lime (Ca(OH) <sub>2</sub> )	2	4	5	10–29	1–15
CaCO <sub>3</sub>	NR°	NR	NR	15–33	4.5–13.7
CaCl (Calcium Chloride)	NR	NR	NR	NR	0.8–6.3
Moisture (Free Water)	1	2	2	NR	NR
Source(s)	[36]	[10]	[10]	[38, 48]	[49]

Table 2-9 Typical Composition of SDA Material Containing Fly Ash as Noted in the Reviewed Literature, wt%

<sup>a</sup> Mixed hydrates.

<sup>b</sup> Includes some CaCO<sub>3</sub>.

As shown in Tables 2-10 and 2-11, precollection of fly ash does change the composition of the final SDA material. The impact of  $SO_2$  collection efficiency on SDA material composition is shown in Table 2-11.

# **Chemical Analyses**

Bulk chemical compositional data of SDA materials as reported in the reviewed literature are compiled in Appendix A. Conventionally, major/minor components of CCPs are reported as oxides. A typical report may include a weight percent value for SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, SO<sub>3</sub>, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, BaO, MnO<sub>2</sub>, SrO, moisture content, and loss-on-ignition (LOI). These data are summarized in Table 2-12 for SDA material containing fly ash and in Table 2-13 for SDA material with precollection of fly ash.

#### **Main Components Typical Range**<sup>a</sup> Range Fly Ash/Lime Inerts 3 – 10 <8 Calcium Sulfite (CaSO<sub>3</sub>) 55 - 7017 - 68Calcium Sulfate (CaSO<sub>4</sub>) 5 – 15 3.5 - 29Unreacted Lime (Ca[OH],) 2 – 10 0.5 – 15 CaCO<sub>2</sub> 5 – 15 5 – 13 CaCl, • n H,O 1 - 4 $0.8 - 9.5^{\circ}$ Moisture (Free H<sub>2</sub>O) 1 – 3 NR Source [16] [49] <sup>a</sup> 0.7%–2% sulfur coal and precollection of fly ash with efficient ESP.

# Table 2-10

Typical Range of Main Components of SDA Material with Precollection of Fly Ash, wt%

<sup>b</sup> Reported as CaCl.

Table 2-11
Composition (wt%) of SDA Material Overall and as a Function of SO <sub>2</sub> Separation Efficiency.
Adapted from Kolar [17]

Main Components	Range with and	SO <sub>2</sub> Separation Efficiency <sup>a</sup>				
Main Components	Without Fly Ash	90%	85%	80%	75%	70%
Fly Ash/Lime Inerts	0–85	15.4	17.0	19.5	21.0	22.8
Calcium Sulfite (CaSO₃)	15–75	33.6	35.8	39.8	40.5	41.5
Calcium Sulfate (CaSO₄)	2–30	5.0	5.3	5.9	6.0	6.15
Unreacted Lime (Ca[OH] <sub>2</sub> )	0–25	38.1	33.4	25.3	22.4	18.8
CaCO <sub>3</sub>	1–30	NR	NR	NR	NR	NR
$CaCl_2 \cdot 4 H_2O$	1–15⁵	4.9	5.5	6.5	7.1	7.75
Moisture (Free H <sub>2</sub> O)	1–4	3.0	3.0	3.0	3.0	3.0

<sup>a</sup>Prerequisites: SO<sub>2</sub>=1600 mg/m<sup>3</sup>; fly ash=1000 mg/m<sup>3</sup>; and HCl=160 mg/m<sup>3</sup> (all standard temperature and pressure, dry). <sup>b</sup>Reported as CaCl<sub>2</sub>  $\cdot$  n H<sub>2</sub>O.

#### Table 2-12

Summary of Bulk Chemical Composition,	Reported as Oxides	, of SDA Material Containing
Fly Ash Reported in Literature Reviewed,	wt%	

Parameter	Range	Sources
SiO <sub>2</sub>	6 - 46	[2, 14, 30, 31, 33, 34, 35, 40, 44, 49, 50, 51, 52]
$Al_2O_3$	4 – 44	[2, 14, 30, 31, 33, 34, 35, 40, 44, 49, 50, 51, 52]
Fe <sub>2</sub> O <sub>3</sub>	1 – 44	[2, 14, 30, 31, 33, 34, 35, 40, 44, 49, 50, 51, 52]
CaO	0.2 – 52	[2, 14, 30, 31, 33, 34, 35, 40, 44, 49, 50, 51, 52]
SO3	0 - 32	[2, 14, 33, 34, 35, 40, 44, 49, 50, 51, 52]
MgO	0.1 – 14	[2, 14, 30, 31, 33, 34, 35, 40, 44, 49, 50, 51, 52]
Na₂O	0.1 – 46	[2, 14, 30, 31, 33, 34, 35, 40, 44, 49, 50, 51, 52]
K₂O	0.1 – 6.37	[2, 14, 30, 31, 33, 34, 35, 40, 44, 49, 50, 51, 52]
$P_2O_5$	0.03 – 1.2	[2, 14, 31, 33, 35, 40, 44, 50, 51, 52]
TiO <sub>2</sub>	0.2 – 1.19	[2, 14, 30, 33, 35, 40, 44, 49, 50, 51, 52]
BaO	0.39 – 0.85	[44, 50]
MnO <sub>2</sub>	0-0.12	[2ª, 14, 44, 50]
SrO	0.11 – 0.46	[2, 44, 50]
Moisture	<0.1 – 13.2	[31, 33, 35, 40, 44, 50, 51, 52]
LOI or C	0.19 – 20.5	[14, 31, 35, 44, 50]
Unaccounted	1.7 – 6.2	[40, 51, 52]
<sup>a</sup> Mn <sub>3</sub> O <sub>4</sub>		

When reviewing compositional data on CCPs, 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. One important example of this is found in the reported calcium oxide concentration. In fly ash or bottom ash, the calcium is usually present as a component of the glassy phase with other elements and is not present as primarily CaO as reported. In FGD materials, calcium is likely associated with sulfur and is present as calcium sulfite or calcium sulfate. When calcium oxide is present as lime in any CCPs and is exposed to water by sluicing or storage in a pond situation, that lime will be converted to calcium hydroxide or hydrated lime. However, the bulk compositional data are useful in evaluating CCPs for various use applications because of the voluminous comparative historical data, empirical evaluations, and comparison with other tests and standards.

Results and Discussion of the Literature Review

Additional chemical parameters were reported as a weight percent of the evaluated SDA material in the reviewed literature. These included  $CaSO_3$ ,  $CaSO_3 \cdot \frac{1}{2}H_2O$ ,  $CaSO_4$ ,  $CaSO_4 \cdot 2H_2O$ ,

Parameter	Range	Source(s)
SiO₂	1.4 – 11.1	[41 <sup>ª</sup> , 45, 49]
$Al_2O_3$	0.8 - 5.4	[41ª, 45, 49]
Fe <sub>2</sub> O <sub>3</sub>	0.4 - 4.4	[41ª, 45, 49]
CaO	32.9 - 60	[41ª, 45, 49]
SO3	2 – 30	[41ª, 49]
MgO	0.4 – 1.9	[41ª, 45, 49]
Na₂O	<0.1 – 0.3	[41ª, 49]
K₂O	<0.2 - 0.6	[41 <sup>ª</sup> , 49]
TiO <sub>2</sub>	0-0.2	[45, 49]
LOI or C	1.3 – 2.1	[45]
<sup>a</sup> May contain up to 20% fly ash content.		

#### Table 2-13

Summary of Bulk Chemical Composition, Reported as Oxides, of SDA Material with Precollection of Fly Ash Reported in Literature Reviewed, wt%

 $CaCO_3$ ,  $CaCl_2$ ,  $SO_4$ , organic carbon, total sulfur, free lime, hydroxide,  $Ca(OH)_2$ , Cl, Ca as available CaO,  $CO_2$ ,  $SO_2$ ,  $SO_3^{-2}$ ,  $SO_4^{-2}$ ,  $CO_3^{-2}$ ,  $Cl^-$ , loss at 500°C, and loss at 900°C. Loss at 500°C determines free moisture and moisture of hydration; at 900°C, other compounds such as carbonates decompose to oxides.

The total elemental composition of SDA materials as reported in the reviewed literature are compiled in Appendix B. The highly variable data for SDA material containing fly ash are summarized in Table 2-14.

The trace metal content of SDA material with precollection of fly ash is, as a rule, lower than that of fly ash and comparable to that of soil [16]. The limited data available in the reviewed literature for SDA material with precollection of fly ash are summarized in Table 2-15. The narrow range of concentrations for each element is within the range for SDA material containing fly ash.

# pН

Kost et al. suggest that the pH of dry FGD products depends primarily on the sorbent used and secondarily on the FGD technology [37]. They concluded that the high pH values of most FGD samples were due to the presence of oxides and hydroxides of Ca and Mg. When these products are exposed to water and  $CO_2$ , they will convert to carbonates by carbonation reactions and the pH will decrease. The pH values reported in the reviewed literature, shown in Table 2-16, ranged from 9 to 13.

Element	Range	Source(s)
Aluminum (Al)	10,000 - 230,000	[12, 13, 30, 31, 35, 37, 46, 53, 54]
Antimony (Sb)	0.8 – 29	[12, 13, 30, 31, 35, 55, 56]
Arsenic (As)	0.4 – 1200	[12, 13, 17, 30, 31, 35, 37, 44, 46, 47, 54, 55, 56]
Barium (Ba)	0.76 – 12,000	[12, 13, 30, 31, 35, 44, 46, 54, 55, 56]
Beryllium (Be)	0.7 – 63	[12, 13, 30, 31, 35, 37, 46, 54, 55, 56]
Boron (B)	<10 - 1460	[12, 13, 30, 31, 35, 37, 44, 46, 47, 50, 54, 55, 56]
Bromide (Br)	0.3 – 21	[31, 35]
Cadmium (Cd)	0.01 – 70	[12, 13, 17, 30, 31, 35, 37, 44, 46, 49, 54, 55, 56]
Calcium (Ca)	7100 - 401,000	[12, 13, 30, 35, 37, 46, 53, 54]
Cesium (Cs)	1 – 22	[35]
Chloride (Cl)	<0.1 - 10,200	[35]
Chromium (Cr)	3 – 1000	[12, 13, 30, 31, 35, 37, 44, 46, 49, 54, 55, 56]
Cobalt (Co)	<0.5 – 172	[12, 13, 17, 30, 31, 35, 37, 46, 54, 55, 56]
Copper (Cu)	3 – 655	[12, 13, 30, 31, 35, 37, 44, 46, 47, 49, 55]
Fluoride (F)	0.4 - 1000	[31, 35]
lodine (I)	0.1 - 0.6	[35]
Iron (Fe)	6300 - 367,000	[12, 13, 30, 31, 35, 37, 44, 46, 53, 54, 55, 56]
Lead (Pb)	<0.3 - 800	[12, 13, 17, 30, 31, 35, 37, 44, 46, 49, 54, 55, 56]
Lithium (Li)	15.1 – 530	[12, 13, 30, 35, 37, 46, 54]
Magnesium (Mg)	3000 - 151,300	[12, 13, 30, 31, 35, 37, 46, 53, 54]

#### Table 2-14

Summary of Total Elemental Composition of SDA Material Containing Fly Ash Reported in Literature Reviewed, ppm

#### Table 2-14 (continued) Summary of Total Elemental Composition of SDA Material Containing Fly Ash Reported in Literature Reviewed, ppm

Element	Range	Source(s)
Manganese (Mn)	24.5 – 1432	[12, 13, 30, 31, 35, 37, 46, 47, 54, 55, 56]
Mercury (Hg)	<0.001 – 10	[12, 13, 17, 30, 31, 35, 44, 46, 49, 55, 56]
Molybdenum (Mo)	<0.018 – 514	[12, 13, 30, 31, 35, 37, 46, 47, 54, 55, 56]
Nickel (Ni)	1.4 – 460	[12, 13, 17, 30, 31, 35, 37, 44, 46, 47, 49, 54, 55, 56]
Phosphorus (P)	21 – 2200	[37, 46, 54]
Potassium (K)	1600 – 9300	[12, 13, 30, 35, 37, 46, 54]
Rubidium (Rb)	48 – 530	[35]
Selenium (Se)	<0.4 - 760	[12, 13, 17, 30, 31, 35, 37, 44, 46, 47, 50, 54, 55, 56]
Silicon (Si)	22,000 – 157,200	[12, 13, 30, 35, 37, 46, 54]
Silver (Ag)	<0.024 – 8	[12, 13, 30, 31, 35, 44, 46, 54, 55, 56]
Sodium (Na)	710 – 240,000	[12, 13, 30, 35, 46]
Strontium (Sr)	30 – 13,000	[12, 13, 30, 31, 35, 37, 46, 54]
Sulfur (S)	3000 - 170,000	[37, 53, 54]
Thallium (TI)	0.1 – 42	[12, 13, 17, 30, 31, 35, 46, 55, 56]
Tin (Sn)	0.01 – 962	[12, 13, 30, 31, 35]
Titanium (Ti)	1050 – 6700	[12, 13, 30, 35, 46]
Uranium (U)	0.8 – 140	[12, 13, 30, 35]
Vanadium (V)	0.4 – 950	[12, 13, 30, 31, 35, 37, 46, 44, 54, 55, 56]
Zinc (Zn)	<6 – 9000	[12, 13, 30, 31, 35, 37, 44, 46, 49, 54, 55, 56]

# **Current and Potential Uses of SDA Material**

When SDA material was first produced, there were no obvious uses for it because of the novelty of the process, a lack of applications for the main component calcium sulfite, the undesirable calcium chloride content, a wide range in chemical composition, and the low volume per location [17]. The literature reviewed contained numerous references to current commercial and potential uses of SDA material. Many of the uses have commercial potential but are still in the research and development phase. The following is a summary of current commercial and potential uses of SDA material noted in literature reviewed. It should be noted that this summary is not exhaustive and only represents uses reported in the reviewed literature.

