

# Alternative By-Products from Flue Gas Desulfurization Systems

Utilization of Clean Coal By-Products from SO2 Control Processes

Technology Review

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Utilization of Clean Coal By-Products from SO<sub>2</sub> Control Process

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## **REPORT SUMMARY**

This white paper discusses the potential for using clean coal technology (CCT) by-products and describes evaluation methods used to determine their suitability for various applications. The assessment—an update of a 1997 EPRI study—is separated by wet flue gas desulfurization (FGD) and dry FGD by-products.

#### Background

FGD by-products are not widely reused, even though there are a large number of sulfur dioxide (SO<sub>2</sub>) control systems in the United States. Yet, the general trend in SO<sub>2</sub> control continues to be the use of non-regenerable systems, which produce large volumes of by-products. The cost and environmental impact of disposing of these by-products provides inducement for utilization rather than disposal. Disposal costs are likely to increase in the United States and the world in general, as they have in the countries of the Organization for Economic Cooperation and Development (OECD). This increase is largely due to stricter environmental regulations and, in some locations, limited space for suitable landfill. These factors are likely to make the economics of utilization more favorable.

#### Objective

To describe potential uses of CCT by-products and methods to judge their applicability for different applications.

## Approach

The project team researched opportunities for using CCT by-products from wet FGD, spray dryer (SD), sodium sorbent injection (SSI), calcium sorbent injection (CSI), furnace sorbent injection (FSI), and atmospheric fluidized-bed combustion (AFBC). The team's work was an update of a study originally prepared for EPRI in 1997, the results of which were published in a technical paper included in the proceedings of the 1999 American Coal Ash Association (ACAA) Symposium.

## Results

This technology assessment white paper discusses the utilization potential and evaluation methods for CCT by-products. The discussions are separated by wet FGD and dry FGD by-products. The white paper will serve as an update to previous EPRI reports published under the Advanced SO<sub>2</sub> Control By-Products Project (RP2708), which provided detailed assessments of the utilization potential of conventional SO<sub>2</sub> and advanced control processes available until 1991.

The paper presents potential uses of FGD by-products from wet FGD, spray dryers (SD), and furnace sorbent injection (FSI). Also discussed are combined ash/FGD by-products from both atmospheric and pressurized fluidized-bed combustion (AFBC and PFBC). Given the maturity of

fly ash utilization technology in the United States, the only fly ash topic discussed in this paper is for those applications that combine fly ash and CCT by-products.

#### **EPRI** Perspective

The general trend in  $SO_2$  control continues to be toward non-regenerable systems, which produce large volume waste products. The cost of disposing waste provides inducement for utilization rather than disposal. As disposal costs increase due to a variety of reasons, including limited land availability and stricter environmental regulations, the economics of utilization become more favorable. Finding industrial applications for coal combustion by-products (CCBs) as raw materials can provide a "hook" for co-locating industries and job creation opportunities.

#### Keywords

Clean coal byproducts FGD byproducts Byproduct reuse Reuse applications

## ABSTRACT

This technology assessment white paper discusses opportunities for using clean coal technology (CCT) by-products from wet flue gas desulfurization (FGD), spray dryer (SD), sodium sorbent injection (SSI), calcium sorbent injection (CSI), furnace sorbent injection (FSI), and atmospheric fluidized-bed combustion (AFBC). It is an update of a 1997 EPRI study. This white paper discusses CCT by-products utilization potential and evaluation methods for determining their suitability for various applications. The assessment is separated into wet FGD and dry FGD by-products.

The United States now reuses a third of its coal ash in productive uses, according to the most recent survey published by the American Coal Ash Association. The utilization potential is generally not limited by technological barriers or lack of understanding use options. Rather, coal ash is not used in greater volume due to the low cost of disposal, the wide availability of natural materials, and transportation costs from the point of production to the point of use.

In contrast, FGD by-products are not widely reused, even though there are a large number of sulfur dioxide  $(SO_2)$  control systems in the United States. Yet, the general trend in SO<sub>2</sub> control continues to be use of non-regenerable systems, which produce large volumes of by-products. The cost and environmental impact to dispose of these by-products provides inducement for utilization rather than disposal. Disposal costs are likely to increase in the United States and the world in general, as they have in the countries of the Organization for Economic Cooperation and Development (OECD). This increase is largely due to stricter environmental regulations and, in some locations, limited space for suitable landfill. These changes are likely to make economics of utilization more favorable.

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# **1** INTRODUCTION

This technology assessment white paper provides the information relative to opportunities for utilization of clean coal technology (CCT) by-products from wet flue gas desulfurization (wet FGD), spray dryer (SD), sodium sorbent injection (SSI), calcium sorbent injection (CSI), furnace sorbent injection (FSI), and atmospheric fluidized bed combustion (AFBC). It is an update of a study originally prepared for EPRI in 1997 by GAI Consultants, the results of which were published in a technical paper included in the proceedings of the 1999 ACAA Symposium [1]. The general trend in sulfur dioxide (SO<sub>2</sub>) control continues to be toward non-regenerable systems, which produce large volume waste products. The cost of disposing waste provides inducement for utilization rather than disposal. As disposal costs increase due to a variety of reasons, including limited land availability and stricter environmental regulations, the economics of utilization become more favorable.

This white paper discusses the utilization potential and evaluation methods for CCT by-products. The discussions are separated by wet FGD and dry FGD by-products. The white paper will serve as an update to the previous EPRI reports published under the Advanced SO<sub>2</sub> Control By-Products Project (RP2708), which provided detailed assessments of the utilization potential of the conventional SO<sub>2</sub> and advanced control processes available up until 1991. An annotated listing of the reports prepared under that project is provided in the bibliography [1-18].

The United States now reuses a third of its coal ash in productive uses, according to the most recent survey published by the American Coal Ash Association. The utilization potential is generally not limited by technological barriers or lack of understanding of the use options. Rather, coal ash is not used in greater volume due to the low cost of disposal, the wide availability of natural materials, and transportation costs from the point of production to the point of use.

In contrast, flue gas desulfurization (FGD) by-products are not widely reused, notwithstanding the large number of sulfur dioxide (SO<sub>2</sub>) control systems in the US. Yet the general trend in SO<sub>2</sub> control continues to be the use of non-regenerable systems, which produce large volumes of by-products. The cost and environmental impact of disposing of these by-products provides inducement for utilization rather than disposal. Disposal costs are likely to increase in the U.S. and the world in general, as they have in the OECD countries, largely due to stricter environmental regulations and, in some locations, limited space for suitable landfill. These changes are likely to make the economics of utilization more favorable. The lack of electric generation capacity in many parts of the U.S. is likely to increase the number of coal-fired generation in the next several years. Plants which do not require large land areas for disposal of Coal Combustion By-products (CCBs) are going find it easier to obtain the necessary regulatory

#### Introduction

approvals and citizen acceptance. Finding industrial applications for the CCBs as raw materials can provide a "hook" for the co-location of industries and job creation opportunities.

Given the maturity of fly ash utilization technology in US, the only fly ash topic discussed in this paper is for those applications that combine fly ash and the CCT by-products. The balance of the discussion presents potential uses of FGD by-products from wet flue gas desulfurization (wet FGD), spray dryers (SD), and furnace sorbent injection (FSI). Also discussed are the combined ash/FGD by-products from both atmospheric and pressurized fluidized-bed combustion (AFBC and PFBC).

# **2** WET FGD BY-PRODUCTS

Wet FGD sludge is the liquid/solids bleed stream from the scrubber, which carries away the reaction products and contains water, dissolved solids, and suspended solids (predominantly calcium sulfite, calcium sulfate, and sometimes fly ash). These sludges are the waste products from lime, limestone, alkaline fly ash–enhanced, magnesium-enhanced lime, and dual-alkali wet scrubbers. The utilization potential of wet FGD sludge is related to its quality and characteristics. Because of this, the type and degree of processing largely determine the uses of sludge that merit consideration. Producing a useful by-product from FGD sludge often requires additional processing, such as forced oxidation (usually within the SO<sub>2</sub> absorber reactor in the limestone forced oxidation systems) or fixation/stabilization.

Oxidizing FGD sludge allows it to compete for the current uses of naturally occurring gypsum. The following markets have been identified as potential primary applications for FGD by-product gypsum: (1) wallboard production, (2) cement production, and (3) agricultural use.

Fixing or stabilizing FGD sludge can enhance its physical properties for potential structural uses. Demonstrated uses include (1) structural fill, (2) road construction, (3) soil stabilization, (4) liner cap material (5) artificial reefs, and (6) mine reclamation.

## 2.1 Utilization of Oxidized FGD Sludge

Calcium sulfate (gypsum) is a principal by-product generated in lime- or limestone-based FGD scrubbing systems. Often, both calcium sulfate and calcium sulfite are produced, although it is possible to employ forced oxidation either in the scrubber or as a separate step to convert the sulfite to sulfate. FGD sludges high in calcium sulfate can be used in lieu of natural gypsum for wallboard, plasters, cement additives, and other products.