# Agriculture

It is widely know that gypsum (CaSO<sub>4</sub>  $\cdot$  H<sub>2</sub>O) has been used to improve soil conditions for centuries. Gypsum has been shown to improve water retention characteristics, increase infiltration rates, reduce soil crusting, and mitigate salinity and sodicity in alkaline soils or arid and semiarid regions [58]. Studies on the use of FGD gypsum compare it to natural gypsum in terms of the benefits when applied to agriculture soil. Although FGD gypsum is widely used in agriculture, other FGD products, including SDA material, contain very little mineral gypsum; therefore, their suitability for agriculture applications is different and should not be compared to gypsum. ACAA reported 168,190 short tons of FGD gypsum and 846 short tons of dry FGD material were used in agriculture applications in 2006, down drastically from 19,259 short tons in 2005, possibly because of variations in respondents to the ACAA survey [22, 59]. ECOBA reported 36,376 short tons of SDA material used for plant nutrition in 2004 [23]. The low solubility of calcium sulfite (CaSO<sub>3</sub>  $\cdot$   $\frac{1}{2}$ H<sub>2</sub>O) in SDA material makes it a poor source of calcium and sulfur for agriculture use. The sulfites may be harmful to plants, by producing hydrogen sulfide gas under anaerobic conditions, unless placed far in advance of planting [60]. However, the substitution of alkaline sulfite-rich dry FGD products for conventional liming materials in agriculture is a potential use for these products, as noted in the research studies summarized below. It is important to note that there are instances in the literature of agricultural use of SDA material in Europe, but the authors focused primarily on literature from the United States.

#### Table 2-15

Summary of Total Elemental Composition of SDA Material with Precollection of Fly Ash Reported in Literature Reviewed, ppm

Element	Range	Source(s)
Arsenic (As)	4.8 – 11	[41ª]
Barium (Ba)	270 – 4000	[41ª]
Boron (B)	100 – 150	[41 <sup>ª</sup> ]
Cadmium (Cd)	0.9 - 6.9	[41ª, 49]
Chromium (Cr)	34 – 60	[41ª, 49]
Copper (Cu)	43 – 80	[41ª, 49]
Lead (Pb)	28 – 110	[41ª, 49]
Manganese (Mn)	170 – 420	[41ª]
Mercury (Hg)	<0.3	[41ª, 49]
Molybdenum (Mo)	2.7 – 5.4	[41ª]
Nickel (Ni)	32 – 80	[41ª, 49]
Selenium (Se)	3.9 – 6.5	[41 <sup>ª</sup> ]
Vanadium (V)	60 – 70	[41ª]
Zinc (Zn)	94 – 380	[41ª, 49]

<sup>a</sup> May contain up to 20% fly ash content.

Table 2-16
pH Values of SDA Material Reported in Literature Reviewed

рН	Source(s)
9.7 – 12.8	[2]
11.8 – 12.5	[37, 57]
9.3	[47]
9 – 13	[34ª, 41 <sup>b</sup> ]
12.4	[53]
11.7 – 12.4	[39]

<sup>a</sup>Literature review reported within source.

<sup>b</sup>Precollection of fly ash; up to 20% fly ash content.

Calcium sulfite phytotoxicity is a concern when applying SDA material to agriculture soils, as evident below in the literature cited. Strategies for reducing toxicity are also examined. Decreased maize growth was reported in an acid soil when levels of an FGD product containing CaSO<sub>3</sub> exceeded 2 g/kg in a soil initially at pH 4.2 [61]. Toxicity from volatile sulfur compounds and increased aluminum toxicity were suspected, but the relative contribution of each could not be quantified. The  $SO_{3}^{-2}$  ion is thermodynamically unstable in the presence of oxygen. It as been reported that rapid CaSO<sub>3</sub> oxidation to CaSO<sub>4</sub> is expected in the oxidizing atmosphere of most agronomic soils, and additional reactions that generate SO<sub>2</sub> may occur with CaSO<sub>2</sub> addition to low-pH media [62]. The oxidation of sulfite to sulfate at near-neutral to alkaline pH values is extremely slow at atmospheric pressure. The fact that oxidation is relatively rapid in soils leads to the conclusion that other mechanisms may play a crucial role. It is likely that in an agricultural soil, fungi, bacteria, and microfauna may aid in the ultimate oxidation of sulfite to sulfate through metabolic processes. Sulfite and SO<sub>2</sub> both are phytotoxic, but toxicity effects may be temporary, subsiding when most  $SO_3^{-2}$  has been oxidized to  $SO_4^{-2}$  [58]. Research by others indicated that raising the soil pH or allowing oxidation of sulfite to sulfate to occur are two effective strategies for reducing calcium sulfite phytotoxicity [63]. The toxic effects resulting from calcium sulfite use in soils were related to low soil pH and can be considerably diminished by applying an acidity-neutralizing amendment such as hydrated lime. In addition, the oxidation of sulfite to sulfate in water and soil systems can occur in approximately 3–5 weeks. Others also demonstrated that both sulfate and sulfite FGD products can be used to reduce toxicity in acidic subsoil layers. Although short-term phytotoxicity was observed in the sulfite-rich sample, the addition of small amounts achieved the goal of mitigating soil aluminum toxicity and increasing plant growth. This suggests that application of the sulfite-rich sample or similar materials to soils in autumn may improve crop growth the following growing season [58]. The lower toxicity of sulfite in alkaline environments is likely due to the reduced concentrations of bisulfite ions, which are pH-dependent and maximum at below pH 5. Bisulfite combining with atmospheric oxygen is the mechanism used in much of the forced oxidation found in the production of gypsum from sulfite scrubber material.

The impact SDA material has on the environment and plant growth was studied by the University of Georgia and by Argonne National Laboratory. The University of Georgia study showed the incorporation of SDA material into native soils had no impact on germination rates of corn, soybeans, and cotton [47]. Concerning the effect on the elemental composition of plant tissues, arsenic, selenium, molybdenum, boron and, to some extent, calcium increased within all crops grown in Year 1. Tissue concentrations of manganese and sodium decreased, and nickel, lead, iron, and copper levels were not affected. Leachate salinity and soil salinity rose immediately (from 0.2 to 2.9–3.3 dS/m) after the application and remained elevated over the two years of the study. The leachate pH was not affected by the application of SDA material, but the application did produce a stable increase in soil pH (from 5.5 to 8.1). Arsenic, selenium, and boron tended to accumulate in the plants. Boron emerged in the leachate, indicating possible impacts to groundwater quality. Plant growth experiments using soil treated with SDA material were conducted at Argonne National Laboratory. Three different soil types and soybean and corn crops were tested, using a combination of SDA material with soil at 0%–4% by weight. For both corn and soybeans, growth decreased as the amount of SDA material increased. Soybeans grown in soil with 4% SDA material exhibited stunted growth when compared to the control crop. For corn, a similar reduction in growth was noticed, although not to the same degree as for soybeans. Boron concentration in the leaves of the corn and soybeans grown in soil treated with SDA

#### Results and Discussion of the Literature Review

material were found to be up to 20 times greater than those found in the leaves of the control grown in soil containing no SDA material [64].

The use of SDA material as a liming agent has been studied. The British Coal Corporation analyzed the use of a European SDA material as a liming agent [41]. Pure limestone has a liming or neutralizing value (calcium oxide content equivalent) of 56, and the SDA material tested had a neutralizing value of 25. The study concluded that if an appropriate amount of the SDA material were added to achieve adequate liming, the recommended upper limits for trace element concentrations in soils after sewage sludge application would not be exceeded. The use of CCPs (including SDA material) as compared to CaCO, as a liming agent in strongly acidic soils was studied, and it was concluded that CCPs functioned similarly to CaCO<sub>2</sub> and that they had very few adverse effects on soil enzyme activities compared with those of CaCO<sub>2</sub> [53]. In order of effectiveness for increasing soil pH were FBC ash > LIMB ash > SDA material > fly ash. Because CCPs contain CaO and MgO, the study concluded that it seems likely that the ability of CCPs to act as liming agents may be related to their content of these oxides. For example, the high initial alkalinity associated with the application of CCPs to soil was reduced by conversion of CaO to CaCO, in soils exposed to atmospheric CO,. The results of this study also provide information on the use of soil enzyme activities as indicators of soil quality. They clearly demonstrate that caution is required in such use because the relationships between soil qualities are complex and measurements of the changes in enzyme activities without reference to proper controls can be misleading.

Several commercial uses of SDA material in fertilizer applications were identified in Europe; however, the use of SDA material as a fertilizer has not reached the commercial stage in the United States.

Many soils throughout northern Europe are experiencing a growing sulfur deficiency, and therefore, fertilizer companies are increasing the amount of sulfur in commercial fertilizers. The application of SDA material as fertilizer for sulfur deficiency is now permitted in Germany, Denmark, and Austria, as described below [16].

SDA material with low fly ash content has been used as a sulfur fertilizer since 1994 in Denmark, and it has been used as an admixture to and spread with liquid manure. The Lanskontoret for planteavl (Agricultural Research Institute) has carried out tests that indicate that SDA material, collected without fly ash, is suitable for use on farm soils, and the Danish Ministry of Environmental Protection has given permission for this application, with certain conditions. In commercial applications, the residues are mixed with dolomitic lime to prevent dusting and to allow application of the two materials simultaneously. It is necessary to apply the two materials together because the fertilizing potential of the SDA material is too small to make separate application viable. Dolomitic lime contains magnesium and acts slowly and continuously. The SDA material can also be mixed with liquid manure, agricultural lime, or wastewater sludge [65].

A three-year VGB Group research project under the "Waste Management of Residues from Coal-Fired Power Plants and Waste Incineration Plants" (known as ERKOM) research program yielded results that gained approval of SDA material as a fertilizer in Germany in 1999 by the Scientific Advisory Board of the Federal Ministry of Agriculture [66, 67]. The minimum sulfur content of a fertilizer of this type is to be 10%, which is achieved by SDA material when the major amount of fly ash is precollected before the SO<sub>2</sub> removal. The German Ministry of Food, Agriculture, and Forestry has specified SDA material as a sulfur–calcium fertilizer in legislation. The SDA material was also licensed in Austria based on the research results in Germany. The total cost of the VGB Group research project of approximately 0.5 million Deutsche Mark (DM) has produced annual savings for the operators in the region of 2.8 million DM [66].

# Binders

A novel binder for interior plasters is described in U.S. Patent 5,522,928 using a calcium sulfite component, water, and a finely divided residual material component comprising primarily calcium sulfite. SDA material is called out specifically as the calcium sulfite component [68]. Kolar summarizes a multiphase binder described in German Patent DE 3 82 16 57 C2 [17]. SDA material is mixed with fly ash, and precalcination, oxidation, and calcination are carried out. A salable binder is produced by adding additives and grinding. The use of the 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. Binder applications have not reached commercialization in the United States.

# **Cement Manufacture**

SDA material has been used commercially to manufacture cement in Germany. A German coalfired power plant treats SDA material using a fluidized-bed process. Pelletized anhydrite is produced that can be used as a substitute for natural anhydrite in industrial processes such as cement manufacture [69]. Two anhydrite production processes using SDA material are the Fläkt-Dorr-Oliver Process and the Vereinigte Aluminium-Werke AG, Lünen (VAW) Process [17]. Another process used dry FGD material to manufacture cement, once utilized in the Müller-Kühne Process at WSZ Wolfener S.u.Z. in Bitterfeld in Germany [16].

U.S. Patent 4,470,850 claims that a dry FGD material (likely SDA material) can be used in the place of fly ash and gypsum as a solidification regulator in the production of fly ash cement [70]. The essential reaction product in the dry FGD material that functions as the solidification regulator is the calcium sulfite hemihydrate. Although this application appears to be technically feasible, no dry FGD material has been reported as used for cement manufacture in the United States since 2003 [71].

# **Cement Replacement in Concrete**

Research has been conducted on the use of SDA material as a concrete admixture. Below is a summary of the research studies found in the literature reviewed, which consisted primarily of European sources. It is not known if the limited amount of literature pertaining to commercial or demonstrated use of SDA material as a concrete admixture is due to technical constraints or a lack of market development. ACAA reported 9660 short tons of dry scrubber FGD material used in concrete, concrete products, and grout in 2006 [22].

Research carried out at KEMA, Netherlands, has investigated the use of SDA material as a partial replacement for sand and cement in concrete [45, 72]. The SDA materials tested had no precollection of fly ash and contained a mixture of about 70% fly ash and 30% sorbent reaction products. For initial comparative tests, 20% of the portland cement in the concrete was substituted by SDA material. Except for a slight retardation in setting times, concretes in which cement was partly substituted by SDA material showed strength and durability performances comparable to or superior to reference concretes. No destructive ettringite  $(Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26 H_2O)$  reactions were observed in tests carried out with an exposure time of two years. The presence of chloride was noted in some SDA materials, restricting their application in reinforced concretes [45]. The study concluded that the compositions could be applied successfully to concrete products, but that further verification under real conditions was required. Long-term tests were still being carried out when the report was published.

A demonstration project was carried out by the Technical University of Denmark to assess the use of SDA material as a cement and concrete admixture [73]. Three precast, reinforced concrete front elements containing 20 and 30 wt% SDA material were manufactured. Additives, such as superplasticizers and an air-entraining agent, were added to some specimens. After a period of 1 year, corrosion tests indicated a low probability of corrosion for most of the specimens. The results suggest that when SDA material is used as an admixture in mortar to replace part or all of the usual fly ash, increased compressive strength is achieved. The grain size of the SDA material has some influence on strength. Progressive substitution of cement by SDA material will result in gradually decreasing strength. During this project, it was found that the mineral thaumasite  $(Ca_3Si(CO_3)(SO_4)(OH)_6 \cdot 12H_2O)$  formed under certain conditions. Because thaumasite greatly reduces the strength of cement and concrete, the project was abandoned.

A review of studies in Europe by Kolar indicated that nonreinforced concrete might be a more suitable application for SDA materials than reinforced concrete [17]. Chloride poses a risk of corrosion of steel reinforcement. Concrete pipes produced containing SDA material in Austria had swelling attributed to the formation of ettringite. Prevention of this was not successful. Additionally, the product was not frost-resistant. It was concluded that these factors limited the use of SDA material-containing concretes in building to solid or hollow bricks for interior walls or backing. Dry storage of the bricks would also be necessary.

The use of dry FGD material as a raw material for cellular or gas concrete was studied in Denmark and Poland [16]. Cellular concrete is made of cement and/or white lime and ground quartz sand and steam-hardened at 180°–200°C (356°–392°F), resulting in a porous structure. There are over 20 factories for the production of cellular concrete in Poland, many of which use fly ash as a raw material. Testing has concluded that the addition of approximately 20% dry FGD material is positive and that it can be used for cellular concrete manufacturing. However, the market incentive is low, and further development work is required. Earlier work in Denmark used up to 30% SDA material, resulting in problems including chlorine corrosion in the autoclaves and thaumasite formation [17].

Two sources of SDA material and one source of limestone FSI product were tested for partial cement replacement in concrete. The products were substituted for 30 wt% Type I cement. Three product concrete mixtures, one fly ash concrete mixture, and one control concrete mixture were prepared. One SDA sample met the ASTM International C618 criteria except for SO<sub>3</sub> content, which was higher than the criterion. The other SDA material and the limestone FSI product did not meet ASTM International C618 criteria for silica, alumina, iron oxides, SO<sub>3</sub>, and LOI. However, for all samples, their fineness and pozzolanic activity indices met ASTM International C618 criteria. In addition, the autoclave expansion test results were within the ASTM International C618 limits. The concrete mixtures made with SDA material achieved a higher compressive strength than that of the control mixture at all testing ages (3, 7, 28, and 90 days). The SDA mixtures had longer setting times than the LIMB mixtures and controls [34].

In one project, portland cement concrete incorporated with 10% SDA material was used on a test section of road pavement [46]. Prior to the field placement, laboratory specimens were made using 5% and 10% SDA material. Laboratory and field results indicated that compressive strengths increased with increased percent of SDA material for all test ages (7, 14, 21, and 28 days). A comparison of the laboratory and field concrete mixes shows a similar 28-day compressive strength.

# **Civil Engineering**

Dry FGD material, including SDA material, mixed with fly ash has been used commercially in civil engineering in Europe and has been a topic of study in research projects. Civil engineering applications including landfill construction, embankments, structural fill, and road base have been documented in the literature. ECOBA reported 61,729 short tons of SDA material used for general engineering fill in 2004 [23]. ACAA reported 249 short tons of dry scrubber FGD material used in the road base/subbase/pavement category but no use in the structural fill/embankment category in 2006 [22].

In Nordic countries, there are six blending stations at coal-fired power plants blending dry FGD material and fly ash, sometimes with the addition of cement. These blends are referred to in the literature generically as stabilisate product.<sup>1</sup> An example is Cefill (or Cefyll), produced by the Swedish company Cementa AB, which was developed in the 1980s and has been producing Cefill since at coal-fired combined heat and power (CHP) power plants in Västerås, Sweden.

<sup>&</sup>lt;sup>1</sup> This is similar to the process used in the United States whereby wet FGD material is mixed with fly ash to produce fixated scrubber solids (FSS) or Pozzotec.

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Three qualities of Cefill are typically produced with 30%-70% dry FGD material, 30%-70% fly ash, and 0%-8% cement. Compressive strengths vary from 5 to 30 MPa (725–4350 psi) and water permeabilities vary from  $10^{-10}$  to  $10^{-12}$  cm/sec. A similar stabilisate product called REALIT is produced at coal-fired power plants in Dürnrohr, Austria [16].

A few commercial examples of the use of Cefill and REALIT as a capping material are provided by Bengtsson [16]. Cefill has frequently been used as a bottom- and top-capping material for hazardous waste such as metal ore mine residues and as a vertical seal for preventing horizontal groundwater flow contamination. Many other projects have been carried out in Sweden based on the tight and flexible nature of the cured Cefill material. REALIT was used to seal off a sludge deposit.

The construction of road dams, filling of foundation cavities and cable trenches, and sealing of waste disposal sites using Cefill are applications that have been abandoned in Denmark but are being intensively pursued in Sweden and Finland [17].

In Europe, stabilisate products have been used extensively as a base course material in applications such as storage areas, coal yards, road banks, parking lots, and noise protection walls. An example is a 2-km-long road built at a coal-fired CHP station in Finland using a 1-m-thick layer of a 50% dry FGD material and 50% fly ash without cement addition covered with 0.5–1.5-m fly ash and a 0.24-m layer of crushed stone [16]. This test road has been tested annually for important engineering parameters. Results have been very satisfactory, showing high frost resistance. REALIT was used in the base liner of a squeezed sewage sludge disposal site in Austria [74].

A common European application of stabilisate products is for landscaping and land reclamation [16]. Examples include fill for reclamation of destroyed land and old/closed quarries, fill in an area behind a new quay in a harbor, and reclamation of lignite pit mines. It is common practice to recultivate the top surface of reclaimed land with a layer of soil for planting trees and grass.

In addition, utilization of a stabilisate product is under consideration in the Czech Republic as embankment material for roads and railways.

The fine-grain Dutch SDA material is suitable for use in the stabilized layer of road construction, whereas the artificially prepared grains (lumps) did not meet Dutch standard technical requirements [45]. However, research in Denmark has shown that problems may occur with swelling during application as a foundation material [65]. The expansion of several types of FGD materials was measured, and it was concluded that compacts containing SDA material, alone and in combination with fly ash, expanded by less than 0.2% after a year of exposure, with no evidence of structural deterioration after that time [41].

The use of SDA material in a truck ramp for vehicles to unload trash [57]. Difficulties in achieving uniform conditions during construction were experienced; however, no problems with performance and no evidence of failure were reported.

Dawson et al. evaluated literature on the potential for SDA material to be used as structural fill and concluded that all but the nonreactive SDA material has potential to be used as a structural fill [10]. For reactive SDA material, compressive strengths in excess of 2000 psi can be achieved, whereas low-reactive SDA material strengths greater than 100 psi can be expected.

Swell properties of the material and the strength that can be achieved when compacted are factors in the application of FGD materials for engineering purposes. Swelling primarily occurred in FGD samples containing free lime and occurred in two episodes [38]. The first episode occurred almost immediately upon water addition and is attributed to hydration reactions such as the hydration of lime (CaO) to portlandite (Ca[OH<sub>2</sub>]) and of anhydrite (CaSO<sub>4</sub>) to hemihydrate (CaSO<sub>4</sub> ·  $\frac{1}{2}$  H<sub>2</sub>O). The second swelling episode usually began after about 10 days and is thought to be a result of the formation of secondary minerals such as ettringite. The strengths achieved varied when FGD samples were compacted at optimum water content.

The use of SDA material for cured compacted products suitable for use as landfill materials, embankments, roadbase compositions, and similar applications is described in U.S. Patent 4,354,876 [8]. It is specifically stated that the material used is obtained from a lime-based dry-scrubbing FGD operation containing fly ash. The material is mixed with water and compacted under sufficient load to achieve at least 70% of the laboratory dry density. The resulting cured compacted products have compressive strengths of at least ~25 psi and permeabilities of less than  $1 \times 10^{-5}$  cm/sec. The process of the invention is designed to take full advantage of the unique self-bonding capabilities of the material. The SDA material may need to be conditioned for this use. Cementitious additives may be required for unreactive to moderately reactive SDA materials.

A test road used SDA material in the pavement layers, the pavement, the subbase, and the embankment [46]. SDA material proved useful; especially as replacement for common earthen borrow material<sup>2</sup> in embankments. The granular and select granular borrow material met or exceeded Minnesota Department of Transportation (MnDOT) specifications. Environmental testing showed the placement had no adverse impact on groundwater quality; however, barium in the SDA material–common borrow mixture slightly exceeded Minnesota drinking water limits. Although the placement was successful from an engineering and environmental standpoint, it did not offer economic advantages because additional costs were incurred for mixing and transporting the SDA material. The SDA material might have an economical advantage if lime or lime kiln dust was required for borrow stabilization.

In Kansas, SDA material (containing about 80% fly ash) has been mixed with dry economizer ash, moistened with water, and used to create a lining layer (~1.25 m thick) for a landfill site. The conditioned SDA material was spread in layers about 0.5–0.75 m thick and compacted to give a layer with a permeability of  $<10^{-6}$  cm/sec. Wet boiler slag was brought separately to the landfill and encapsulated in the conditioned SDA material [65].

<sup>&</sup>lt;sup>2</sup> Earthen borrow is sand, gravel, or other material used for grading.

# Flowable Fill

Flowable fill is a material that flows like a liquid, is self-leveling, requires no compaction or vibration to achieve maximum density, and hardens to a predetermined strength [28]. Controlled low-strength material (CLSM), controlled density fill (CDF), and infill are names used to describe flowable fill that comprises a blend of cement, fly ash, sand, and water. ACAA and ECOBA have reported commercial uses for dry scrubber FGD material (9843 short tons in 2006) and SDA material (45,195 short tons in 2004), respectively, in flowable fill applications [22, 23]. Research conducted to date indicates that SDA material can be an effective component in the production of flowable fill.

The potential for SDA material to be used in flowable fill as a replacement for conventional fly ash was examined. The design mixes consisted of varying amounts of SDA material, cement, lime, admixtures, and water. The mixes were tested in the laboratory for flowability, unity weight, moisture content, unconfined compressive strength, erodiblity, set time, penetration, and long-term strength characteristics. Tests were conducted for up to 90 days of curing. The study concluded that flowable fill containing SDA material can be an economical alternative to conventional materials. SDA flowable fill mixtures tested gained good strength (400 psi obtained in 1–2 days for standard flowable fill and 400 psi obtained in 1/3–6 hours for quick-set flowable fill) and had excellent placeability. The authors suggested, especially for high-cementitious-content flowable fill, that long-term strength tests be conducted to estimate the potential for later excavation. Furthermore, chemical reaction and mechanisms that accelerate initial set time need to be studied. Long-term strength tests for more than 1 year are needed, and full-scale field tests would be valuable. Resilient modulus, stress–strain behavior, freeze–thaw, swell potential, and corrosivity characteristics also need to be studied [75].

Others mixed SDA material with an additional fly ash and stabilized the mixture by adding about 3 wt% lime kiln dust [76]. The stabilized product was either used as a flowable fill or left in a storage yard for several years. Samples extracted from these sites were analyzed using x-ray diffraction and scanning electron microscopy. The analytical results show the formation of thaumasite, ettringite, and an intermediate phase with varying chemical composition of calcium, aluminum, silicon, and sulfur. Ettringite and thaumasite are not present in CCPs but are secondary minerals formed from the reaction of the CCPs with water. Most of the thaumasite formed in the system was growing directly from the gypsum matrix. Thaumasite was also growing in the void space. Thaumasite grown in the system occur as short, stubby crystals. Ettringite crystals, on the other hand, grow in isolated pockets when the conditions of a saturated lime environment are available.

# Fixating Agent for Waste

SDA material, and other alkaline-rich FGD materials have the potential to solidify or fixate wastes. Alkaline FGD materials may be useful to stabilize metals in acidic hazardous wastes that have reduced solubilities at higher pH, such as cadmium, iron, manganese, zinc, copper, and cobalt [34]. Waste sludge stabilization is similar to soil and road base stabilization; however, since the sludges generally have a high moisture content and low solids content, more FGD material needs to be used to fixate waste. Research studies that have evaluated the use of SDA material as a fixating agent for waste are summarized here.

The great fineness of SDA material, especially with low fly ash content, yields a high water retention capacity, which could be used for the thickening of sewage sludge and river or harbor silt. Some applications have been successful; however, negative experiences have occurred in Denmark because calcium hydroxide appears to cause early hardening [17].

In one study, different waste materials (cadmium and chromium plating precipitation sludges, waste oil digestion sludge, and a sedimentation slurry from an aluminum can reclamation center) were mixed with SDA material [77]. In all mix designs, a ridged structural material evolved as a result of the expansive and pozzolanic reactions occurring from the wetted SDA material. Structural and physical characteristics and leaching were evaluated. The cadmium plating waste-SDA material mix exhibited a 7-day unconfined compressive strength of up to 5.221 MPa (759 psi) and the chromium plating sludge–SDA material mix reached 7.587 MPa (1103 psi). The SDA material mixed with water exhibited a 7-day unconfined compressive strength up to 5.035 MPa (762 psi). The unconfined compressive strength for weak concrete is 10.346 MPa (1504 psi). The raw and waste materials fixated with SDA material were leached with acetic acid and with deionized water. The SDA material did not leach above Resource Conservation and Recovery Act (RCRA) regulations. The cadmium waste and aluminum can-processing waste heavy metal leaching characteristics were reduced from hazardous to nonhazardous by fixation with SDA material, as was chromium plating waste at mass ratios of 1:1, 2:1, and 25:1 (SDA material to dry chromium waste). The oil sludge was not affected by SDA material fixation with regard to inhibiting leaching.

A study on the leachability of SDA material from Argonne National Laboratory concluded that if proper fixation techniques can be developed, SDA material has the potential to be used as an impounding agent in the codisposal of chemical wastes containing lead, cadmium, and other elements whose leachability decreases with increasing pH [64].

A laboratory study conducted at the Western Research Institute evaluated the ability of FGD materials to stabilize the organic and inorganic constituents of hazardous wastes. Two sources of atmospheric fluidized-bed combustion (AFBC) material and two sources of SDA material were used in this study, and four types of hazardous waste streams were obtained including separator sludge, mixed metal oxide–hydroxide waste, metal-plating sludge, and creosote-contaminated soil. Each product was mixed with each hazardous waste, allowed to equilibrate, and then leached using the toxicity characteristic leaching procedure (TCLP). It was found that chromium was leached from both SDA material-stabilized mixtures. However, the products tested can be used to stabilize the cadmium found in the metal oxide–hydroxide hazardous waste. Mineralogy tests were performed on a number of products and hazardous waste mixtures. Quartz and

ettringite were the most dominant mineral phases; others included gypsum, portlandite, and calcite [34].

This application has not reached commercialization in the United States.

# Marine Applications

It has been suggested that SDA material could be used in marine applications such as artificial reefs and offshore sea defenses, although ACAA does not report this as a separate use application. The literature reviewed, and summarized here, showed positive results when reefs and blocks were prepared using SDA material and placed in a seawater environment. All studies showed that artificial reefs and blocks could provide a favorable habitat for marine life without adverse impacts to the environment. Tests carried out in the United Kingdom by the Coal Research Establishment show that blocks containing SDA material, exposed to both tidal and totally submerged conditions, showed no evidence of surface friability or cracking [41]. Block weights generally increased with time to levels compatible with water adsorption values found in laboratory tests. The strength of blocks containing a proportion of portland cement and fly ash increased compared with those containing only SDA material, but all specimens behaved adequately. Similarly, the Marine Sciences Research Center conducted an investigation on the preparation and evaluation of blocks prepared from a variety of CCPs and placed in a seawater environment. Testing indicated that properly designed reef blocks possessed adequate structural integrity for marine environments, exhibited no adverse environmental effects, and functioned acceptably as habitat for marine life [10, 78]. Dump blocks from SDA material and fly ash mixtures bonded with 7.5% portland cement were produced. It was indicated that the blocks could be used for artificial reef construction. The compressive strength was 5  $\text{Nm/m}^2$ , and very low leaching was observed [45].