Production of gypsum worldwide has been estimated at over 100,000,000 metric tons for the past two years. In some years the increases have been spectacular. For example, sales of by-product gypsum increased by 26% in 1996/97 worldwide as consumption has dramatically increased in North America, Western Europe and Japan. US sales have increase from 630,000 metric tons in 1992 to 2,240,000 metric tons in 1996. The majority of this increase has been due to the manufacture of plaster and plasterboard using FGD gypsum. FGD gypsum is becoming increasingly used in regions where it is available, due to its low cost and high purity. The increasing availability of by-product gypsum may depress output of natural gypsum in those regions, but production of natural gypsum in less industrialised countries is likely to increase steadily in the near future. The market for this material is closely tied to the home building construction boom that has occurred during the past half-decade.

#### Wallboard Production

In the United States, the largest consumer of gypsum is the wallboard industry (~75%), followed by the portland cement industry (~15%), agricultural applications (~6%) and plaster manufacture (~4%). In Europe and Japan the different methods of construction, and consequent differences in the products manufactured, give a slightly different breakdown of gypsum uses. Plasters consume a much higher proportion of gypsum than does wallboard in Europe, while Japan has developed a reinforced wallboard design suitable for its thinner walls. On a worldwide basis, the proportion of uses are about 80% for walls (wallboard or plaster), 15% for cement, and 5% for agricultural uses.

In substituting FGD gypsum for naturally occurring gypsum in wallboard production, the following product variables are of concern: free water, fly ash, soluble salt contents (particularly chlorides), and crystal size and shape. The free water content of natural gypsum is approximately 3%, while that of FGD gypsum is typically much greater, at times exceeding 10%, depending on the efficiency of the dewatering equipment used. This excessive moisture can be a problem in handling FGD gypsum in the calcining step of wallboard production, since free water must be driven off. In addition, a high moisture content may indicate poorly formed crystals.

In wallboard manufacturing, the unit operations can be sensitive to changes in the raw materials. Therefore, direct substitution of synthetic gypsum for natural gypsum is not always possible. The characteristics of the feed material and its subsequent impact on the materials handling and process chemistry must be fully understood to facilitate by-product substitution. On the other hand, one advantage of FGD gypsum is its typical high purity (CaSO<sub>4</sub>•H<sub>2</sub>O content) which, when added as a portion of the board line feed, may improve some board properties with only minor changes to the operating parameters. FGD gypsum has been used successfully in the manufacture of wallboard in the United States and Europe, and its use is continuing to grow.

Fly ash is present in FGD gypsum in varying amounts, depending on the type of particulate removal system. A fly ash content of more than 2% will affect the color of wallboard. In particular, iron, manganese, and unburned carbon in the fly ash are responsible for contributing color to the wallboard. Discoloration due to fly ash may render the wallboard unattractive to potential consumers.

FGD gypsum may contain varying amounts of soluble salts depending on the coal type and process conditions. The presence of soluble salts in by-product gypsum reduces the required calcination temperature. If the concentration is excessive, the gypsum may begin to recalcine during the wallboard drying process, thus disrupting the paper-gypsum bond. Excessive salt concentrations can also corrode nails used to install the wallboard and can cause efflorescence, the deposition of a white powdery residue on the wallboard surface during humid weather.

Making quality wallboard requires large gypsum crystals and a blocky crystal shape. Smaller crystals make it necessary to use more water when the calcined gypsum is rewetted in the production process. This may result in increased drying costs and decreased board strength.

## **Other Board Processes**

Attempts are continuously made to improve or modify gypsum board. In these new board products, the properties provided by the paper liner are replaced by other materials. These materials are either less costly or provide improvements in the board quality and possibly enhance the variety of applications for the gypsum board product. Successful modifications to the structure of the board from a commercial point of view consist of either distributing paper fiber throughout the gypsum matrix rather than applying paper to the surface, or replacing the paper surface liner with a fiberglass sheet or mat. These alternative gypsum board process include: (1) fiber-reinforced board, where fibers provide improved tensile, flexural, and impact strength to board products; (2) filler-reinforced board, where modifications of gypsum wallboard with inorganic fillers might be particularly compatible with the utilization of a combined gypsum and fly ash FGD scrubber waste; and (3) polymer-modified board, which was developed to improve moisture resistance, freeze-thaw durability, strength, and abrasion resistance.

## Plasters

FGD gypsum has good potential for plaster manufacture because of its high purity. However, the plaster market is relatively small, accounting for only about 1 million tonnes annually in the OECD countries. In the United States, there are two main types of plasters, designated as alphaand beta-plaster. Alpha-plaster is a higher-value material (up to \$350 per tonne, f.o.b. plant) and is produced under different and more costly conditions than beta-plaster. Alpha-plaster is used for specialty applications including industrial molding, dental and medical plasters, and possibly mining mortars. Due to their higher cost, alpha-plaster is a lower-value material (ranging from \$16 to \$100 per tonne, f.o.b. plant in the U.S.) produced via more conventional "dry" calcination methods. In addition to wallboard manufacture, beta-plaster is used in wallplasters and as a fireproof coating.

## Filler Material

Natural gypsum has not seen significant application as a filler material in the world, although several grades of calcium sulfate fillers are commercially available in North America. However, certain qualities of FGD gypsum (i.e., high purity, fineness, whiteness) may make it suitable for specific filler applications. Therefore, Section 3.8.3.3 includes a discussion of mineral fillers, describing the properties of fillers required for different applications. The use of gypsum as a filler in some applications is also reviewed.

## **Cement Production**

The use of by-product gypsum as a set retarder for portland cement appears to be quite viable. In the manufacture and use of portland cement, gypsum is an important and essential component that serves two main functions. First, during grinding of the clinker, the finely ground clinker particles have a tendency to adhere to the grinding media and walls of the mill. Gypsum is used as a grinding aid and its action has been theorized to be based on the release of water from the

gypsum during grinding. Reportedly, this allows for the conduction of electricity and a reduction in the buildup of static electricity on the cement particles. Gypsum, being a softer mineral, also contributes to the measured fineness of the final product.

Second and more important, gypsum serves as a set regulator for portland cement to prevent flash set during the early stages of mixing and placement. Flash set of cement is the irreversible, early stiffening of the cement paste which occurs as a result of the rapid reaction of tricalcium aluminate ( $3CaO \cdot Al_2O_3$ ) with water. The level of gypsum added to the cement clinker (i.e.,  $SO_3$  content) will directly influence the early setting behavior of the cement paste. Gypsum can also control the rate of early strength development and shrinkage during drying.

When natural gypsum is used in the manufacture of portland cement, the rock is crushed to pass 5-cm screening and then fed through chutes to a vibrating pan/conveyor. Handling of the finer-sized FGD gypsum may be an issue, as cement plants are designed for using gypsum as a coarsely crushed rock which is added directly to the clinker for grinding.

Cement plants offer the greatest utilization potential for FGD gypsum. A typical cement plant can use 80,000–100,000 metric tons of gypsum per year. Several cases are known where FGD gypsum has been used successfully in the manufacture of cement in the United States. This practice is becoming more common in the U.S. Boral Materials reports that it is selling about 40,000 tons per year of FGD gypsum into this market [28]. In the midwestern U.S. where Powder River Basin coal ash is prevalent, the use of gypsum for set retarding is more common also.

There are fewer problems in producing gypsum for cement than for wallboard use. Impurities are not as critical; gypsum with a higher fly ash content can be used and chloride content of up to 1% can be tolerated. The major differences between natural and FGD gypsum are particle size/shape and moisture content as related to materials handling. In some cases, it may be necessary to dry and/or agglomerate the gypsum in order to provide a material that is more compatible with existing equipment. Another difference is the absence of insoluble anhydrite (anhydrous calcium sulfate) which can occur in natural deposits of gypsum. If the cement plant is accustomed to using a gypsum/anhydrite blend to control the setting of cement, some developmental work may be required prior to substituting FGD gypsum for natural gypsum.

## 2.2 Agricultural Use of Gypsum

The use of natural gypsum in agriculture has a long history, and ground gypsum is commonly referred to as landplaster. By-product gypsum also has considerable potential for use in agriculture as a soil amendment, soil conditioner, fertilizer, or soil stabilizer. In agricultural applications, the gypsum is either in the form of the dihydrate or the anhydrite and is used for both chemical and physical conditioning of soils. Gypsum also provides a supplemental source of sulfur and calcium for specific crops, particularly peanuts, legumes, potatoes, and cotton. Additionally, gypsum can serve as a composting aid for use with stored manures prior to their application in the soil. Finally, gypsum is also used to some degree as an extender for animal feeds and as a carrier for nutrients, insecticides, and herbicides.

The use of FGD gypsum in agriculture is relatively straightforward. The specifications for this application relate mainly to toxic impurities, particularly limits on the heavy metals content. Market penetration depends mainly on transportation costs and the cost and availability of natural gypsum sources at the user locations. In some areas the price of agriculture gypsum exceeds that of gypsum used in the wallboard industry, so utilities should explore this option in the local markets that surround the power plants producing FGD gypsum.

As a soil conditioner, gypsum improves soil structure by loosening heavy, compacted soils and clays to increase permeability and thus improve aeration, drainage, and the penetration and retention of water in the soil. This can result in better growth and higher yields through improved germination and increased root growth. Also, surface-applied fertilizers can penetrate into the roots more readily.

Another widely used application is as a soil conditioner in the amendment of high-salt (sodium) and/or sodic (alkaline) soils. High salt content in soils can interfere with the water uptake of plants, and can also adversely affect soil permeability and thus penetration of water into the soil. The soils can become crusty, restricting seedling emergence and root extension. In this case, the calcium ions of the gypsum undergo anion exchange with the sodium ions, leaving the sodium ions free to be leached out. This lowers the pH and buffers soils against excessive alkalinity. In these applications, the gypsum is typically applied and intermixed as a finely ground powder (80–90% through 100 mesh) but in some cases, products are graded (i.e., multisized) such that solubilization occurs over an extended period to provide a "time-release" effect over the growing season.