# Masonry

SDA material has shown promise for use as a raw material to manufacture masonry products; however, only one reference to the commercial manufacture of masonry was found in the literature. Based on results by KEMA and on further testing in Germany, considerable amounts of dry FGD material were used in German and Dutch sand–lime brick manufacturing [16]. However, the manufacturing of sand–lime bricks seems to have ceased (as of the writing of that report). Detailed information of the application is limited, both for competitive reasons and because of the risk of unfavorable publicity regarding the use of "waste products" in a high-quality application. ACAA reported 9660 short tons of dry scrubber FGD material used in concrete, concrete products, and grout in 2006 [22].

International patent WO 82/00819 and U.S. Patent 4,377,414 describe a method to use SDA material in the production of shaped cementitious products such as pellets, bricks, tiles, and blocks [79, 80]. The method uses a closely controlled compaction process. First, an SDA material containing fly ash is uniformly contacted with a critical amount of water and then immediately compacted at a critical compaction ratio to provide a manageable green body in which the fly ash particles are positioned with respect to one another so that the interstitial spaces are sufficient to accommodate the volumetric changes in the cementitious materials without any

deleterious expansion of the product. The product is then cured in as little as two days at  $120^{\circ}$ – $180^{\circ}F$  (49°– $82^{\circ}C$ ).

Evaluation of the use of SDA material in sand-lime bricks has been carried out in the Netherlands by KEMA [45, 81]. Sand–lime bricks are made of fine white lime and high-quartz sand molded, pressed, and steam-cured in autoclaves at 175°-214°C (347°-417°F). About 3000 sand-lime bricks were manufactured and tested. The test bricks were manufactured with mixtures of SDA material and fly ash replacing about 20% of the sand in the conventional bricks. The quality of the bricks containing SDA material was satisfactory in comparison to conventional bricks, with higher compressive strength and splitting-tensile strength. The results were good with respect to compressive strength and splitting-tensile strength, porosity, and absorption coefficient with capillary action of water. No efflorescence was found when only moderate amounts of sodium sulfate (<0.4 wt%) or potassium sulfate (<2.2 wt%) were present. The carbon content of the fly ash must be limited to <7 wt%. The oxidation rate of calcium sulfite to calcium sulfate is extremely low, particularly in air. SDA materials have also been used in the manufacture of sand-lime bricks in Germany [69]. It has been noted that laboratory tests showed that the best results were obtained by replacing 50% of the sand with SDA material containing 70% fly ash [17]. For the pressing of solid bricks, it is necessary to reduce the SDA material proportion to 20%.

# **Mineral Wool**

SDA material can be used to manufacture mineral wool used in insulation and ceiling tiles, as described in the research study conducted by the EERC [82]. SDA material with a high level of fly ash was used to prepare mineral wool in a pilot-scale cupola furnace. The SDA material was formed into balls, melted at 2600°–3000°F (1430°–1650°C) in the cupola, and fiberized by means of a compressed airstream. The mineral wool product was easily fabricated and appeared to be comparable in fiber diameter to that of commercial mineral wool. There were no reported commercial uses of this application in the United States, and ACAA does not report this as a separate use application.

# **Mining Applications**

One large-volume use for alkaline, dry FGD material is in reclamation of acidic minespoils. Dry FGD material could be used to neutralize the spoil acidity and reestablish the vegetative cover to stabilize soils and reduce erosion [83]. It has been indicated that SDA material could potentially be used in a grout mix design to fill mine voids [34]. ECOBA reported 181,881 short tons of SDA material used for mine reclamation and restoration in 2004 [23]. Mining applications are the largest reported use of dry scrubber FGD material in the United States. ACAA reported 115,696 short tons of dry scrubber FGD material used in mining applications in 2006 [22].

Brendel et al. summarized the findings from an EPRI study entitled *Advanced SO*<sub>2</sub> *Control By*-*Product Utilization: Laboratory Evaluation*, EPRI CS-60443 [34]. In this study, grout mixes were prepared with cement and FGD materials (including SDA material) at various proportions with sufficient water to achieve a flow in the range of 5–35 seconds. Three mix designs were created with SDA material including 3:1, 1:1, and 1:2 (cement to SDA material) ratios. Data show increased strength gain from 7 days [2.3–16.1 MPa (334–2335 psi)] to 28 days [4.5– 26.1 MPa (652–3785 psi)]. Data show that more cement does not always improve strength.

SDA material has been used as a mine fill in the United States and Europe. Instances cited in literature are described below.

A former limestone room and pillar mine in Sugar Creek, Missouri, is being stabilized using up to 700 tons of SDA material per day. The SDA material is mixed with water to create a slurry that is injected into the mine through 10-inch-diameter cased boreholes drilled through 160 feet or more of overburden. Because this particular SDA material contains ammonia, ventilation during mine stabilization was provided by constructing steel reinforced shotcrete walls between selected pillars to control airflow. As of September 2002, over 71,000 tons of the SDA material/water slurry had been injected into the mine [84].

In North Dakota, SDA material (containing about 75% fly ash) has been mixed with wet bottom ash to a water content of 20%–25% and used to backfill an old lignite strip mine. The mine was lined with clay (0.5–1.5 m thick) and capped with a clay layer (~1.5 m thick), overburden, and top soil [65].

In Germany and Poland, SDA material has been used successfully in the mining industry as filler in packing and backfill operations and as an additive in mining mortars [16, 69]. SDA material has been used in the backfilling of gravel pits without bottom sealing in Austria. Mining mortar from SDA material and fly ash was used in 1990 in Germany for the construction of underground retaining walls, for backfilling and consolidation, and for special uses. The use of SDA material for filling abandoned tunnels in lime, ore, and coal mines has been officially sanctioned and approved by German court decisions (OVwG (Oberverwaltungsgericht: Administrative Court of Appeals) Saarlouis, File 1-W 125/89; 1 F 17/89) [17].

# Soil Stabilization

SDA material has physical and chemical characteristics similar to those of a lime–fly ash mix and, thus, has the potential to be used in soil stabilization. The ability for the SDA material to form ettringite without swelling is key to its engineering performance. It also needs to be durable enough to withstand potential damage due to freezing and thawing and wetting and drying action. ACAA reported 299 short tons of dry scrubber FGD material used in soil modification and stabilization in 2006 [22]. Soil stabilization with SDA material has been documented in only a few laboratory and field demonstration projects. OSU performed laboratory experiments to characterize the engineering properties of silty clay stabilized with SDA material and FSI products. Tests were conducted to evaluate compressive strength, permeability, swelling potential, compressibility, and leachate composition. These tests were performed on compacted samples of SDA material–soil mixtures at the optimum moisture content. The FGD materials tested substantially improved the strength and stiffness of soil, which was dependent on the mix ratio. All stabilized soil mixtures developed strength of at least 0.69 MPa (100 psi) by 28 days. Generally, the permeability of the stabilized soil decreased with time as a result of the chemical reaction occurring within the mixture. Every sample showed an increase in volume over time due to ettringite formation. Consolidated test results showed low compressibility of stabilized soils. The concentration of heavy metals in the leachate was considerably lower compared to EPA drinking water standards [34].

ICF Northwest Inc. performed tests on a variety of FGD materials, including SDA material, mixed with A-7 clay, with and without additional lime. Soil had a liquid limit of 28.5 and a plastic limit of 24. The mixtures consisted of a) 90% soil, 7% FGD material, and 3% lime; b) 90% soil and 10% FGD material; and c) 90% soil, 7% fly ash, and 3% lime. The 28-day compressive strength of SDA material mixed with lime was 4.34 MPa (630 psi) and without lime was 2.83 MPa (410 psi) [34].

# Sulfuric Acid Production

The Müller-Kühne process is based on Müller's tests to produce sulfuric acid from anhydrite and Kühne's idea to produce cement at the same time by adding carbon (coke), clay, and sand. As early as 1985, investigations were started to substitute natural raw materials with products such as SDA material [17]. Dry FGD material was processed into sulfuric acid in the Müller-Kühne Process at WSZ Wolfener S.u.Z. in Bitterfeld in Germany until recently [16]. No information was found to indicate why this process is not currently used.

No instances of sulfuric acid production research in the United States were noted in the reviewed literature, and ACAA does not report this as a separate use application.

# Synthetic Aggregate

The production of synthetic aggregate using SDA material has been demonstrated in several countries on a commercial level. However, other commercial attempts have not been as successful or were only demonstrated on a laboratory scale. Production methods tend to use mixtures of fly ash and SDA material, either pelletized or briquetted. Most synthetic aggregates are lighter than natural aggregates, and are suitable for the manufacture of lightweight precast products such as roofing tiles, masonry blocks, or as a concrete and asphalt paving material. Although synthetic aggregate was not reported as an application for SDA material by ACAA in 2006 [22] or ECOBA in 2004 [23], numerous instances of commercial use and research projects were noted in the reviewed literature.

In the United States, a manufacturing plant is being operated at the Birchwood Power Facility by Universal Aggregates, LLC. The plant is turning CCPs, including SDA material, into 1,667,000 tons of lightweight aggregate annually [85]. The process used by Universal Aggregates, LLC, is described in U.S. Patent 6,054,074 [86]. The method mixes a sulfurcontaining CCP, recycle fines containing calcium hydroxide, an aluminum-containing material, and water to produce an agglomerated product. This is then combined with curing fines that contain calcium oxide and is cured. The cured material is screened to separate dry fines, which are recycled, and the aggregate, which is used as a product. CCPs used in the method can include wet FGD material with fly ash, dry FGD material such as SDA material, wet lime kiln dust with dry lime kiln dust, or FBC material with fly ash. Specifications are provided for the various materials. Further investigation of the end product is being conducted by the Research and Development Department of CONSOL Energy (CONSOL R&D) with Universal Aggregates, LLC, under a DOE cooperative agreement. The objective is to conduct a systematic study of the durability of manufactured aggregates using a variety of CCPs, including SDA material, with different chemical and physical properties. The manufactured aggregates and aggregate product materials were tested under different freeze-thaw, wet-dry, and long-term natural weathering conditions [33].

Sherburne EnviRock initiated production of manufactured, lightweight aggregate intended for use in the concrete masonry block market in 2001. A year later EcoBlend, a concrete mineral admixture also intended for use in concrete masonry, was added to production. SDA material containing fly ash is used as the primary feedstock [87].

A study performed by ICF Northwest Laboratory to produce synthetic aggregate from five different FGD materials, including SDA material, using two production processes: 1) agglomeration followed by sintering and 2) briquetting followed by  $CO_2$  environment curing. The SDA material and FSI material produced the strongest briquettes, with an average strength of 10.71 and 7.43 MPa (1554 and 1077 psi), respectively [34].

SDA material was used as an aggregate in asphaltic concrete pavement in a test road. Type 31B base course and Type 41A wear course mixes were made in the lab with 5% SDA material and 5.5% or 5.8% asphalt, respectively. The asphalt content needed to be decreased to meet MnDOT air void specifications. However, no conclusions can be drawn from these data, because it was difficult for the batch operators to meter the amount of SDA material and other aggregates used. An addition of 5% of SDA material caused a decrease in both stability and percent air voids compared to the control mixes. It was noted that less compactive effort was required to achieve the 95% of maximum density when using the SDA material containing bituminous material [46].

Synthetic aggregate production using the Aardelite process has been used commercially to manufacture synthetic aggregate. Aardelite is a proprietary technology owned by Danieli Corus but licensed to Aarding Lightweight Granulates B.V. in the Netherlands. The technology and equipment are sold by Aarding Lightweight Granulates B.V. to power plants. To date, four Aardelite plants have been built [88]. To make Aardelite, SDA material can be mixed with water and pelletized [65]. The pellets are then embedded in fly ash, so the final pellet has a core of SDA material surrounded by fly ash. The composite pellets are hardened with steam at 90°C and size-graded by sieving. The four plants use a different embedding material. However, according to a company representative, there are no commercial plants using SDA material in operation

[89]. Aardelite pellets can be used as raw material in a variety of building applications including the following [88]:

- Masonry (building) blocks
- Ready mix concrete
- Prefabricated concrete elements
- Concrete piles
- Bitumen-bonded asphalt for road construction
- Paving stones

It has been suggested that these aggregates could also be used in structural concrete. However, research carried out in Denmark by ELSAM indicates that the pellets do not have sufficient strength for this application [65]. When mixed with fly ash, the SDA material can form the mineral thaumasite, which has poor strength characteristics. Low-grade aggregates and pellets may be suitable for use in road base and as filler in asphaltic concrete.

Research initiated in Denmark has examined using the self-hardening properties of SDA material to form pellets [36]. Additives, such as portland cement or hydrated lime, may be added to SDA material with a low reactivity so that the pellets acquire adequate strength and density. Pellets (5–15 mm) were manufactured in the laboratory using a continuous roll mill pelletizing machine, and cured in a water-saturated environment. Despite encouraging results, the demonstration work did not result in the commercial production of aggregates.

It is possible to produce artificial gravel and chippings by mixing SDA material with 10%–20% water and compacting it in a pelletizing plant to a density of 2 t/m<sup>3</sup> and curing. A 5% addition of cement is required for low-fly ash SDA materials. The artificial gravel and chippings can be used as a substitute for natural gravel or chippings for cement or bitumen-bound road surfaces and cement-bound building brick. Development work in Denmark has been discontinued because of long setting times, reduced frost resistance, and an increase in volume due to thaumasite formation [17].

# Wallboard

The use of SDA material in wallboard has been demonstrated in Denmark by DURACON ApS [65]. The process uses the same production facilities as other fiber–cement boards that are fire-resistant. The boards consist of a mixture of SDA material (~40%), fly ash (~10%), recycled paper (10%), cement, and additives. The finished panels should be cured in an autoclave. The raw materials are low in cost, minimizing production costs compared with similar wallboards. The panels are strong enough, with sufficient stiffness, for normal handling and working, and fire resistance tests show good performance. The product was undergoing full-scale testing in 1992, with a potential daily production capacity of about 4000 m<sup>2</sup> of board. Instances of this product reaching full commercial implementation were not found.

Kolar also reported that several authors have described the production of wallboard made of SDA material, fly ash, fibers, and portland cement or lime hydrate [17]. The board is autoclaved and dried. The boards are claimed to be suitable for interior applications in residential buildings, hospitals, schools, and industrial buildings.

ACAA has not reported dry scrubber FGD material use in wallboard applications since dry scrubber FGD materials have been categorized.

# Wet FGD Sorbent

Dry FGD material is used as a sorbent in the wet FGD process in both Germany and Denmark; although it has not reached commercialization in the United States [16, 22]. The excess alkali in the dry FGD material serves as a sorbent for the  $SO_2$  in the flue gas, and the sulfite in the material is simultaneously converted to commercial-grade gypsum. A prerequisite for this use is a very low fly ash content. It has been reported that the gypsum quality has improved when operating on dry FGD material as compared to using limestone powder and typically contains 98%–99% calcium sulfate dihydrate (gypsum) [16].

# **3** SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

An extensive literature review was performed that provided information on:

- SDA systems and their operation and the impacts of system components and operation on the SDA material composition.
- The production and use statistics for SDA material produced in the United States and Europe.
- SDA material characteristics.
- Commercial and potential uses of SDA material.

The literature review brought into focus several issues evident to producers and users of SDA material that have an impact on the status of this material in commercial markets. These issues are summarized here and include a list of barriers to the commercial utilization of SDA material.

## **SDA Production and Material Characteristics**

SDA systems have two primary configurations. In the United States, the most common system configuration has the spray dryer chamber located so the flue gas is combined with the sorbent before it is introduced into the primary particulate collection system. In this configuration, the fly ash and dry SDA material are mixed in the spray dryer chamber, and in cases where the fly ash is alkaline, the fly ash actually serves as a sorbent so the fly ash particles are coated with calcium sulfite/sulfate. Recycle of this mixture is frequently used to optimize sorbent utilization. Variables in this system include the amount of fresh lime sorbent that is introduced, the fly ash characteristics, the recycle rate, and the spent sorbent–fly ash ratio.

The typical European SDA system configuration includes a fly ash precollection unit that removes the fly ash from the flue gas before it enters the spray dryer chamber. The variables in this system configuration are fewer resulting in a more consistent material between plants.

The SDA material that results from these two primary system configurations have obvious compositional differences. The systems with fly ash precollection produce an SDA material that is composed primarily of calcium sulfite, calcium sulfate, and other minor calcium-based compounds. The systems that incorporate the fly ash stream into the sorbent stream in the spray dryer chamber produce SDA materials that are composed of these same calcium compounds with fly ash that may or may not be coated with calcium sulfite or sulfate, depending on the alkalinity and composition of the fly ash. Even without accounting for varying chemical composition of the fly ash, it is apparent that SDA materials produced from these two configurations will be

significantly different in composition performance. In European literature, SDA materials are frequently referred to as dry FGD material. This term is used more generically in the United States but does include SDA material. Unfortunately, in most of the literature reviewed, the system configuration was not described nor was the percentage of fly ash, if present, noted. However, the variability of the materials investigated and/or used is evident in the results of the literature review by the variability of the composition and properties reported. Wide variability for these materials was documented for every physical property for which literature was found and for the chemical composition to include the trace element concentrations. Although mineralogical characterizations were limited, it is expected that similar crystalline phases would be present in all types of SDA materials, but that those with fly ash present would also contain a significant amorphous phase. On review of the characterization data from the literature review, it was noted that varying conclusions were drawn by individual authors. The variability of samples used in the studies likely contributed to the divergence in conclusions. Another factor that likely played a role in the differences was the methodology used to evaluate specific parameters. This serves as a caution in relating literature data and conclusions as representative of SDA materials without a clear understanding of the specific material(s) referred to in the literature.

## **Utilization of SDA Material**

As described in Section 2 under "Current and Potential Uses of SDA Material," SDA material is commercially used in a variety of applications in the United States and Europe. A review of the ACAA production and use survey results also provides an indication of utilization in the United States. These applications are noted in Table 3-1.

European Commercial Applications	U.S. Commercial Applications
Agriculture (e.g., sulfur fertilizer)	Agriculture
Flowable fill	Concrete, concrete products, and flowable fill
Raw material for cement manufacture	Soil stabilization
Raw material for sulfuric acid production	Structural fills/embankments
Wet FGD sorbent	Synthetic aggregatea
	Mining applications

Table 3-1Commercial Applications for SDA Material in the United States and Europe

<sup>a</sup> Although not listed in the 2006 ACAA statistics [22], this is a current SDA material use.

The utilization profiles for SDA material in the United States and Europe are different at least in part because of the different chemical composition resulting from the inclusion of fly ash in the United States, while in Europe, SDA material typically does not include a fly ash component. Additionally, the more stringent European disposal regulations encourage utilization of CCPs, and likely encouraged utilization of SDA materials. Some commercial applications, such as mine fill and wet FGD sorbent, may have less stringent composition or quality control criteria.

Based on the commercial applications reported and research on utilization of SDA material, a list of applications was assembled, ranking applications as having high, moderate, and low potential for the U.S. market relative to the technical achievability of the applications. Key technical issues that were considered in ranking these applications were:

- Variability of SDA materials Most U.S. current and projected SDA systems incorporate some fly ash into the final SDA material. The level of fly ash present and the specific chemistry of that fly ash results in a variability in the chemical composition of the final SDA material, and that is expected to result in a variability in the physical and engineering performance of the material for many of the use applications noted.
- Sulfur content Since SDA is used to remove sulfur gases from flue gas, the total sulfur content of SDA materials can be significantly higher than fly ash. For some applications, this elevated concentration of sulfur may limit the use. Additionally, most of the sulfur present in SDA material is present both as sulfite and as sulfate, with sulfite being the prevalent form. For some applications, the potential for oxidation of the sulfite to sulfate could limit use of SDA materials and needs to be considered.
- Potential for expansion SDA material that contains fly ash has the potential to expand, especially when exposed to water. The composition of SDA materials containing fly ash includes the primary building blocks for ettringite formation, a key secondary hydrated phase that can cause expansion if it forms in finished products or final placements. The pH of SDA material is not considered conducive to ettringite formation, but free lime present in SDA material may provide enough alkalinity to allow ettringite formation to occur. Expansion needs to be considered in any use applications for SDA material. While expansion can be predicted by use of appropriate tests, many tests currently available for determining expansion potential may not be adequate to predict field or full-scale performance. This is due to many factors, but laboratory studies indicated that expansion may be taking place into material voids. A simple test based on density changes of materials that will with great certainty predict expansion under laboratory conditions has been developed by the EERC [90].

Economic feasibility was not used in this ranking process, but in order for any material to be commercially viable in a utilization application, the economics need to be advantageous and should be considered in feasibility investigations. For some applications, the environmental suitability of SDA materials, or any other CCP or industrial resource, may need to be evaluated. Environmental performance of SDA materials was outside the scope of this literature review, but the issues associated with use applications that may result in impacts to human health and the environment are prevalent in public reports and technical literature.

#### **High-Potential Applications**

High-potential applications for the U.S. market are estimated to be those that take advantage of the presence of the fly ash component of the SDA material, can tolerate relatively high sulfur content, and have limited susceptibility to expansion or reduce expansion potential in the production process. These applications fall into two categories: 1) cementitious products and 2) mining.

#### **Cementitious Products**

ACAA's 2005 utilization rate for dry scrubbing materials in concrete and concrete products was ~14,000 tons, or ~1% of the 2005 U.S. production. It is unlikely that this utilization rate includes significant quantities of sodium-based dry scrubber materials because of the technical and performance issues associated with high levels of available alkali in materials used for formulation of concrete. Therefore, it is assumed that the 2005 1% utilization rate refers almost exclusively to SDA material. Anecdotal evidence suggests that this utilization is likely primarily in concrete products such as masonry. ACAA also reported that nearly 10,000 tons of dry scrubbing materials were used for flowable fill in 2005 (0.7% of the amount produced) [59]. It is also assumed that the bulk of the dry scrubber material reported in flowable fill is also likely SDA material. Literature and anecdotal evidence indicated that some of these cementitious products or applications have specific requirements for the SDA material to be used most effectively. It is predicted that these use applications have high potential for growth as more SDA materials become available. Based on the prediction of 13–14 M tons of SDA material to be produced annually in the United States by 2017, it is estimated that the utilization rate should be maintained at the current approximate 2% level and could reach 5% or higher of production if industry develops technical and performance data and markets the product effectively. This equates to about 260,000 to 700,000 tons annually. Location of material and markets will have a definitive impact on market development and penetration. Much of this growth is anticipated after 2012 as installations increase in number.

#### Masonry

Although SDA material has been shown to be an effective component of masonry products, most commonly concrete blocks, the SDA material may need to be conditioned prior to use, and cementitious additives may be required for unreactive to moderately reactive SDA materials. Use of alkaline activation and the elevated-temperature curing of these products has been shown to result in good performance of the SDA material in these products.

#### 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 properties, swell potential, and corrosivity.

#### Synthetic Aggregate

SDA material is currently being used to manufacture synthetic aggregate in the United States; however, there is also evidence that some synthetic aggregate-manufacturing processes developed to use SDA material have not had commercial success. Successful aggregate production from SDA material indicates the potential for use in concrete block, brick, and other shaped compacted product production. Much like the masonry application, it may be necessary to activate the SDA or use an elevated-temperature curing to facilitate good product performance.

#### **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 on mine spoils did cause excessively high pH and cementation. The technical issues associated with the use of SDA material in mine applications can be addressed through an understanding of the experience already reported in the literature, characterization of the material, and careful attention to the methods for applications and quantities of material applied. Statistics from 2005 indicate that approximately 8% of dry scrubber materials produced in the United States were used in mining applications [59]. This represented by far the largest current use of dry scrubber materials. It is reasonable to assume that much of the dry scrubber materials included in the 2005 statistics were SDA materials simply because of the very limited number of other dry scrubber systems currently being used as compared to SDA systems reported. Since projected SDA installations are expected to be in the Midwest and western United States, it is likely that mining applications of SDA materials will remain a good utilization candidate and will increase proportionately to the amount of material produced in the western states. Contingent on rules currently under development by the Office of Surface Mining, it is anticipated that the utilization rate of 8% can be readily maintained and could be expected to increase to 15% during the period from 2007 to 2012. During that period, most of the new installations will be in western states, where mine placement is expected to be economically feasible. Between 2012 and 2017, this use application could continue to increase but on a more limited basis because later SDA installations are anticipated to be in the Midwest and the advantage of location is not expected to favor mine reclamation as much as western installations. It is estimated that a maximum utilization rate of 20% could be realized by 2017. This would equate to 2.6–2.8 million tons annually, a more than 10-fold increase over current utilization volumes.

#### **Moderate-Potential Applications**

#### Cement Replacement in Concrete

SDA material should be evaluated for suitability as a cement replacement in concrete, especially as groups like ASTM International and the American Association of State Highway and Transportation Officials (AASHTO) 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 superior to traditional concrete. This application is most promising when SDA material and fly ash are collected together with a high percentage of fly ash, as is common in U.S. installations. The technical issues that require some continued evaluation can be readily addressed using protocols similar to the ones developed and used for fly ash and other supplementary cementitious materials. It will be possible to determine the appropriateness and amounts of specific SDA materials for use in concrete, and there is technical evidence that it can offer good performance. Much like fly ash qualification for use in concrete, the producer or potential marketer will need to take the responsibility of evaluating their specific material, developing the market, and educating the users. This process will require time, so although the market has high potential to be technically successful, it is expected to take time to develop that market.

The potential for large volumes of SDA material to be used in this application will likely be dependent on a number of factors, including potential reductions in the availability of fly ash for use in concrete, which is expected to be impacted by the installation of mercury control technologies that use activated carbon and combine the activated carbon with the fly ash stream. If even some of the current concrete-quality fly ash being produced becomes unsuitable for use in concrete, there may be a market need for alternate materials. Of course, if activated carbon is used and mixed with fly ash on a unit or plant where the fly ash is incorporated into the SDA material, the SDA material may not meet the required specifications for use in concrete.

Current data on dry FGD material utilization do not separate use in concrete or concrete products. It is estimated that only very low quantities of SDA material (<0.5%) are currently being used for cement replacement. This utilization rate is not expected to increase significantly, but at the predicted production rate for 2017 (13–14 M tons/year), a use rate of 0.5%, or 65,000–70,000 tons, would be significant for the overall use of the material.

#### **Engineering Applications**

SDA material has been used commercially in engineering applications in Europe and with limited success in the United States. ACAA reported 2666 tons of dry FGD material were used for structural fills and embankments in the United States in 2005 [59]. This utilization rate of approximately 2% was likely primarily SDA material and indicates that SDA can be successfully utilized in engineered fills. This utilization rate would be expected to be maintained as additional SDA materials are generated.

#### Agriculture

In Europe, SDA material is typically collected separately from fly ash, whereas in the United States, SDA material and fly ash are 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. The leaching of boron could be a potential environmental concern. ACAA reported ~19,000 tons of dry scrubber material used in agricultural applications in 2005, nearly 1.5% of the total production of ~1.4 million tons [59]. This represents the second largest current use of dry scrubber material. It is likely that the dry scrubber material used in agricultural applications was SDA material because the sodium-based dry scrubber materials have potential detrimental effects on many crops and soil types. An effort is currently under way in the United States to demonstrate the effectiveness of FGD gypsum for use as an agricultural soil amendment. Even though SDA material contains fly ash and calcium sulfite, which makes it different from FGD gypsum, the potential for SDA material to be used in agricultural applications may be enhanced by the current efforts on FGD gypsum use. The agricultural use of calcium sulfite, which is toxic to plants under certain conditions, appears to be less problematic than initially expected. Under normal soil pH and with a limited supply of air for oxidation, it would be expected that the oxidation of sulfite to sulfate, which is not toxic to plants, would be extremely slow. However, in field studies, this conversion occurs rapidly. This anomaly is likely due to microbial transformations of sulfite to sulfate. It has been demonstrated that simply placing the sulfite-rich material in the agricultural soils a few weeks in advance of planting mitigates any detrimental effects of sulfite. There is moderate potential for SDA material to be used in agriculture in the western United States, where FGD gypsum is expected to be less available. The trace element concentrations of SDA materials are likely one technical and regulatory issue that will need to be addressed. Utilization rates are predicted to be maintained at near 1% based on the increased production.

#### Soil Stabilization

SDA material has physical and chemical characteristics that are similar to a lime-fly ash mix and, thus, has the potential to be used in soil stabilization even though mixed results have been found in the expansion potential of SDA material used as a road foundation. The ability for the SDA material to form ettringite without swelling is key to its engineering performance. It also needs to be durable enough to withstand potential damage due to freezing and thawing and wetting and drying action. Soil stabilization with SDA material has been documented in only a few laboratory and field demonstration projects, and no commercial uses were found in the reviewed literature even though marketers indicated the successful use of specific SDA materials in soil stabilization in certain regions of the United States. There is the potential for the technical issues related to the use of SDA material in soil stabilization to be addressed, so this application has moderate potential. Currently, there is only anecdotal evidence of SDA material being used for soil stabilization in the United States, but if the technical issues are adequately addressed, it is projected that the utilization rate could reach 0.5%-1.0% of the production rate.