Many agricultural-grade products are commercially available. Recently a U.S. firm, Domtar, introduced a solution-grade agricultural gypsum for use with its gypsum solution system. The gypsum is specially milled to allow for dissolution in irrigation water and application through common irrigation equipment. The gypsum used for this product is of high purity so as to prevent plugging of application equipment.

A further interesting application for gypsum in agriculture has been demonstrated by U.S. research showing that gypsum granules are a good substrate for carrying nutrients, insecticides, and herbicides. The use of granules has eliminated the difficulties associated with blending pesticides with the fine grades of gypsum. When the gypsum granules are impregnated with pesticides and nutrients, the result is a combined soil conditioner, fertilizer, and pesticide with more efficient bulk handling and distribution characteristics.

## 2.3 Miscellaneous uses of FGD Gypsum

## **Mining Mortars**

Cut and fill mining practice—in which depleted mines are backfilled with tailings and mortar is an important method for mining silver, lead, zinc, copper, tungsten, gold, and to a lesser extent, mercury, asbestos, and talc. This method is increasing in popularity due to three factors. First, it is environmentally acceptable, as all the tailings and other wastes stay in the mine.

Second, productivity is increased, as the yield from the vein is effectively 100%. Third, the method is safe, since only a portion of the mine is open at one time, thereby decreasing the chance of subsidence (i.e., gradual settling). As this practice becomes more popular, the need for cheap mortar materials will increase.

In Europe, alpha-plaster or portland cement mixed with pozzolanic materials such as fly ash is commonly used for mortar applications. However, in North America, the use of alpha-plaster, fly ash, or slags as binders for mining mortars has not been fully developed. While guidelines for these materials do not yet exist in the United States, leachability seems to be the most important criterion when considering their use in this application.

## Self-Leveling Flooring Material

To ensure proper application of final flooring materials (ceramic tiles, linoleum, and carpet), the smoothness and consistent level of the entire subfloor must be assured. Commonly, floor underlayment such as plywood sheets, with one side smooth-finished, is used to provide an adequate surface. However, plywood is expensive and provides little fire resistance. To reduce cost, particle resin board is sometimes used as a replacement for plywood. This product also has little fire resistance, and inhalation of the volatile organics used to fabricate the board may be harmful. Alternatively, slurries of calcium sulfate mortars using anhydrite or alpha-plaster can be applied over the subfloor to provide a level, smooth, hard, dimensionally stable, seam-free surface, in addition to providing substantial fire resistance.

## Fillers

Although calcium sulfate–based filler products are currently available in OECD countries, use of these fillers has not been fully exploited. As an example of the potential market, the mineral extender and filler consumption in North America alone is estimated to exceed 12 million tonnes, with a value of \$4 billion.

Extender and filler minerals fall into two classes, chemical or physical. Chemical fillers are used when their chemical nature and reactivity are important. Examples of these are lime, salt, soda ash, and phosphates. Physical extenders and fillers, such as talc and calcium carbonate (CaCO<sub>3</sub>), have found widespread application for two reasons. First, as extenders, they reduce the amount of the typically more costly host matrix material, thus improving the cost-effectiveness of the product. Second, as functional fillers, they can be used to enhance existing properties of the host matrix or to introduce new properties. Specific mineral properties can be used to improve casting characteristics and strength, reduce thermal expansion, and better control density, thermal conductivity, and electrical properties. Calcium sulfates are chiefly used as physical fillers and have found their largest markets in the structural fillers and extender/filler pigment categories.

These two categories for gypsum filler applications can be further segregated into the principal industries that consume the largest quantities of these minerals:

- Paper
- Paints and coatings

- Putties, caulks, sealants, and gypsum-based joint compounds
- Adhesives
- Rubbers and plastics
- Carpet backing

Traditionally, these industries have primarily used six minerals, namely, calcium carbonate, kaolin, barite, mica, silica, and talc. Gypsum-based extenders and fillers will be in direct competition with these minerals in terms of properties and price.

Although large-scale use of gypsum in any extender or filler application has not been realized to date, recent developments seem promising. Gypsum is a soft mineral with a relatively high whiteness. Its crystal shape and size are variable, and it is relatively resistant to acid and alkali materials, as compared to calcium carbonate. A high whiteness and refractive index are beneficial when color is an important criterion. Good resistance to acids and alkali is required for many applications.

Matching the physical properties of gypsum with those of other minerals is not the only consideration for the substitution of gypsum in a particular application. For example, a guaranteed supply with consistent quality is also imperative to gain user acceptability of gypsum as a mineral extender or filler, and synthetic gypsum provides this consistent quality. Although the market in OECD countries is beginning to recognize this value of synthetic gypsum, the cost and performance differences between synthetic and natural gypsum are not large enough to induce the users to change their buying habits quickly.

## Plastics

After the 1973–74 fuel shortage in OECD countries sparked the need for more economic utilization of expensive oil-based resins, the use of minerals in plastics increased dramatically. At that time, minerals were only used in the non-functional sense. However, extensive research has since been conducted realizing that minerals can impart useful properties to the final product. For example, minerals can serve as low-cost inert fillers, extenders, and reinforcement in plastics. The minerals commonly used in plastics, rubbers, and molding compounds are calcium carbonate, talc, silica, kaolin, wollastonite, aluminum trihydrate, and more recently gypsum. Fibrous calcium sulfate (both hemihydrate and insoluble anhydrite) has demonstrated suitability for use in urethanes and polyurea reaction injection molding, offering both improved surface appearance and dimensional stability.

Each form of calcium sulfate offers specific properties suitable to different end uses. The dihydrates serve as a flame-retarding filler in unsaturated room temperature cure polyesters, while insoluble anhydrite has demonstrated good compatibility in thermoplastic systems. It can improve impact resistance and stiffness, allowing redesign of parts to lower their costs.

In rigid PVCs, higher loading levels of insoluble anhydrite improve impact resistance and tensile strength, and increase throughput rates–without necessarily sacrificing other physical properties.

Insoluble anhydrite can also be used to replace barites in PVC plastisols, offering cost savings for many food contact applications.

Insoluble anhydrite has been used in thermosets for microwaveware because of its flow characteristics and resistance to food acids. Both its electrical properties and resistance to breakage from impacts rival those of materials used as industry standards.

## 2.4 Utilization of Fixed/Stabilized FGD Sludge

FGD sludge can be stabilized by adding dry fly ash, soil, or another dry additive to reduce the moisture content and improve handling characteristics without a chemical interaction between the sludge components and the additive. Fixation or chemical treatment is a type of stabilization that involves the addition of lime or other reactive material such as blast furnace slag, alkaline fly ash, or portland cement, which cause cementitious-type reactions with the sludge. These reactions bind the sludge particles together, thus increasing shear strength and reducing permeability. The structural stability and environmental characteristics of the waste product are thereby improved.

Treated FGD sludge produced as a dry product has valuable structural properties. Similar to soil but somewhat cementitious, fixed/stabilized sludge makes excellent fill. In general, it could be used for road fill, dikes, berms, general fill, and similar local construction uses. In addition, fixed/stabilized sludge has been demonstrated to be of beneficial use as a base for paving material (roads and parking lots), wearing surfaces in some cases, embankments, wastewater pond or landfill liner, blocks for artificial ocean reefs, and fill for mine reclamation.

Proper planning and design of the disposal area for fixed/stabilized sludge may allow for eventual residential, recreational, or light industrial development on top of the fill. The potential for utilizing such a fill for structural purposes is largely dependent upon structural integrity. Compressive strength should be at least 10 tonnes/m<sup>2</sup>, and permeability should be less than  $5 \times 10^{-5}$  cm/s. In addition to uses for light structural developments, fixed/stabilized sludge could be used in a variety of construction projects requiring stable fill material, such as roadways. In utilizing fixed/stabilized sludge as borrow material in construction, similar requirements for structural integrity would apply.

As is the case for some of the dry CCT by-products, land recovery, especially mine or quarry backfill, may be a promising use for fixed/stabilized FGD sludge in selected areas. As an added benefit in this application, depending on the type of coal burned and scrubber efficiency, the sludge may contain free lime, which can mitigate acid formation in depleted mines.

## Other Potential uses

Through research activities and small-scale applications, a number of other potential uses of sludge have been explored. These include:

Artificial reefs

Production of lightweight aggregate

Brick and concrete block

Mineralizer in metals extraction

Cement replacement at levels as high as 60% (compared to the current practice of 20%)

Producing brick from a mixture of FGD sludge, silica sand, and lime may be viable. Experiments have indicated that autoclaving such a mixture can result in a product of satisfactory quality. FGD sludge also can be used as a cementing agent or a partial cement replacement in producing concrete blocks that are lighter than conventional blocks. Such blocks would be used as low-cost, non-load-bearing construction materials (e.g., interior walls, decorative walls, patios, thermal insulating walls, and acoustic insulating walls).