#### Wet FGD Sorbent

Dry FGD material has been used commercially as a sorbent in the wet FGD process in Germany and Denmark. Since there is alkalinity still available in SDA material, it is possible that it could be a good candidate for use in wet FGD systems in the United States, likely in inhibited or natural oxidation systems. The technical issues would need to be addressed, and the actual use would likely be dependent on locations of an SDA producer and wet FGD system. Currently, there is no SDA material being used in this application, but it could reach a utilization rate of up to 1% or greater by 2017. This application warrants investigation to evaluate the impact of the presence of fly ash in the SDA material, and it is likely that this application has the highest potential for a region where an SDA material producer and wet FGD system user are in close proximity.

### Low-Potential Applications

The following applications are expected to have low utilization potential. Predictions for utilization rates have not been made.

#### Binder

SDA material used as a binder for interior plasters was noted in U.S. and German patents. The use of SDA material 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; however, it is not anticipated that the process will reach commercialization.

#### Fixating Agent for Hazardous Waste Sludge

Research has shown that SDA material has the potential to solidify or fixate hazardous wastes if proper fixation techniques can be developed. The mechanism for this is likely due to the excess alkaline materials present in SDA material. Although SDA material particles are generally coated with sulfite and sulfate, the grinding action of a pug mill would likely activate the material by exposing alkaline surfaces through abrasion of particles.

#### **Marine Applications**

Research conducted to date has shown that SDA material can be used in marine applications such as artificial reefs and offshore sea defenses. SDA materials exposed to marine environments appear to show no evidence of surface friability or cracking and are a favorable habitat for marine life. The economical and environmental feasibility of this application should be further evaluated.

#### **Mineral Wool**

The production of mineral wool from SDA material is technically feasible if the SDA material contains a high percentage of fly ash. However, the market is not demanding this process at this time.

#### Sulfuric Acid Production

The use of SDA material in the production of sulfuric acid may be technically feasible; however, the authors believe this is not an economical beneficial use option.

#### Wallboard

Using SDA material as a source of gypsum in traditional wallboard is not a promising utilization option. However, research conducted in Denmark showed that SDA material, when mixed with fly ash, cement, and other additives and cured in an autoclave can produce good-quality fiber–cement board. The economics of this application need to be considered.

#### **Barriers to SDA Material Utilization**

The European and U.S. production and utilization statistics for SDA material clearly indicate that SDA materials are currently underutilized, especially in the United States, even though this report summarized a number of commercial applications and several applications that have high potential to become commercial. 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 inconsistency with regard to the terms used to describe SDA materials and FGD materials in general. The discrepancies were so broad that, in some cases, the authors could not determine the specific product to which the reports referred. Inconsistent terminology makes it difficult for those in the industry, particularly government entities, to define the material and its potential uses properly. In any area, a well-defined vocabulary is the cornerstone of effective communication, and this is essential in technical fields. This lack of consistent terminology is a barrier to both the commercialization and to 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 CCPs, 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 affect 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, products from FGD systems are relatively new in comparison to other products, and specifications have not been written that deal specifically with SDA material. In European countries where regulations have been adopted, most progress has been made with regard to SDA material utilization.
- Economics Economic factors are an overriding issue in utility ash management decisions. Currently, the potential to produce revenue from the sale of SDA material is limited; therefore, most utilities 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 presence of significant levels of calcium sulfite and the natural oxidation of sulfite to sulfate has the potential to affect 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 so the fly ash can also act as an SO<sub>2</sub> sorbent.
- U.S. SDA material utilization rates are lower than European utilization rates, likely because of higher variability of the U.S. material, incorporation of fly ash into the material, and current 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 markets identified.

## Recommendations

As U.S. coal-fired power plants install additional FGD systems to reduce  $SO_2$  emissions in coming years, it is anticipated that a number of plants will elect to use SDA systems, resulting in an associated increase in the volume of SDA material produced in the United States. Although disposal is currently the predominant management option for SDA material in the United States, the potential exists that viable commercial options can be developed for this material. In order to optimize SDA material use in existing commercial applications and develop the potential commercial options in the United States, technical, environmental, and economic evaluations will be required. The following recommendations present an outline for the CCP industry to maintain existing commercial markets and develop new markets for U.S. SDA materials:

- Work within existing organizations such as ASTM International and ACAA to develop and put into use appropriate terminology and definitions for SDA materials.
- Develop an understanding of the impact of compositional variability on the performance characteristics of SDA materials.

- Develop an understanding of the oxidation profiles of SDA materials and evaluate the impacts of oxidation on product performance.
- Educate potential users, regulatory representatives, and other stakeholders about SDA materials.
- Address quality, compositional, environmental, and performance criteria in research, development, and demonstration efforts.

# **4** REFERENCES

- Berland, T.D., D.F. Pflughoeft-Hassett, B.A. Dockter, K.E. Eylands, D.J. Hassett, L.V. Heebink. *Review of Handling and Use of FGD Material;* CARRC Final Report for Utility Solid Waste Activities Group, EERC Publication No. 2003-EERC-04-04; Grand Forks, ND: Energy & Environmental Research Center, April 2003.
- Redinger, K. "Spray Dryer Atomization (SDA) Byproducts: Production, Characteristics, and Management Options." In *Proceedings of the 20th Symposium on Western Fuels;* Denver, CO, October 24–26, 2006.
- 3. Pflughoeft-Hassett, D.F. *Utilization of Sulfite-Rich FGD Material: Summary of References Under Review;* Topical Report for CARRC Members; Grand Forks, ND: Energy & Environmental Research Center, February 2006.
- U.S. Environmental Protection Agency. *Air Pollution Control Technology*; Fact Sheet No. EPA-452/F-03-034; U.S. Environmental Protection Agency, Washington, DC: U.S. Government Printing Office, 2006. <u>www.epa.gov/ttn/catc/dir1/ffdg.pdf</u> (accessed July 2006).
- 5. Stultz, S.C., and J.B. Kitto. "Sulfur Dioxide Control." In *Steam: Its Generation and Use*, 40th ed.; Barberton, OH: Babcock & Wilcox, 1992; pp 35-1 to 35-15.
- 6. Brown, E.S. "Overview of the Utility MACT Development and Issues." Presented at What We Know About Mercury Part II: Regulatory and Legislative Policy Options Being Proposed to Deal with Mercury Contamination, March 7, 2003.
- 7. National Energy Technology Laboratory. Combustion Fluidized-Bed Combustion: An Overview. <u>www.netl.doe.gov/technologies/coalpower/advresearch/combustion/FBC/fbc-overview.html</u> (accessed June 2007).
- 8. Webster, W.C. Utilization of Dry Scrubber Waste Materials. U.S. Patent 4,354,876. October 19, 1982.
- 9. Bird, J.F. Dry Scrubbing Technologies for Flue Gas Desulfurization; Norwell: Kluwer, 1998.
- 10. Dawson, G., J.S. Perri, J.R. Daley. *Utilization Potential of Advanced SO*<sub>2</sub> *Control By-Products*; EPRI-CS-5269; Palo Alto, CA: Electric Power Research Institute, June 1987.
- Katzberger, S.M., and W.J. Rymarczyk. "Treatment and Disposal of Wastes from Dry SO<sub>2</sub> Control Processes." Presented at the American Institute of Chemical Engineers Annual Meeting, Chicago, IL, November 1985.

#### References

- Klimek, A.P., A.G. Eklund, G.W. Dawson, and D.W. Golden. "Design of Waste Management Systems for Calcium Spray Dryer FGD Technology." In *Proceedings of the Tenth Symposium of Flue Gas Desulfurization*, Volume 2, Atlanta, GA, November 17–21, 1986; Emmel, B.B., Ed.; Palo Alto, CA: Electric Power Research Institute, May 1987; EPRI-CS-2801, pp 10-79 to 10-100.
- Klimek, A.P., M.G. Lees, E.H. McMeekin, and MM. Stewart. *Calcium Spray Dryer Waste Management: Design Guidelines*; EPRI-CS-5312; Palo Alto, CA: Electric Power Research Institute, September 1987.
- Beidleman, W., and J.D. Hilbert. "Material Handling Considerations for FGD Solid By-Products." *Coal Technology, International Coal Utilization Conference and Exhibition* 1985, *I & II*, 343–370.
- 15. Soud, H.N. FGD Installations on Coal-Fired Power Plants; London: IEA Coal Research, 1994.
- 16. Bengtsson, S. "Semi-Dry FGD End Product Utilization European Experiences." Presented at the Mega Symposium, Chicago, IL, August 20–23, 2001; Paper 219.
- 17. Kolar, J. "Possibilities of Using Residual Products of the Spray Absorption Processes." *VGB Kraftwerkstechnik* 2 (1995): 153–159.
- 18. Babcock & Wilcox Company, personal communication, July 2007.
- 19. American Coal Ash Association, Glossary of Terms Concerning the Management and Use of Coal Combustion Products (CCPs) Effective: April 2003.
- 20. American Coal Ash Association. 2002 Coal Combustion Product Production and Use Survey; Aurora, CO, November 24, 2003.
- 21. American Coal Ash Association. 2004 Coal Combustion Product Production and Use Survey; Aurora, CO, September 9, 2005.
- 22. American Coal Ash Association. 2006 Coal Combustion Product Production and Use Survey; Aurora, CO, August 24, 2007.
- 23. European Coal Combustion Products Association (ECOBA). www.ecoba.com/index.html (accessed August 2006).
- Brennan, P., H.-J. Feuerborn, W. vom Berg. "Recent Developments in European CCP Utilization." In Proceedings of the 15th International American Coal Ash Association Symposium on Management & Use of Coal Combustion Products, Lexington, KY, October 20–22, 2003.
- 25. vom Berg, W., and H.-J. Feuerborn. CCPs in Europe. In *Proceedings of Clean Coal Day in Japan 2001*; Tokyo, Japan, September 3–6, 2001, ECOBA European Coal Combustion Products Association, <u>www.energiaskor.se/rapporter/ECOBA\_paper.pdf</u>.
- 26. vom Berg, W., and H.-J. Feuerborn. "Present Situation and Perspectives of CCP Management in Europe." In 2005 World of Coal Ash Conference Proceedings; Lexington, KY, April 11–15, 2005.
- 27. Naik, T.R., and Y. Chun. "International Coal Combustion Products Generation and Use." Presented at the Tenth International Conference on "Ashes from Power Generation," Warsaw, Poland, October 2003: Report No. CBU-2003-34.

- 28. ASTM International, Active Standard: E2201-02a Standard Terminology for Coal Combustion Products, 2005.
- Korcak, R.F. "Agricultural Uses of Coal Combustion Byproducts." In Agricultural Uses of Municipal, Animal, and Industrial Byproducts; Wright, R.W., Kemper, W.D., Millner, P.D., Power, J.F., Korcak, R.F., Eds.; Washington, DC: U.S. Department of Agriculture Agriculture Research Service: pp 103–119.
- Dawson, G.W., A.G. Eklund, R.D. Delleney, C.M. Thompson, R.D. Achord, and G.M. Blythe. *Laboratory Characterization of Advanced SO<sub>2</sub> Control By-Products: Spray Dryer Wastes*; EPRI-CS-5782; Palo Alto, CA: Electric Power Research Institute, May 1988.
- Boyd, R.H., Jr., H.A. Frediani Jr., and A.R. Kimbro. Advanced SO<sub>2</sub> Control Solid-Waste Management Planning Study; EPRI-CS-4402; Palo Alto, CA: Electric Power Research Institute, February 1986.
- Perri, J.S., J.S. Laskey, and R.J. Collins. Advanced SO<sub>2</sub> Control By-Product Utilization-Laboratory Evaluation; EPRI-CS-6044, Palo Alto, CA: Electric Power Research Institute, September 1988.
- 33. Wu, M.M. Durability Evaluation and Production of Manufactured Aggregates from Coal Combustion By-Products; Final Report (October 1, 2000 through February 28, 2005) for U.S. Department of Energy Cooperative Agreement DE-FC26-00NT40910; South Park, PA: CONSOL Energy, February 2005.
- 34. Brendel, G.F., N.J. Balsamo, and L.H. Wei. Guidelines for the Beneficial Use of Advanced SO<sub>2</sub> Control By-Products; TR-108403; Palo Alto, CA: Electric Power Research Institute, August 1997.
- 35. Dawson, G.W., A.G. Eklund, G.D. Gumtz. *Management of Solid By-Products from Advanced SO*<sub>2</sub> *Control Systems*; EPRI-CS-5076; Palo Alto, CA: Electric Power Research Institute, April 1987.
- Donnelly, J.R., E.S. Jøns, and W.C. Webster. "Synthetic Gravel from Dry Flue Gas Desulfurization End-Product." In *Sixth International Ash Use Symposium*, Volume 2, Reno, NV, March 1982. DOE/METC-82-52-Vol.2.
- 37. Kost, D.A., J.M. Bigham, R.C. Stehouwer, J.H. Beeghly, R. Fowler, S.J. Traina, W.E. Wolfe, and W.A. Dick. "Chemical and Physical Properties of Dry Flue Gas Desulfurization Products." *Journal of Environmental Quality* 34 (2005): 676–686.
- 38. Dick, W., J. Bigham, R. Forster, F. Hitzhusen, R. Lal, R. Stehouwer, S. Traina, S., W. Wolfe, R. Haefner, and G. Rowe. *Land Application Uses for Dry Flue Gas Desulfurization By-Products*; Executive Summary; Ohio State University: Wooster, OH; Columbus, OH: United States Geological Survey, January 1999.
- Janssen, K.E., and R.L. Erikson. "Basin Electric's Involvement with Dry Flue Gas Desulfurization." EPA Symposium on Flue Gas Desulfurization, Las Vegas, NV, March 1979; EPA-600/7-79-1676. pp 629–653.
- 40. Stearns, Conrad and Schmidt Consulting Engineers, Inc. Recovery, Utilization, and Disposal of Solid By-Products Generated by Dry Flue Gas Desulfurization Systems: State of the Art and Research Needs; EPRI-CS-1765; Palo Alto, CA: Electric Power Research Institute, March 1981.

#### References

- 41. British Coal Corporation Coal Research Establishment. *Disposal and Utilization of Flue Gas Desulphurisation (FGD) Residues*; EUR Report EUR-14071-EN; Luxembourg: Commission of the European Communities, 1992.
- 42. Jøns, E. Summary Report on SDA End Product; Report for A/S Niro Atomizer, Soeborg, Denmark, January 1987.
- 43. Dick, W., J. Bigham, F. Forster, R. Hitzhusen, R. Lal, R. Stehouwer, S. Traina, and W. Wolfe. Land Application Uses of Dry FGD By-Products: Phase 3 Report; Final Technical Report, EPRI Project RP2796-02; Columbus, OH: The Ohio State University, May 1998.
- 44. Pflughoeft-Hassett, D.F., B.A. Dockter, K.E. Eylands, D.J. Hassett. Survey and Demonstration of Utilization Potential of North Dakota Lignite Ash Resources; Final Report; EERC Publication 96-EERC-04-01; Grand Forks, ND: Energy & Environmental Research Center, April 1996.
- 45. Bloem, P.J.C., B.J.G. Sciarone. "Applications of Spray-Dry Products in Building Materials." In *Proceedings of the Second International Conference on FGD and Chemical Gypsum*, Toronto, Canada, May 12–15, 1991.
- 46. Behrens, G.P., W.A. Weigand, and M.R. Curtis. *Use of Spray Dryer Product in Road Construction: Minnesota Demonstration*; TR-108402; Palo Alto, CA: Electric Power Research Institute, August 1997.
- 47. Punshon, T., and D.C. Adriano. Soil Amendment with Flue-Gas Desulfurization Residue: Mid-term Physical and Chemical Effects on Plants and Soils; Advanced Analytical Center for Environmental Sciences; Savannah River Ecology Laboratory: Drawer E. Aiken, SC, November 2001.
- 48. Bigham, J.M., D.A. Kost, R.C. Stehouwer, J.H. Beeghley, R. Fowler, S.J. Traina, W.E. Wolfe, and W.A. Dick. "Mineralogical and Engineering Characteristics of Dry Flue Gas Desulfurization Products." *Fuel* 84 (2005): 1839–1848.
- 49. Peters, F., and W. vom Berg. "Origin and Properties of Power Plant Residues." *VGB Kraftwerkstichnik* 4 (1992): 353–357.
- Solem-Tishmack, J.K. Use of Coal Conversion Solid Residuals in Solidification/Stabilization Technology. Thesis, North Dakota State University of Agriculture and Applied Science: Fargo, ND, March 1993.
- 51. Wu, M.M., R.A. Winschel, and G.E. Wasson. "Composition Effects on Durability of Aggregates Made from Coal Combustion By-Products." In *Proceedings of the Twelfth Annual International Pittsburgh Coal Conference*, Pittsburgh, PA, September 11–15, 1995; pp 132–137.
- 52. Wu, M.M., R.A. Winschel, and G.E. Wasson. Composition Effects on Durability of Aggregates Made from Coal Combustion By-Products. In *Proceedings of the 1995 International Ash Utilization Symposium*, Lexington, KY, October 23–25, 1995.
- 53. McCarty, G.W., R. Siddaramappa, R.J. Wright, E.E. Codling, and G. Gao. "Evaluation of Coal Combustion Byproducts as Soil Liming Materials: Their Influence on Soil pH and Enzyme Activities." *Biol Fertil Soil* 17 (1994): 167–172.

- 54. Stehouwer, R., W. Dick, J. Bigham, L. Forster, F. Hitzhusen, E. McCoy, S. Traina, and W. Wolfe. Land Application Uses of Dry FGD By-Products: Phase 1 Report; EPRI TR-105264; Palo Alto, CA: Electric Power Research Institute, 1995.
- 55. Coal Ash Resources Research Consortium<sup>®</sup> (CARRC<sup>®</sup>). Coal Ash Properties Database. Grand Forks, ND: Energy & Environmental Research Center, 2006.
- 56. Hassett, D., L. Heebink, P. Bloom, and F. Gustin. *Environmental Evaluation for Utilization of Ash in Soil Stabilization*; Final Report (August 11, 1999 Nov 30, 2001) for U.S. Department of Energy Contract No. DE-FC26-09FT40321; EPRI No. 1005213; EERC Publication No. 2001-EERC-08-06; Grand Forks, ND: Energy & Environmental Research Center, August 2001.
- 57. Dick, W.A., Y. Hao, R.C. Stehouwer, J.M. Bigham, W.E. Wolfe, D. Adriano, J.H. Beeghly, and R.J. Haefner. Beneficial Uses of Flue Gas Desulfurization By-Products: Examples and Case Studies of Land Application. In *Land Application of Agricultural, Industrial, and Municipal By-Products*; Power, J.F., Dick, W.A., Bartels, J.M., Eds.; Soil Science Society of America Book Series No. 6; Soil Science Society of America: Madison, WI, 2000; pp 505–536.
- Wendell, R.R., and K.D. Ritchey. "High-Calcium Flue Gas Desulfurization Products Reduce Aluminum Toxicity in an Appalachian Soil." *Journal of Environmental Quality* 25 (6) (1996): 1401–1410.
- 59. American Coal Ash Association. 2005 Coal Combustion Product Production and Use Survey; Aurora, CO, September 29, 2006.
- 60. Alcordo, I.S., and J.E. Rechcigl. "Phosphogypsum and Other By-Product Gypsums." In Soil Amendments and Environmental Quality; Rechcigl, J.E., Ona, FL, Ed.; Agriculture and Environment Series; Boca Raton, FL: CRC Press, Inc., 1995: pp 365–425.
- 61. Clark, R.B., K.D. Ritchey, and V.C. Baligar. "Dry Matter Yields of Maize Grown with Coal Combustion By-Products." In *Proceedings of the 10<sup>th</sup> International Ash Use Symposium*, Orlando, FL, January 17-22, 1993; Volume 1: High Volume Uses/Concrete Applications. EPRI Rep. TR-101774. American Coal Ash Association, Washington, D.C.
- 62. Wedzicha, B.L. *Chemistry of Sulfur Dioxide in Foods;* Amsterdam: Elsevier Applied Science Publ., 1984.
- 63. Ritchey, K.D., T.B. Kinraide, R.R. Wendell, R.B. Clark, and V.C. Baligar. "Strategies for Overcoming Temporary Phytotoxic Effects of Calcium Sulfite Applied to Agricultural Soils." In *Proceedings of the 11th Annual International Pittsburgh Coal Conference*, Volume 2; Pittsburgh, PA, September 12–16, 1994.
- 64. Farber, P.S., C.D. Livengood, J.L. Anderson. "Leachate of Dry Scrubber Wastes." Presented at the 76th Annual Meeting of the Air Pollution Control Agency, Atlanta, Georgia, June 19–24, 1983.
- 65. Clarke, L.B. Management of FGD Residues; IEACR/62; London: IEA Coal Research, 1993.
- 66. vom Berg, W. "Aims and Results of VGB's ERKOM Research Programme for the Utilization of Coal Combustion By-Products." *VGB PowerTech* 81 (7) (2001): 85–88.

- vom Berg, W. "By-Products." In Brief Report on the Activities of the Technical Association of Large Power Plant Operators, VGB TECHNISCHE VEREINIGUND DER GROSSKRAFTWERKSBETREIBER E.V. 1998/1999. VGB PowerTech 79 (10) (1999): 37– 39.
- 68. Koslowski, T., and H. Roggendorf. Binder for Interior Plasters. U.S. Patent 5,522,928. June 4, 1996.
- 69. vom Berg, W., F. Peters, K.-H. Puch, U. Taubert. "Use of Residues from Coal-Fired Power Stations in the Federal Republic of Germany." In *UNIPEDE/IEA Conference on Thermal Power Generation and the Environment* (Paper 933en3.6), Hamburg, Germany, September 1–3, 1993.
- Bloss, W. Process with Calcium Sulfite Hemihydrate in a Powdery Byproduct from Dry Flue Gas Desulfurization for the Production of Fly Ash Cement. U.S. Patent 4,470,850. September 11, 1984.
- 71. American Coal Ash Association. 2003 Coal Combustion Product Production and Use Survey; Aurora, CO, October 1, 2004.
- Cornelissen, H.A.W. "Spray Dry Absorption Residue in Concrete Products." In *Studies in Environmental Sciences 48—Waste Materials in Construction*; Goumans, J.J.J.M., van der Sloot, H.A., Aalbers, Th.G., Eds.; Amsterdam: Elsevier, 1991; pp 499–506.
- 73. Jeppesen, K.G. "The Effect on Cement Mortar and Concrete by Admixture of Spray Drying Absorption Products." In *Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal VI*, Boston, MA, November 29–December 1, 1989. Materials Research Society Symposium Proceedings, Volume 178, Day, R.L., Glasser, F.B., Eds.; Materials Research Society: Pittsburgh, PA, 1990; pp 267–278.
- 74. Adam, D., and F. Kopf. "Sophisticated Roller Compaction Technologies and Roller-Integrated Compaction Control." In Compaction of Soils, Granulates and Powders: International Workshop on Compaction of Soils, Granulates and Powders, Innsbruck, 28–29 February 2000; Kolymbas, D.; Fellin, W., Eds.; Taylor & Francis Group, 2000.
- 75. Butalia, T.S., W.E. Wolfe, J.W. Lee. "Evaluation of a Dry FGD Material as a Flowable Fill." *Fuel* 80, (2001): 845–850.
- 76. Sahu, S., S.A. Brown, and R.J. Lee. "Thaumasite Formation in Stabilized Coal Combustion By-Products." *Cement & Concrete Composites* 24 (2002): 385–391.
- 77. Weeter, D.W. "Hazardous Waste Fixation Using Dry Flue Gas Desulfurization Waste." *Resources and Conservation* 9 (1982): 143–148.
- 78. Woodhead, P.M.J., J.H. Parker, and Duedall. "Environmental Compatibility and Engineering for Utilization of FGD Waste in Artificial Fishing Reef Construction." In *Proceedings of EPA Symposium on Flue Gas Desulfurization*, Houston, TX, October 1982.
- 79. Niro Atomizer, Inc. Shaped Cementitious Products. International Patent WO 82/00819, March 18, 1982.
- 80. Buschmann, J.C., E.L. Rasmussen, W.C. Webster, and P.L. Veltman, P.L. Shaped Cementitious Products. U.S. Patent 4,377,414, March 22, 1983.

- Bloem, P.J.C., and B.J.G. Sciarone. "Application of Pulverized Fly-Ash and Spray-Dry Absorption Products in Sand/Lime-Brick Production." *Kema Scientific & Technical Reports* 7 (1989): 35-45.
- Manz, O.E. "Utilization of By-Products from Western Coal Combustion in the Manufacture of Mineral Wool and Other Ceramic Materials." *Cement and Concrete Research* 14 (1984): 513–520.
- Stehouwer, R.C., P. Sutton, and W.A. Dick. "Minespoil Amendment with Dry Flue Gas Desulfurization By-Products: Plant Growth." *Journal of Environmental Quality* 24 (1995): 861–869.
- 84. Voss, L.B., R.L. Moberly, and M.L. Mings. "Stabilization of a Former Limestone Mine Using Dry Scrubber Ash." In *Proceedings: 15th International American Coal Ash Association Symposium on Management & Use of Coal Combustion Products (CCPs)*, St. Petersburg, FL, January 27–30, 2003.
- 85. U.S. Department of Energy. *Commercial Demonstration of the Manufactured Aggregate Processing Technology Utilizing Spray Dryer Ash*; Project Fact Sheet; U.S. Department of Energy; Washington, DC: U.S. Government Printing Office, 2006.
- 86. Wu, M.M., and G.E. Wasson. Method for Making Manufactured Aggregates from Coal Combustion By-Products. U.S. Patent 6,054,074. April 25, 2000.
- U.S. Environmental Protection Agency. *Sherburne EnviRock and EcoBlend*; C2P2 Case Study 06; U.S. Environmental Protection Agency; Washington, DC: U.S. Government Printing Office, 2003. <u>www.epa.gov/epaoswer/osw/conserve/c2p2/cases/sherburne.pdf</u> (accessed July 2006).
- 88. Aarding Lightweight Granulates B.V. *Aardelite Technology*. <u>www.aardinglg.com/aardelite-intro.html</u> (accessed July 2006).
- 89. van den Bos, René. Aarding Lightweight Granulates BV, private communication, 2006.
- Hassett, D.J., E.J. Zacher, and L.V. Heebink. "Determination of Expansion Potential of Coal Combustion By-Products." In *Proceedings of the World Coal Ash Conference*; Lexington, KY, April 11–15, 2005.

## **A** BULK CHEMICAL COMPOSITION – REPORTED AS OXIDES – OF SDA MATERIAL REPORTED IN LITERATURE REVIEWED

Bulk Chemical Composition – Reported as Oxides – of SDA Material Reported in Literature Reviewed

Source	[2]	[14]	[30]	[31]	[33]	[34]	[35]	[40]	[44]	[49]	[50]	[52]
No. of Samples	3	2 – 5	7	Unknown	2	Unknown	Up To 7 Of 24 References For Each	Unknown	1	Unknown	1	1
Units	wt%, Dry Basis	wt%, Dry Basis	wt%	%	wt%, Dry Basis	%	%	%	wt%	wt%	wt%	wt%, Dry Basis
SiO <sub>2</sub>	38.78 – 46.26	22.05 - 33.10	16 – 26	21.1 – 32.4	24.05 - 30.22	16 – 32	6 – 68	21.1	26.52	10 - 40	32.0	21.5
$Al_2O_3$	17.51 – 20.57	9.84 – 18.26	6.3 – 13	8.5 – 23	11.52 – 15.89	6 – 23	4 – 44	8.5	8.26	6 – 15	15.3	10.7
Fe <sub>2</sub> O <sub>3</sub>	2.83 - 3.63	2.55 – 5.82	1.6 – 7.7	4.2 - 6.8	2.21 – 3.79	2 – 8	1 – 44	6.8	4.91	1.5 – 5	3.8	6.4
CaO	13.12 – 18.34	21.59 – 29.27	18 – 31	19.7 – 32.2	25.66 - 34.13	18 – 32	0.2 – 52	18.1	27.16	20 – 28	24.1	28.4
SO3	3.35 – 10.07	5.96 – 20.05	_	_	7.92 – 11.98	6 – 22	0 – 32	3.4	16.48	1 – 10	13.0	24.3
MgO	1.34 – 1.47	2.184.33	0.65 – 4.6	5.8 - 6.0	0.89 - 3.90	0.6 – 6	0.1 – 14	5.8	4.62	0.5 – 1.5	2.9	0.73
Na₂O	1.02 – 1.39	0.49 – 1.52	0.9 - 46	2.7 – 4.7	0.13 – –1.82	0.9 – 5	0.2 – 28	4.7	2.60	0.1 – 0.4	1.67	0.25
K <sub>2</sub> O	0.83 – 0.97	0.36 - 0.50	0.2 - 0.84	0.37 – 0.5	0.43 – 1.10	0.2 - 0.8	0.1 – 6.37	0.5	0.87	0.5 – 1.5	0.52	0.81
P <sub>2</sub> O <sub>5</sub>	0.68 – 1.18	0.15 – 1.10	_	0.4	0.03 – 1.01	_	0.2 – 1.2	0.4	0.09	_	0.43	0.27
TiO <sub>2</sub>	0.54 – 0.70	0.41 – 1.16	0.27 – 0.92	_	0.57 – –1.19	_	0.5 – 1.0	0.5	0.41	0.2 - 0.8	0.67	0.45
BaO	_	_	_	_	_		_	_	0.85		0.39	
MnO <sub>2</sub>	0.03ª	0.00 - 0.12	_	_	_	_	_	_	0.09	_	0.10	_
SrO	0.11 – 0.19	_	_	_	_	_	_	_	0.46	_	0.44	_
Moisture	_	_	_	1 – 5	1.22 – 1.71	_	<0.1 – 13.2	1.3	1.10	_	0.55	0.61
LOI or C	_	0.19 – 6.90	_	0.8	_	_	0.32 – 20.5	_	1.64	_	1.41	_
Unaccounted	_	_	_	_	_	_	_	1.7		_		6.2
CaSO₃	_	_	_	_	11.89 – 17.96 <sup>⊳</sup>	_	_	14.6	_	_	_	_