## 2.5 Utilization of Fixed/Stabilized FGD Sludge with Fly Ash

During the 7<sup>th</sup> International Conference on Fly Ash Use in Concretes, held in Chennai, India, in July, 2001, a paper was presented by an Indian firm that has developed a high strength building material that contains both FGD gypsum and fly ash which had been formulated to make a high strength material. The material is called Fal-G. It derives its name from its components, namely Fly Ash (fa), Lime (l) and gypsum (G).

Although gypsum is not usually considered an additive in concrete, it has commonly been added to cement to improve early strength and as a set retarder. This is accomplished by the formation of calcium trisulphoaluminate hydrite (more commonly called ettringite) which gives early strength to the mixture. These so-called "good ettringites" are transitory minerals, and do not cause the expansive reactions often associated with the delayed ettringite formation (DEF) that typically occur after 60 days age in some concrete mixes. Strength acceleration by the addition of gypsum to ash-lime mixtures has had little research interest, but not much is discussed in previously published literature [41].

The pre-cast concrete market in the U.S. could be a potential market for a "Fal-G" type material. The added strength gain from the gypsum would be an appreciable asset. In some warm climates of the Southwest or Southeast US it would be possible to dispense with the heating cycle used in pre-cast materials, and utilize the Fal-G technique used in India. This approach would negate the need for heavy-duty presses, autoclaves, etc used in pre-casting, which would make the material cost effective and energy-conservative. The gypsum used in the production of the Fal-G material in India was the gypsum anhydrite by-product of the aluminum fluoride industry, which has a purity of 96%, and was ground to a Blaine fineness of 3,800 cm<sup>2</sup>/g. Bricks and blocks manufactured according to the Fal-G technology are rapidly replacing fired bricks used in masonry construction due to their cost advantage.

# **3** DRY BY-PRODUCTS FROM CLEAN COAL TECHNOLOGIES

The by-products generated from dry CCT processes (dry SO<sub>2</sub> controls and fluidized-bed combustion systems) have some chemical, physical, and engineering properties similar to conventional fly ash. Generally, the differences between the properties of CCT by-products and those of conventional fly ash and bottom ash result from the sorbent addition/injection for SO<sub>2</sub> removal. The exact composition of a by-product is determined by the type of sorbent or reagent, the injection process, and the coal source. But in general, the primary components include fly ash, unspent sorbent (lime, limestone, or dolomite), and reaction products (calcium sulfate/sulfite).\* The high percentage of fly ash in the by-products indicates the potential for pozzolanic activity. The unreacted lime or limestone contributes to the self-hardening characteristics of the by-products. Unlike Class F coal ash, SO<sub>2</sub> control by-products contain significant quantities of calcium or sodium oxide (CaO or Na<sub>2</sub>O) and calcium or sodium sulfate/sulfite (CaSO<sub>4</sub> and Ca SO<sub>3</sub> or Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>3</sub>). Like many sources of Class C fly ash, these compounds react exothermically with the addition of water. The by-products produced by the FSI, SD, SSI, or CSI technologies, in addition to the AFBC fly ash, are dry powders which are collected in an electrostatic precipitator or baghouse.

In view of the physical and chemical characteristics of the dry CCT by-products, it is believed that there are potential uses for these materials in highway construction, mining, soil amendment, etc. The dry CCT by-products are dry powders and have physical properties similar to those of conventional fly ash. Their chemical properties are somewhat different from conventional fly ash, however, due to the alkaline reagents. These differences will require some changes in utilization practices relative to fly ash alone. The most promising utilization options are listed here and discussed briefly below:

- Road base stabilization
- Soil stabilization
- Sludge stabilization
- Structural fill
- Grout

<sup>\*</sup> Sodium-based compounds would, of course, be a significant constituent of the by-products from processes using these materials as a sorbent. However, the relatively high cost of sodium compounds and the potential environmental issues associated with the by-product (its high solubility leads to leaching of sodium salts, which need to be treated to avoid contamination of surface or ground waters) have restrained the market penetration of this technology. Therefore, this section does not discuss by-products from sodium injection processes.

Dry By-Products from Clean Coal Technologies

- Asphalt mineral filler
- Filler in carpet backing
- Aggregate
- Cement production and replacement
- Soil amendment

Advantages of dry CCT by-products for utilization include:

- Dry particles
- Cementitious/pozzolanic reactivity
- Grain size distribution similar to conventional fly ash
- Nonhazardous
- High pH, calcium, and sulfur (for soil amendment)

Disadvantages of dry CCT by-products for utilization include:

- Exothermic hydration
- Potential for expansion
- High soluble sodium salt content of sodium sorbent injection by-products
- Potential for corrosion or sulfate attack on concrete
- Limited understanding of long-term performance characteristics
- High sulfur

The dry CCT by-products contain significant portions of aluminous and siliceous compounds as well as alkali (calcium or sodium) ions. These chemical species (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CaO) give the dry CCT by-products self-hardening or cementing characteristics when they come in contact with water. The strength developed depends on the quantity of cementitious materials produced, with the calcium sulfate contributing to early strength gains through the formation of ettringite and thaumasite. In general, the pozzolanic reactions are similar to those of other lime-fly ash mixtures, with reactivity dependent on the fly ash percentage and alkali content. The high sulfate/sulfite composition may contribute to the strength, but may also cause expansion. Also, the by-products contain high percentages of alkali (calcium or sodium) ions. The chemical species SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaO give the dry CCT by-products self-hardening or cementing characteristics when in contact with water. The hydration reactions are complex, with the major hydration products being cementitious materials. The strength developed is dependent on the quantity of cementitious materials produced. The principal reactions are:

 $CaO + H_2O \sim Ca(OH)_2$ 

 $xCa(OH)_2 + ySiO_2 + zH_2O \sim xCaO \bullet ySiO_3 \bullet zH_2O$ 

 $xCa(OH)_2 + yAI_2O_3 + zH_2O \sim xCaO yAI_2O_3 zH_2O$ 

 $xCa(OH)_2 + ySiO_2 + zAI_2O_3 + wH_2O \sim xCaO \cdot yAI_2O_3 \cdot zSiO_3 \cdot wH_2O$ 

Further, the high calcium sulfate concentrations cause these by-products to fail existing U.S. materials standards for conventional coal combustion fly ashes in certain reuse applications, and may cause the long-term strength loss observed with some by-products. Major, minor, and trace elements will partition so that elements from coal ash will be enriched in the entrained solids (the fly ash) and depleted in the spent bed material. Nevertheless, these solids would pass the U.S. leachate tests and not be classified as hazardous materials. Calcium from limestone will preferentially remain in the spent bed material.

The properties of the AFBC by-products indicate that some changes will need to be made to conventional by-product management practices. Dry transport systems are preferable to liquid transport systems, and reactions with water will need to be considered when by-product management systems are designed. AFBC by-products tend to be more abrasive than conventional fly ashes, so special transport designs with few, smooth, abrasion-resistant elbows are needed. The AFBC by-products should develop adequate strength for placement in a landfill, but leachate generation controls may be required, depending on local conditions.

## 3.1 Road Base

Dry CCT by-products have potential as substitutes for lime or fly ash in road base construction. A possible advantage would be faster strength development and less sensitivity to cold weather during curing. However, the potential for expansion (dimensional instability) should be explored for each by-product source and mix. Also, a separate hydration step may be required prior to mixing and placement. A dry CCT by-product road base would be required to fulfill design and performance criteria similar to a cement-stabilized road base. While it would provide pavement support, it may not be appropriate where a free-draining base course is required. When used as base course beneath a portland cement–based concrete pavement, the potential for sulfate attack on the concrete should be considered.

Application of spray dryer by-product in the embankment layer offers the best opportunity for high-volume use in road construction. The by-product can provide a low-cost alternative to the use of common borrow when a borrow pit is not readily accessible. The strength gained from the spray dryer by-product will provide a more solid foundation for the upper road materials. In a 1991 demonstration, EPRI found that the average common borrow strength of the spray dryer by-product used on a section of roadway was 17.6 MPa, which is similar to the strength of natural borrow material. However, spray dryer by-product should not be mixed with the granular and select granular materials that are placed beneath the surface pavements, because it will reduce the permeability of that layer.

Several EPRI demonstration projects have shown that mixtures of the by-product from a dry FGD process with either soil or the by-products from other CCTs produces an excellent material for road construction. A program completed in 1999 has shown that a mixture with the by-product from a PFBC plant can be used successfully in highway construction to stabilize the

local soil [24, 25]. This by-product mixture demonstrated high strength and ease of installation, and no special equipment or training was necessary for its use. Performance during construction demonstrated that the level of care normally required on any construction project should be adequate when working with this material. In other projects, EPRI found that a mixture of the by-products from wet and dry FGD systems can yield a material this has excellent strength properties and workability. Lastly, in Ohio, dry FGD by-product and soil were mixed on site in approximately equal proportions and used to repair a state highway; the resulting strengths were close to those obtained with the FGD by-product alone. This specific FGD material appears to be well suited as a soil stabilizer, and the mixes can be blended in the field and modifications easily made.

## 3.2 Soil Stabilization

Similar to stabilization of FGD sludge, soil stabilization increases soil strength and bearing capacity while decreasing its water sensitivity and volume change potential. Stabilized soil can be used in the construction of roadways, parking areas, foundations for pavement, embankments, and other structural applications. Soil stabilization can eliminate the need to obtain and transport expensive, better-quality borrow materials, expedite construction by improving wet or unstable soil, and reduce pavement thicknesses by improving subgrade conditions.

Cement and lime are the most effective stabilizers for a wide range of soils. Fly ash has also been used to stabilize soils in recent years. Since many fly ashes are low in CaO content, lime or cement is commonly added. The use of dry CCT by-products in soil stabilization is similar in many respects to the use of Class C fly ash or lime/cement–fly ash, since the main compositions of dry CCT by-products are fly ash, calcium sulfate/sulfite, and unreacted lime. The resulting mixtures have been found to be serviceable as subgrade in highway construction.

The primary method of physical stabilization is compaction. However, because compaction alone is sometimes not enough to provide soil stability, especially for fine-grained cohesive soil, chemical stabilization using a calcium-based material is often needed. Lime–fly ash and cement–fly ash mixtures were developed as stabilizers in the past decade. Class F fly ash requires the addition of cement or lime because it is not self-hardening. Class C fly ash is usually used alone as stabilizer. However, if its free lime content is low, the Class C fly ash may need to be combined with small quantities of lime or cement.

With the exception of sodium sorbent injection by-product, dry CCT by-products have a high calcium content which may lead to self-cementing characteristics similar to most Class C fly ash. The presence of unreacted lime in the by-products helps the moisture reduction, plasticity modification, and pH adjustment of soils. In addition, the calcium components will react with siliceous and aluminous components in the fly ash to induce a cementing action and develop long-term strength gains due to the pozzolanic reaction. And the presence of sulfate/sulfite may contribute to moderate early strength gains of the stabilized soil due to the beneficial formation of ettringite. However, these same sulfur compounds may also cause unexpected expansion. The expansion problem has been previously observed when using lime to stabilize soil high in sulfate content. This reaction usually occurs slowly and may not become apparent until six months to

two years or more after construction. Since the dry CCT by-products contain high sulfate/sulfite and abundant aluminum contents, dimensional stability should be one of the durability criteria.

The basic design criteria for stabilized soils are unconfined compressive strength and durability, or ability to resist damage caused by freeze-thaw and wet-dry cycles. In the United States, for example, the American Society for Testing and Materials (ASTM) has developed a specification for the use of lime–fly ash–soil mixtures that establishes minimum unconfined compressive strength and durability requirements.

The above strength and durability criteria are directed toward soil stabilization with emphasis on its use in highway construction. Dry CCT by-products can also be used for soil modification to improve the characteristics of wet, muddy sites to expedite construction. Strength and durability criteria are not normally applied to this use as they are in highway use. An evaluation of the effectiveness of stabilizers can be done simply by monitoring the improvement in the soil characteristics or properties of concern as the amount of stabilizer is varied.

## 3.3 Stabilization of Waste Sludge

Fly ash has already been used as a stabilizer for various sludges, and the solid by-products from dry CCT processes also show promise for stabilizing wet FGD, industrial waste, and hazardous waste sludges.

The selection of a stabilizing agent depends on the characteristics of the sludge and cost. For FGD sludge and nonhazardous waste sludge, fly ash alone or together with lime is frequently used as a stabilizing agent. In this case, the silica and aluminum in fly ash react with the calcium in lime to form a low-strength solid. Lime may also raise the pH value of the sludge. For hazardous waste sludge, fly ash together with lime or cement can be used as a stabilizing agent. Hydration of the by-product reduces the sludge moisture content and results in a strength gain.

However, in many cases, blending dry CCT by-products with sludge may make a more stable and readily used material than sludges stabilized with conventional fly ash. Of particular benefit is the ability of CCT by-product to immobilize trace elements in sludge by causing them to be trapped in the ettringite/thaumasite crystal structure formed from the calcium, aluminum, silica, and sulfur in the CCT by-products. In addition, the high alkalinity of the by-products will chemically stabilize hazardous waste sludge.

Sludge stabilization is similar to soil and road base stabilization in many respects. However, since most sludges generally have a high moisture and low solids content, the percentage of dry CCT by-products used in sludge stabilization is considerably higher than that used in soil or road base stabilization.

In an EPRI study completed in 1994, four clean CCT by-products were tested to stabilize organic and inorganic constituents of four hazardous waste stream materials and evaluated using several different techniques [34]. The CCT by-products included: (1) the Tennessee Valley Authority (TVA) atmospheric fluidized bed combustor (AFBC) residue, (2) the TVA spray dryer residue, (3) the Laramie River Station spray dryer residue, and (4) the Colorado-Ute AFBC residue.

#### Dry By-Products from Clean Coal Technologies

The evaluation methods included: (1) Toxicity Characteristic Leaching Procedure, (2) X-ray diffraction and scanning electron microscopy/energy dispersive X-ray analyses, and (3) solid-state 13C nuclear magnetic resonance (NMR) spectroscopy. Simulated weathering experiments were performed on some of the mixtures of CCT by-products and hazardous waste stream materials.

In this project four types of hazardous waste stream materials were obtained and chemically characterized for use in evaluating the ability of the CCT by-products to stabilize hazardous organic and inorganic wastes. The wastes included an API separator sludge, mixed metal oxide-hydroxide waste, metal-plating sludge, and creosote-contaminated soil. The API separator sludge and creosote-contaminated soil are U.S. Environmental Protection Agency (EPA)-listed hazardous wastes and contain organic contaminants. The mixed metal oxide-hydroxide waste and metal-plating sludge (also an EPA-listed waste) contain high concentrations of heavy metals.

It was found that chromium was leached from spray dryer CCT by-products, therefore, these by-products cannot be used in stabilizing hazardous materials containing chromium. However, cadmium found in hazardous waste can be stabilized by all four CCT by-products. The high pH of the CCT by-products suggest that these materials may be used to stabilize acidic components of the hazardous waste materials.

Using diffraction and dispersive X-ray analyses, quartz and ettringite were the most significant mineral phases in most mixtures of CCT by-products and hazardous waste materials. Preliminary solid-state NMR adsorption studies of a hazardous waste adsorbed on a CCT by-product have shown that this technique may be used to determine the relative strength of the bonding interactions between these materials.

The stabilizing effects of the CCT by-products on a variety of hazardous wastes provides confirmation that the alkaline by-products can be very useful in the treatment of hazardous wastes. This EPRI study has demonstrated a promising area for commercial development [34]. These CCT by-products have even been proven for use in chemically enhanced "designer" liners.

## 3.4 Structural Fills

The major advantage to using a dry CCT by-product as fill material is its high unconfined compressive strength relative to soil. The major disadvantage is that it is a new material, and its long-term behavior is relatively unknown. Laboratory tests indicate leachate concentrations are well below toxicity levels for hazardous waste, but the pH is high, generally about 12. A potential concern with these by-products is dimensional stability (expansion). Although no reports of expansion of these by-products in fills have been identified, fluidized-bed materials have in some cases been expansive in road base, and erratic unconfined compressive strengths have been observed over time in some laboratory samples.

Finally, these by-products need to be used when they are available; otherwise they may be impractical to recover from the storage facility because they are self-hardening (unless stored dry in silos—typical silo volumes are 300 to 500 cubic meters). Further, exposed stockpiles may experience changes in by-product reactivity.

## 3.5 Grout

Grouts are fluids used to fill voids or fissures accessible only by injection. Their purpose is either to increase the structural strength or reduce the permeability of a subsurface location.

Suspension grouts are typically cement and water based, and may contain combinations of fly ash, lime, and/or sand. Admixtures may also be used to control set or improve workability. In grout, dry CCT by-products may be used to replace fly ash, lime, and/or cement. Granular spent bed material from AFBC and PFBC may also serve as a replacement for sand in a grout mix.

Potential advantages of dry CCT by-products include:

- Fine particle size
- Reduced segregation
- Low cost
- Excellent strength development
- Possible limitations to be considered include:
- Expansion
- Sulfate attack on concrete
- Time of set
- Heat of hydration
- Hazardous waste stabilization

## 3.6 Brick, Block, and Aggregates

Bricks use mixtures of by-products and clay or sand. In block production, the basic components of the mixture are cement, by-products, sand, aggregate, and water. Sometimes preconditioning of the by-product is needed before mixing the by-product with other materials. Synthetic aggregate can be formed by mechanical agglomeration, briquetting, or forming large blocks/beams. In general, synthetic aggregates should meet ASTM specifications for the expected application. The bricks/blocks should be evaluated for absorption, compressive and flexural strength, efflorescence, freeze-thaw resistance, and dimensional stability.

The calcium sulfate compounds in dry CCT by-product ash pose some potential concerns, including dimensional stability (expansion), long-term strength loss, and sulfate attack on mortar within or between concrete blocks. Use of prehydrated by-product may mitigate long-term changes in dimensional stability and strength; however, a field demonstration wall would be necessary to completely resolve concerns associated with calcium sulfate and related compounds.

## 3.7 Cement Production and Replacement

As with fly ash, there are three potential uses of dry CCT by-products in the cement manufacturing industry:

- Raw feed for cement production (by-product added prior to clinkering)
- Production of a blended cement (by-product added after clinkering)
- Partial substitution for cement in concrete

The self-hardening characteristics of dry CCT by-products and their high percentage of fly ash (up to 70%) are desirable characteristics for utilization in cement and concrete production. However, wherever ASTM specifications are applicable, the use of these by-products in cement production and concrete is severely limited.