# Table A-1 Bulk Chemical Composition of SDA Materials Containing Fly Ash Reported in Literature Reviewed

Table A-1 (continued)
Bulk Chemical Composition of SDA Materials Containing Fly Ash Reported in Literature Reviewed

Source	[2]	[14]	[30]	[31]	[33]	[34]	[35]	[40]	[44]	[49]	[50]	[52]
No. of Samples	3	2 – 5	7	Unknown	2	Unknown	Up To 7 Of 24 References For Each	Unknown	1	Unknown	1	1
Units	wt%, Dry Basis	wt%, Dry Basis	wt%	%	wt%, Dry Basis	%	%	%	wt%	wt%	wt%	wt%, Dry Basis
$CaSO_{_3} \cdot \frac{1}{2} H_{_2}0$	_	_	_	_	_	—	13 – 59	_	_	—		_
CaSO₄	—	—	—	—	—	—	6 - 43	8.9	—	_	_	—
CaCO <sub>3</sub>	—	—	—	—	—	—	2.1	2.1	—	—	_	—
Ca(OH) <sub>2</sub>	—	—	—	—	8.5 – 25.0°	—	4 – 21		—	—	_	—
Free Lime	—	—	—	—	—	—	_	1.6	_	—	_	—
Ca as Available CaO	—	_	_	_	_	_	0 - 5.4	_	—	_	—	_
SO <sub>4</sub>	—	_	12 – 22	_	_	—	_	_	_	_	_	_
SO2	—	_	—	—	_	—	0.1 – 20.5	_	_	5 – 25	_	_
	—	1.77 – 7.54	—	—	—	—	<0.1 – 15 <sup>d</sup>	—	_	—	_	_
Hydroxide	_	_	0.45 – 8.2	_	_	0.5 – 10	<0.1 – 9.5	_	_	_		_
CI	—	—	—	—	—	—	_	—	_	0.5 – 4	_	—

<sup>a</sup> Mn<sub>3</sub>O<sub>4</sub>
 <sup>b</sup> Based on total sulfur content in ash
 <sup>c</sup> Based on thermogravimetric analysis (TGA) or lime index measurement
 <sup>d</sup> Carbonate, as CO<sub>2</sub>

# Table A-2Bulk Chemical Composition of SDA Materials with Precollection of Fly Ash Reported inLiterature Reviewed

Source	[41]	[45]	[49]		
No. of Samples	<b>3</b> ª	4	Unknown		
Units	wt%, Dry Basis	wt%	wt%		
SiO <sub>2</sub>	7.9 – 10.6	1.4 – 11.1	<2.5		
Al <sub>2</sub> O <sub>3</sub>	4.1 – 4.7	0.8 - 5.4	<1.5		
Fe <sub>2</sub> O <sub>3</sub>	1.9 – 4.4	0.4 – 1.8	<0.7		
CaO	33.6 - 37.8	32.9 – 46.9	35–60		
SO <sub>3</sub>	17.4 – 30.0	—	2–17		
MgO	1.0 – 1.9	0.4 – 1.7	<0.8		
Na₂O	0.2 - 0.3	—	<0.1		
K₂O	0.3 – 0.6	_	<0.2		
TiO <sub>2</sub>	_	0.0 - 0.2	<0.1		
LOI or C	_	1.3 – 2.1	—		
Na <sub>2</sub> O/K <sub>2</sub> O	_	0.2 – 0.8	—		
$CaSO_{_3} \cdot \frac{1}{2} H_{_2}0$	_	50.0 - 62.0	—		
$CaSO_4 \cdot 2 H_2O$	_	4.5 – 10.0	—		
CaCO <sub>3</sub>	_	0.5 – 12.5	—		
CaCl <sub>2</sub>	_	0.6 – 7.2	—		
Ca(OH) <sub>2</sub>	_	2.4 – 18.9	—		
Free Lime	<0.5 - 4.0	—	—		
SO <sub>4</sub>	7.0 – 24.6	—	—		
SO <sub>2</sub>	_	_	9 – 40		
Total Sulfur	9.3 – 15.7	—	—		
	10.6 – 20.1	—	—		
C (org.)	0.1 – 0.2	—	_		
SO <sub>3</sub> <sup>-2</sup>	_	29.7 – 38.8	—		

#### Table A-2 (continued) Bulk Chemical Composition of SDA Materials with Precollection of Fly Ash Reported in Literature Reviewed

Source	[41]	[45]	[49]
No. of Samples	3ª	4	Unknown
Units	wt%, Dry Basis	wt%	wt%
SO <sub>4</sub> <sup>-2</sup>	—	2.5 – 6.9	_
CI	0.93 – 3.0	_	0.5 – 6
Cl⁻	_	0.4 - 4.6	
CO <sub>3</sub> <sup>-2</sup>	_	0.3 – 7.5	_

<sup>a</sup> May contain up to 20% fly ash.

# **B** TOTAL ELEMENTAL COMPOSITION OF SDA MATERIAL REPORTED IN LITERATURE REVIEWED

Table B-1 Total Elemental Composition of SDA Materials Containing Fly Ash Reported in Literature Reviewed

Source	[12, 13]	[17]	[30]	[30]	[31]	[35]	[37]	[44]	[46]	[47]	[49]	[50]	[53]	[54]	[55]	[56]
No. of Samples	8	1ª	8	8 (by AA)	Unknown	Unknown	13	1	1	1	Frequent Conc.°	1	1	13	1 – 19	1
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Aluminum (Al)	33,300–66,700	—	33,300–66,700	_	18,000–110,000	18,000–230,000	10,000–86,000	—	92,100		_	—	24,000	10,000-86,000	_	_
Antimony (Sb)	5.6 <sup>b</sup> –29	_	5.6 <sup>b</sup> –29	_	7.5–8	0.8–20	_	_	_		_			_	3.81–6.19	3.8
Arsenic (As)	3.6–48	0.4–380	<12–22 <sup>b</sup>	3.6–48	14.2–47	2.3–1200	6.9–165	28.7	4	68.9	_			6.9–165.5	13.9–82.0	13.9
Barium (Ba)	190–3090	_	190–6060	_	100–2000	20–12,000		0.76	3200		_			100–2400	139	139
Beryllium (Be)	1.4–3.1	_	0.8–3.1	_	4–63	0.94–63	0.7–9.6	_	3		_			0.7–9.6	2.19–2.24	2.2
Boron (B)	<10–230	_	<10–230	_	500	10–1300	292–948	1460	650	42.1		1352		292–948	982-1329	1329
Bromide (Br)	_	_	_	_	0.3–21	0.3–21	_	—	_		_		_	—	_	
Cadmium (Cd)	0.2 <sup>b</sup> -0.63	0.1–5	<0.4–5.8	<0.2–0.63	0.5–70	0.01–70	1.1–40.7	0.88	<4		0.1			1.1–40.7	0.55–1.54	0.55
Calcium (Ca)	14,300–223,000	_	126,200–223,000	_	_	7100–360,000	178,000–401,000	_	159,400		_		245,000	178,000– 401,000		_
Cesium (Cs)		—	_	—		1–22	_	_	_	_	_	—	—	—	_	_
Chloride (Cl)		—		_		<0.1–10,200	_	—	_		_	—	_	—	_	_
Chromium (Cr)	36–210	—	36–210	—	27–130	3.6–1000	11.4–56.3	14	62 [Cr(VI): <6]	_	3	—	_	11.4–56.3	25.3–42.8	35
Cobalt (Co)	9.9–26	<0.5–62	9.9–26	_	4.8–80	4.8–172	8.0–20.8	_	<20			—	_	8.0–20.8	13.4	13.4
Copper (Cu)	20–160	—	20–160	—	8.1–170	7.1–655	13.3–73.2	30	61	111	3	—	_	13.3–139.0	71.8	
Fluoride (F)	_	_		_	0.4–1000	0.4–1000	_	_	_		_	_		—	_	_
lodine (I)		_		_	_	0.1–0.6	_	_	_		_			—		
Iron (Fe)	10,900–53,700	—	10,900–53,700	_	10,000–367,000	6300–367,000	19,000–51,000	—	29,300		_	—	36,000	15,000–51,000	24,825	24,825
Lead (Pb)	<0.3–19	4–550	<16–44 <sup>b</sup>	<0.3–14	4.4–150	3.1–800	6.5–139	16.3	<20		5	_		6.5–139.0	18.6–59.57	21.1
Lithium (Li)	18–42	_	18–42	_	_	48–530	15.1–90.5	_	110		_			15.1–90.5		
Magnesium (Mg)	3880–27,700	_	3880–27,700	_	_	3000–22,000	3800–151,000	_	17,900		_	_	11,000	3800–151,300	_	_
Manganese (Mn)	55–680	—	55–680	_	45–630	24.5–1432	43–501	—	680	200	_	_		43–501	558	558
Mercury (Hg)	<0.05-0.39	<0.1–10	_	<0.05-0.39	BDL-0.5	<0.005–2.5	—	0.631	<0.02	_	<0.1	—	_	—	<0.001–2.553	0.015
Molybdenum (Mo)	2.7–514	_	2.7–514	_	0.5–33	0.5–110	<0.02–50.2	—	<20	32.8		—	_	<0.018–50.2	13.2	13.2
Nickel (Ni)	17–110	1.4–125	17–110	_	13–460	1.8–460	12.4–58.9	13	<20	64.7	2	_	_	12.4–58.9	12.9–30.3	27

# Table B-1 (continued) Total Elemental Composition of SDA Materials Containing Fly Ash Reported in Literature Reviewed

Source	[12, 13]	[17]	[30]	[30]	[31]	[35]	[37]	[44]	[46]	[47]	[49]	[50]	[53]	[54]	[55]	[56]
No. of Samples	8	<b>1</b> ª	8	8 (by AA)	Unknown	Unknown	13	1	1	1	Frequent Conc.°	1	1	13	1 – 19	1
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Phosphorus (P)	—	_	—	—	—	—	21–1752	—	2200	—	—	—	_	21–1752	_	—
Potassium (K)	1760–7020		1760–7020	_	_	1700–9300	1600–5000		4700	—	—	_	_	1600–5000	_	—
Rubidium (Rb)	—	_	—	_	_	48–530	—			—	—	_	_		_	—
Selenium (Se)	<0.4−7.3⁵	3–34	71 <sup>b</sup> –283	<0.4–7.3 <sup>b</sup>	4.7–20	0.6–760	4.9–23.0	5.4	<4	29.2	_	7.6		4.9–23.0	9.15–18.2	18.2
Silicon (Si)	72,800–120,000	_	72,800–120,000	_	_	70,000–99,000	22,000–137,000	_	157,200	_	_	_	_	22,000– 137,000	_	_
Silver (Ag)	1.6 <sup>b</sup> -5.8		1.6 <sup>b</sup> -5.8	_	0.2–0.5	0.04–8	—	0.20	<4			_		<0.024	1.18–1.97	1.18
Sodium (Na)	6540–34,000		6540–34,000	_		710–240,000	_		13,500	_	_	—		_	_	
Strontium (Sr)	184–3040	_	184–3040	_	84–2500	30–13,000	153–1370		4300	_	_	_	_	153–3166	_	_
Sulfur (S)	_	_	_	_	_	_	42,000–163,000	_	_	_	_	_	3000	42,000- 170,000 <sup>d</sup>	_	_
Thallium (TI)	<18	<10	<18	—	20–30	0.1–42	—	—	<1	_	_	—	_		0.47	0.47
Tin (Sn)	<19–349	_	<24–349	—	30–36	0.01–962	—	—		_	—	—	_	_	_	—
Titanium (Ti)	1610–5360	_	1610–5360	—		1050–6700	—	—	3700	_	_	—	_	_	_	_
Uranium (U)	<5–140	_	<25–140	_		0.8–30	—		_	_	_	_	_	_	_	_
Vanadium (V)	72–180	_	72–180	_	0.4–610	0.4–950	22.5-83.9	49.7	86	_		—		22.5-83.9	56	56
Zinc (Zn)	22–110		<6–79	—	12–330	12–9000	52–266	25	70	—	15	—		52–237	48.9–50	50

<sup>a</sup>High fly ash. <sup>b</sup>Indicates less than 5 times the detection limit. <sup>c</sup>Multiplying or dividing by 2 can give the range. <sup>d</sup>Combination of LECO and ICP concentrations.

#### Total Elemental Composition SDA Material Reported in Literature Reviewed

## Table B-2 Total Elemental Composition of SDA Materials with Precollection of Fly Ash Reported in Literature Reviewed

Source	[41]	[49]
No. of Samples	<b>3</b> ª	Frequent Conc. <sup>▶</sup>
Units	mg/kg	mg/kg
Arsenic (As)	4.8–11	—
Barium (Ba)	270–4000	_
Boron (B)	100–150	—
Cadmium (Cd)	0.9–6.9	1
Chromium (Cr)	34–50	60
Copper (Cu)	43–47	80
Lead (Pb)	28–110	100
Manganese (Mn)	170–420	_
Mercury (Hg)	<0.3	<0.1
Molybdenum (Mo)	2.7–5.4	—
Nickel (Ni)	32–36	80
Selenium (Se)	3.9–6.5	_
Vanadium (V)	60–70	_
Zinc (Zn)	94–380	120

<sup>a</sup> May contain up to 20% fly ash.
 <sup>b</sup> Multiplying or dividing by 2 can give the range.

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