ASTM C 150 provides standard specifications for Portland cement, including the chemical criteria for the final cement produced. There are no chemical composition requirements for the raw materials used to produce the cement, but the final product is limited to 4% sulfate (reported as sulfur trioxide). Because dry CCT by-products typically contain more than 4.0% sulfate, only small proportions can be used. In general, the maximum amount of by-product that may be introduced in cement production or as a cement replacement in concrete is often determined by the SO<sub>3</sub> content. A high SO<sub>3</sub> content may contribute to formation of sulfates in the concrete and lead to deterioration of the concrete due to sulfate expansion.

Dry CCT by-product behave as pozzolans, similar to fly ash, when used to replace cement in concrete. To satisfy ASTM C 618 requirements the by-product must contain a minimum of 50% combined content of  $SiO_2 + Al_2O_3 + Fe_2O_3$ . However, this same specification disallows the use of residue resulting from "the injection of lime directly into the boiler for sulfur removal." This is because of the expansive reactions that would be created by the SO<sub>2</sub> sorbent by-products mixed with the conventional fly ash.

ASTM C 618 also states that the material to be used as a mineral admixture should have no more than 5% oxidized sulfur reported as sulfur trioxide. This corresponds to 6% as sulfate/sulfite. Most of the dry CCT by-products have high sulfate/sulfite content, ranging from 6% to 20%. The high concentrations of sulfate/sulfite prohibit by-products from use as a mineral admixture for Portland cement concrete.

The loss-on-ignition (LOI) levels of dry CCT by-products are similar to conventional fly ash and depend on the  $NO_x$  controls used in conjunction with these  $SO_2$  controls. ASTM limits LOI to 6%, but concrete plants typically refuse ash with greater than 4% LOI.

In Japan, 30% (for a total of 12 plants) of cement production plants utilize FBC residues as a replacement for the argillaceous material in cement.

## 3.8 Substitutes for Agricultural Lime

Dry CCT by-products can be used as soil amendments to raise the soil pH of both acidic mine soils and agricultural soils. Natural gypsum has long been used in agriculture for both chemical and physical conditioning of soils. Gypsum provides a supplemental source of sulfur and calcium for legumes, particularly peanuts, and to a lesser degree potatoes and cotton. Similar to natural agricultural gypsum, dry CCT by-products contain calcium and sulfur. However, these elements may or may not exist in the same form as in natural gypsum. Unlike gypsum, dry CCT by-products typically raise soil pH, and may harden rather than loosen soil at high application rates. Some soils may benefit by properly applied dry CCT by-products. Some peanut cropland, for instance, could benefit by an increase in pH, as this would reduce the solubility of zinc and potassium in the soil, two elements which inhibit the growth of peanuts.

Fly ash and dry CCT by-products have been used in many revegetation studies and projects. Combinations of biosolids and alkaline by-products may provide complementary plant nutrients. Concerns with using dry CCT by-products include:

- Variability of calcium carbonate equivalency (CCE), which could result in incorrect application rates
- Contamination of agricultural land by trace elements
- Interference with seed germination on sandy soil by high levels of soluble salts
- Different materials handling methods than used for standard agricultural lime
- Crusting or hardening of the amended soil

The first three "challenges" can be overcome by frequent sampling, testing, and diligent quality assurance practices. The properties that should be tested are CCE, trace elements, soluble salts, and ash variability.

The loading rate of a dry CCT by-product is determined by the rate required for proper pH adjustment. At that loading rate, it must then be determined that the following are not exceeded:

- Soluble salts
- Boron, molybdenum, and selenium
- Heavy metals—both annual and lifetime cumulative loading rates
- Crusting or hardening

Because of their alkalinity, one possible beneficial use for dry FGD by-products is as a limestone substitute for amendment of acidic agricultural soils. Land application of fluidized-bed combustion by-products as a lime substitute and a source of Ca and S has been investigated in a number of studies (Holmes et al., 1979; Korcak, 1980; Stout et al., 1979; Terman et al., 1978), and most recently by EPRI (TR-112916, July 1999). These studies have generally reported positive effects on plant growth and crop yield, with negative effects occurring only at application rates of 25 wt% or higher. Most studies with fluidized-bed materials have investigated soil pH and plant responses, with little emphasis on potential environmental

#### Dry By-Products from Clean Coal Technologies

impacts. EPRI investigated the responses of alfalfa (*Medicago sativa L*.) and corn (*Zea mays L*.) grown on three acidic agricultural soils amended with a dry FGD by-product applied at rates based on the liming requirement of the soils.

In addition to crop responses, soil chemical effects and transport of the FGD material were monitored.

Soil application of dry FGD by-product materials at the recommended liming rate can effectively and rapidly neutralize acidity in the zone of incorporation. An EPRI project even found evidence of increasing pH in underlying soil to a depth of 30 cm within one year of application. This makes the soil more favorable for plant growth because the increased pH in the zone of incorporation produces an immediate decrease in water-soluble concentrations of Al, Fe, and Mn and an increase in Ca, Mg, and S concentrations. In fact, the ability of FGD by-products to accelerate the movement of Ca and Mg, thereby increasing the base-status of sub-soils well below the zone of incorporation, is a benefit not realized with conventional liming materials. In studies to date, EPRI has found no evidence that land application of FGD by-products at the recommended liming rate would lead to elevated levels of potentially toxic trace elements in soil or water. One potential exception is water-soluble boron, which was found to increase in the application of some SO<sub>2</sub> control by-products (from PFBC in this case) to three different soils. However, the concentrations always remained well below phytotoxic levels and decreased with time as the boron was leached from the soil.

With pH-sensitive crops such as alfalfa, application of FGD by-products can increase growth and yield on acidic soils. Even when applied at twice the lime requirement rate of the soils, past studies have found no adverse effect on yield. With a crop such as corn that is less pH sensitive, the potential yield benefit from FGD by-product application may be less than for a more sensitive crop such as alfalfa.

In the study using by-products from a PFBC unit, plant-available phosphorous (P) decreased, and this was attributed to the large amount of added Ca and consequent precipitation of relatively insoluble calcium phosphate. This may require farmers to adjust P fertility programs in soils where available P is low at the time the FGD by-product is applied.

CCT materials with high Ca-carbonate equivalencies make them usable as a liming material (as well as a nutrient source), and thus make them valuable to farmers. The value may be as high as \$25 to \$30 per ton. (TR-102575) [26].

## 3.9 Fertilizer from Mixture of Dry CCT By-Products and Biosolids

Although fly ash and CCT by-products have been used in many revegetation studies and projects, these materials, do not provide essential nitrogen to plants. Some recent research has focused on the use of biosolids (sewage sludge) to provide organic matter and nitrogen. While biosolids can increase a site's biomass, they may not affect the pH, iron, or lead contents of the soils; these could be improved by the addition of an alkali such as a CCT by-product. Under an EPRI sponsored research project at the University of Georgia, soil scientists and agronomists have been developing new mixes of various CCT by-products and biosolids for use in making

horticultural mixes. The biosolids provide the organic nutrients and the CCT by-products absorb the moisture, and control the odor.

### 3.10 Miscellaneous uses of Clean Coal By-Products

#### Farm Feedlot Stabilization

Another use of the by-products from clean coal technologies is to create farm feedlot surfaces that could improve animal production. In areas with humid climates, muddy farm conditions can cause poor animal productivity. There are few economically viable remedies currently available to overcome this problem. In one project, EPRI constructed a feedlot pad by blending dry PFBC material into the top 20 cm of in-place soil and compacting. This procedure created a suitable platform for the placement of an additional 20 cm to 30 cm layer of blended cyclone and bed ash of the PFBC material. Based on laboratory results and the field observations from the PFBC feedlot, two additional 1200 m<sup>2</sup> pads were constructed for hay bale storage using wet FGD by-product material. To achieve the required densities and strengths, an additional 5% to 10% of lime was added at the job site prior to compaction. Some States have regulations that provide for a permit process for the use of by-products in agricultural or ranch environments. In Nebraska for example, according to Nebraska Ash, the use of ash to stabilize feedlots would require a permit. For this reason this application has not been very widespread [21]. A rhinoceros feedlot pad at a wildlife safari park near Cambridge, Ohio was constructed using lime-enriched FGD material from a nearby power plant [30].

#### Abandoned Underground Mine Filling

The chemistry of FGD by-products is ideal for use in reclamation of abandoned mine sites. The high alkalinity content improves soil pH, creating an environment that is acceptable for plant growth. The high gypsum content helps move calcium down into the soil profile so that areas not directly in contact with the applied FGD by-product can also be improved. One of the problems with traditional resoil reclamation technologies is that the surface soil layer is very thin. If any erosion occurs, the rooting depth becomes too shallow to maintain plant growth. FGD by-products help overcome this problem by providing more soluble basic cations that can move into the underlying spoil material, thus increasing plant rooting depth. In addition, use of FGD by-products avoids the problem of having to disturb one area of land to reclaim another. Moreover, EPRI studies have shown that surface water quality can be substantially improved from what existed prior to reclamation, with no change in ground water quality.

#### **Carpet Backing Filler**

The carpet making industry is highly concentrated in a 100 square mile area around Dalton, GA. It represents 80% of the carpet making industry in North America. The use of calcium carbonate and alumina hydrate have long been used as filler materials in carpet backing applications. The particle size distribution of the fillers in carpet backing applications is of critical importance. Fly ash and some spray dryer residues do meet the fineness specifications. The Table below lists

the critical specifications that this industry requires of fillers. Over 600,000 tons of fillers are used each year in this region of Georgia.

# Table 3-1 Critical Specifications, Use Levels, and Pricing for Major Fillers in Carpet Backing

Filler	Specifications	Loading Levels	F.O.B. price	
Calcium Carbonate	325 mesh: 75% to 99% passing.	4 to 5 parts calcium carbonate to one part resin	\$15 to \$60/ton.	
Alumina Hydrate	30 grade exceeds 20 microns.	1 to 5 parts to one part resin.	\$250 to \$320/ton.	

# **4** ENVIRONMENTAL IMPACTS OF COMBUSTION BY-PRODUCT USE

This section provides information on the environmental characteristics of clean coal technology by-products that affect reuse options. The chemical, physical, and engineering characteristics of the CCT by-products determine how each by-product will react with its environment and with the other mixture components involved in specific utilization options. It is also useful to know how the differences in the CCT processes such as process operating conditions, source and type of coal, type of sorbent, etc., change the by-product characteristics.

#### 4.1 General CCT Characteristics

By-products are characterized by chemical reactivity, physical characteristics, and leachate chemistry. All these criteria influence utilization potential and are interrelated. Changes in one property can produce changes in the other properties and affect the utilization potential.

Generally, the differences between the properties of CCT by-products and those of conventional fly ash and bottom ash are due to the addition of alkali to capture SO<sub>2</sub> and the resulting presence of an alkali-sulfur solid product. Chemical compounds related to CCT by-products are listed on Table 4-1. Unlike Class F coal ash, SO<sub>2</sub> control by-products contain significant quantities of calcium or sodium oxide (CaO or Na<sub>2</sub>O) and calcium or sodium sulfate/sulfite (CaSO<sub>4</sub> and CaSO<sub>3</sub> or Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>3</sub>). Like many sources of Class C fly ash, these compounds exhibit self-hardening, or cementing, properties and react exothermically (release heat) with the addition of water. If this heat of reaction is excessive, the material may experience cracking, weakening, or even blowouts. Also, the high alkalinity of these by-products produces a higher-pH leachate than most conventional fly ashes.

It is necessary to understand the leaching characteristics of CCT by-products to properly determine the potential environmental consequences of disposing of the residues. Many countries have laws governing the classification of wastes for handling and disposal based on standardized leaching tests. Laboratory leaching tests include the shake or batch test and the column or lysimeter test. The shake test will usually give a "worst case" result, while the column test, which is designed to determine long-term leaching behavior, provides a more representative idea of leaching behavior under natural conditions. However, column or lysimeter tests are somewhat problematical for most CCT residues, since they tend to consolidate into monoliths leading to very low permeability rates. Therefore, leachates from residues newly created that have not been wetted or conditioned will differ from those older residues.

#### Environmental Impacts of Combustion By-Product use

Leachates from AFBC residues tend to be higher in soluble ions, such as  $SO_4^{2-}$ ,  $Ca^{2+}$ , and  $CI^-$ , than conventional pulverized-coal fly ash. The concentrations of trace elements in the residues are directly related to the initial fuel composition. Although the trace element concentrations of AFBC residues are reported in the literature as similar to pulverized-coal fly ash, their leaching characteristics are different. The solubility of trace elements is decreased due to their adsorption onto the fly ash particles and they may co-precipitate with concentrated salts during the leaching procedure. The solubility is also dependent on the pH of the leaching solution and its buffering capacity.

Previous EPRI work, [35] has determined that combustion temperatures and the operating temperatures of emission control devices are significant controlling parameters that affect the percentage distribution of the trace elements in coal ash. In most cases, the ash produced from different coals burned in the same generating unit under similar operational conditions will have similar distribution of the trace elements in chemical species. Generally, higher ESP temperatures result in the formation of hopper ash with a higher leaching potential for trace elements. Also the combustion of larger coal sizes result in the formation of bottom ashes with higher leaching potential for trace elements [35]. Given the lower combustion temperatures in the NOx controlled boilers, it is likely that the trace element leaching rates will be lower.

Name	Formula			
Alkali	Ca or Na			
Anhydrite	$CaO•SO_3$ or $CaSO_4$			
Calcite or Calcium Carbonate	CaCO <sub>3</sub>			
Calcium Oxide (lime)	CaO			
Calcium Sulfate	CaSO <sub>4</sub>			
Calcium Sulfite	CaSO <sub>3</sub>			
Hannebachite	$CaSO_3 \bullet \frac{1}{2}H_2O$			
Ettringite	3CaO • Al <sub>2</sub> O <sub>3</sub> 3CaSO <sub>4</sub> 32H <sub>2</sub> O or Ca6 Al <sub>2</sub> (SO <sub>4</sub> )3 (OH)12 • 26H <sub>2</sub> O			
Thaumasite	$2CaO \bullet 2SiO_2 \bullet 2CaCO_3 \bullet 2CaSO_4 \bullet 30H_2O$ or Ca6Si <sub>2</sub> (SO <sub>4</sub> )2•(CO <sub>3</sub> )2 (OH)12 • 24H <sub>2</sub> O			
Gypsum	CaO • SO <sub>3</sub> •2H <sub>2</sub> O or CaSO <sub>4</sub> •2H <sub>2</sub> O			
Hematite or Iron Oxide	Fe <sub>2</sub> O <sub>3</sub>			
Hydrated (slaked) Lime or Portlandite	Ca(OH)			
Sodium Hydroxide	NaOH			
Periclase or Mg Oxide	MgO			
Quartz or Silicon Dioxide	SiO <sub>2</sub>			
Sodium Sulfate	Na <sub>2</sub> SO <sub>4</sub>			
Sodium Sulfite	Na <sub>2</sub> SO <sub>3</sub>			

## Table 4-1 Some Chemical Compounds Relevant to CCT By-Product Formation and Utilization

The calcium-sulfur reaction occurs in the boiler in both AFBC and FSI technologies. Because of the lower combustion temperature, AFBC fly ash typically has irregularly shaped particles with low pozzolanic reactivity. However, in the FSI process the sorbent is injected into a higher-temperature region of a conventional boiler, producing spherical, glassy FSI particles. The calcium-sulfur reaction products produced from both technologies are calcium sulfate; little or no calcium sulfite is formed due to the oxidizing atmosphere inside the boiler.

The fly ash content of the by-product from postcombustion dry SO<sub>2</sub> technologies is generally higher than that from the AFBC and FSI technologies. The physical properties of these by-products are similar to those of conventional fly ash, but they are extremely fine. Fly ash is coated by and intermixed with calcium (or sodium)-sulfur reaction product and is collected together with reaction product and unreacted sorbent. Spray dryers produce mainly sulfite components, sodium duct-injection, and calcium duct injection both sulfite and sulfate components. The sodium compounds are much more soluble in water than the calcium compounds, which may result in elevated sodium concentrations in leachate.

These by-products do not exhibit toxic or hazardous characteristics under current U.S. Environmental Protection Agency regulatory definitions. However, the high calcium sulfate concentrations in AFBC by-products can lead to high sulfate concentrations in leachates (which could cause violations of drinking water standards if these sulfates are allowed to reach surface or ground waters untreated).

### 4.2 Environmental Effects of using FGD By-Product for Crop Production

The use of FGD by-products as a soil amendment for crops was discussed previously. Environmental studies of these applications have shown that elemental composition of both alfalfa foliage and corn grain can be affected by FGD by-product application. The largest increases occurred with Mg and S, two major and highly soluble elements in the FGD by-product. There was no evidence of any toxicity problems due to these elements, and the increase was much less in the second growing season than it was in the first application. There were significant increases in Mo concentrations for both alfalfa and corn. Increased Mo uptake is frequently noted when soils are limed and pH is increased; thus the source of the Mo is likely not from the by-product. Although there was some evidence of a small increase in alfalfa boron concentrations resulting from FGD by-product application, concentrations remained well below phytotoxic levels. There was no evidence that the use of the FGD by-product increased any other trace elements. On the other hand, there was some evidence of decreased plant tissue concentrations of Cd, Ni, and Zn in the first year of application. Calcium, the other major element in the by-product, was either unaffected or decreased; its uptake was likely inhibited by the large amount of soluble Mg in the soil following application of the FGD by-product.

Data from an EPRI demonstration showed that application of FGD by-product at the design rate (22.5 Mg/ha) had no significant effect on soil physical properties including soil bulk density, moisture retention characteristics, and saturated conductivity [26]. Similar results were observed for measurements made at different stages of crop growth and for other growing seasons. However, there were differences in total runoff due to the FGD by-product treatment; treatment

Environmental Impacts of Combustion By-Product use

decreased runoff loss by a factor of 2.5. This is attributed primarily to the improved plant growth that was stimulated by amending the soil with this by-product material.

# 4.3 Environmental Effects of using FGD By-Products for Land Reclamation

Consistent results from EPRI field studies suggest that application of FGD by-product as a soil amendment may have the beneficial side effect of reducing soil erosion. The use of alkaline CCT by-products in combination with various biosolids could be an attractive land application in those areas of the country with acid soils.

These applications are regulated by the US EPA. Concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), molybdenum (Mo), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn) currently are regulated by USEPA under the Clean Water Act, section 503. In contrast, boron (B) and major elements like calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) are not regulated. The 503-regulation includes numerical values for maximum (ceiling) metal concentrations in biosolids or biosolids blends, maximum annual loadings of soil, maximum cumulative loadings of soil, and the levels recommended for exceptional quality products (Table 4-2). Under 503 regulations, only biosolids (or their blends) having concentrations of the regulated metals below regulatory limits (ceiling concentrations) can be used on agricultural land.

Element	Clean Sludge <i>mg/kg</i>	Ceiling level <i>mg/kg</i>	Annual loading <i>kg/ha/yr</i>	Cumulative loading <i>kg/ha</i>	Soil level <i>mg/kg</i>	Limiting pathway
As	41	75	2.0	41	20	Ingestion
Cr	1200	3000	150	3000	1500	Plant toxicity
Cd	39	85	1.9	39	20	Food chain
Cu	1500	4300	75	1500	700	Plant toxicity
Hg	17	57	0.85	17	9	Plant toxicity
Мо	18	75	0.90	18	10	Livestock feed
Ni	420	420	21	420	200	Plant toxicity
Pb	300	840	15	300	150	Ingestion
Se	36	100	5.0	100	50	Plant toxicity
Zn	2800	7500	140	2800	1400	Ingestion

#### Table 4-2 EPA limits for Metals in Biosolids to be used on Land

Source: US Environmental Protection Agency, 1993: Standards for the use or disposal of sewage sludge, Federal Register 58, Part 503, 9387-9404.

CCT by-products, because a portion of them consist of fly ash which contain plant nutrients (trace metals), also have capacity to neutralize soil acidity, and can improve physical properties of plant growing media; therefore, they need to be evaluated as to whether or not they be beneficially utilized in agriculture, horticulture, and land reclamation.

The chemical make-up of fly ash, and consequently, possible ash effects on soils and plants, depend on the composition of the parent coal, combustion conditions, and efficiency of emission control devices. The spent sorbent portion of the CCT by-products are lime based compounds. Several studies have been conducted in the last 20 years on utilization of fly ashes and their possible environmental impacts (Adriano et al., 1980; Bilski et al., 1995; Korcak, 1995). It appears from these studies that boron (B) phytotoxicity is probably the greatest potential problem to crop production on land amended with fly ash. In addition, excesses of such micronutrients as molybdenum (Mo) and manganese (Mn), induced phosphorus (P) deficiencies, and negligible nitrogen (N) and potassium (K) supplies in fly ash make fly ash a very unbalanced source of plant nutrients (Molliner and Street, 1982). In addition a long-term study on the use of dry FGD CCT by-products in land based applications was completed for EPRI in December 2000 by Ohio State University (TR-1000721). Many areas drastically disturbed by surface coal mining prior to the Surface Mining Control and Reclamation Act of 1977 (Public Law 95-87) are still in need of reclamation. Where conventional reclamation is expensive or borrow soil is not available, the use of non-hazardous, alkaline flue gas desulfurization (FGD) by-products as an amendment may be an effective method of reclaiming these lands. In that EPRI demonstration project, the results show that the aboveground biomass yields were significantly greater for the conventional reclamation treatment than for the other treatments in 1995 and 1997 but the differences among treatments were not significant in 1996 and 1998. Erosion control was excellent and comparative soil losses decreased for all treatments from < 5.3 Mg ha<sup>-1</sup> in 1995, to < 2.0 Mg ha<sup>-1</sup> in 1996, and then to < 0.7 Mg ha<sup>-1</sup> in 1997 and 1998. In comparison to the conventional reclamation method, FGD with and without addition of compost, was found to be equally effective in ameliorating chemical conditions that were initially extremely acid and phytotoxic.

Monitoring of interstitial water, ground water, and spring water quality was also conducted for four years following reclamation. The EPRI report (TR-1000721) [24] presents data collected from June 1996 through June 1998 but includes some additional data to examine longer-term trends. The beneficial influence of FGD by-product on water quality was evident from lower concentrations of iron, nickel, and zinc in the application-area interstitial waters as compared to interstitial waters from an area reclaimed with conventional reclamation methods. Other trace elements derived from the FGD by-product that could adversely affect water quality were well below Maximum Contaminant Levels (MCLs) set by the USEPA. Furthermore, concentrations of these elements rarely exceeded reporting limits. Reclamation of acid and toxic mine spoil using FGD can be successful accomplished and monitoring of various environmental parameters did not indicated any potential long-term negative impacts of such FGD use.

Successful reclamation of acid surface minelands, such as abandoned mined land sites, require the use of alkaline amendments to ameliorate adverse chemical conditions. Dry Clean Coal by-products have potential for use as liming agents in reclamation of these lands due to their residual alkalinity [22].

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Similarly, land reclamation using biosolids (sewage sludge, composts, etc.) is also problematic because of nutrient imbalances [38]. Therefore, the concept of mixing conventional fly ash with biosolids (sewage sludge, composts) has been investigated under EPRI sponsorship at the University of Georgia, in order to take advantage of the complementary properties of these byproducts. The relatively high alkali metal (Ca, K, Mg) content of ash complements the greater N and P content of biosolids; the alkalinity in the ash offsets the acid-forming tendency of biosolids and immobilizes trace metals present in the organics. Since, dry fly ash adsorbs water strongly, and might be used as a dewatering agent for low-solids organic slurries, such as sewage sludge. In addition, adsorptive capacity of the organics may immobilize certain trace elements (e.g., B) present in fly ash, while fly ash may retard production and leaching of nitrate (NO<sub>3</sub>) and phosphate (PO<sub>4</sub>) from the organic materials. These types of interactions suggest that mixed organic-fly ash products might be formulated as balanced, high-organic fertilizer/soil conditioners free from negative environmental side effects. The main benefits from use of fly ash/biosolids blends for land reclamation include: addition of major nutrients (N, P, K), liming effect, and addition of organic matter and fine particles. The results of this investigation are documented in several EPRI reports published over the last 3 years [37, 38].

### 4.4 Environmental Effects of using Clean Coal By-Products for Underground Mine Reclamation

Clean Coal By-products can mitigate or prevent acid mine drainage (AMD). In the March 1999 Report to Congress, the U.S. EPA states that " under ideal circumstances, placement of wastes in mines could result in net environmental benefits relative to conventional landfills through avoided development of greenfield space for UCCW (utility coal combustion wastes) disposal, improvement of disturbed mine lands through contouring, revegetation, and reduced infiltration to mine workings, and abatement of acid mine drainage through neutralization and diversion" [27].

To date, there have been two EPRI demonstration projects related to the use of Clean Coal By-Products to ameliorate acid mine drainage problems in abandoned underground coal mines. In 1996 an EPRI funded demonstration project at the Indianapolis Power & Light Company Petersburg Generating Station to demonstrate the novel use of a mix of ash and wet FGD scrubber fixated with lime which was injected into the mine underneath the power plant [27]. In a project completed in 2001, the Omega Mine Project near Morgantown, WV was designed to mitigate a serious AMD groundwater problem [29].

In the Petersburg Generating Station project, the fixated FGD scrubber sludge (FSS) was pumped into abandoned underground mine voids to reduce the threat of subsidence as well as to control AMD pollution. In the field demonstration, contractors placed approximately 18,965 yd<sup>3</sup> (14,500 m<sup>3</sup>) of FSS grout in the mines over an eight-week period. Using off-the-shelf equipment that was easily transportable, they injected up to720 yd<sup>3</sup> (550 m<sup>3</sup>) of grout per day, pumping the grout more than 100 ft (30.5 m) at a time. The grout filled both dry and flooded portions of the mines, totaling about 5 a (2 ha). Using conventional low-strength concrete grout, past costs to stabilize underground coal mines at Petersburg Station had ranged from \$370,000/a (\$925,000/ha) above a railroad spur, to as much as \$520,000/a (\$1,300,000/ha) above a coal stockpile reclaimer. Using FSS grout, IP&L was able stabilize 3 a of underground coal mines for approximately \$56,000/a (\$140,000/ha) [28].

Borings confirmed that the FSS grout was in contact with the mine roof and provided grout samples that exhibited unconfined compressive strengths ranging from 99 to 460 psi (683 to 3174 kPa). The samples also had low permeability and showed no deterioration from contact with mine water. Monitoring revealed that the FSS grout had limited chemical effects on mine water, and no chemical effects on surrounding groundwater.

The key to success of any underground injection program is to evaluate various by-product/ash mix variables to optimize flow and strength development characteristics first at a laboratory scale. In the Petersburg project, many mixture variations were investigated ranging from 0.7 to 1.3 (Ash:FGD) and with a solids content ranging from 45 to 75% and a lime content of 0 to 10%. The results showed that strength development of the mix is dependent on the lime content being a minimum of 4% and that variations in the ash:sludge ratio over 50% had little impact [28].

In the Omega Mine Project in West Virginia [29], a coal mine had laid abandoned for over a decade and the AMD pollution coming out it had contaminated the local groundwater. In a joint program with the West Virginia Dept of Environmental Protection, the U.S. DOE, EPRI and local utilities funded a mine reclamation project to demonstrate the technical and environmental benefits of using a combination of 50% coal ash and 50% FBC residue to provide an alkaline material that would gain strength and fill the mine voids to block the formation of new AMD. Investigators conducted an extensive laboratory testing program to evaluate both fly ash and fluidized-bed combustion (FBC) ash as well as mixtures of the two for injection into an abandoned deep mine to reduce AMD. The test program indicated that a blend of the two candidate materials provided an acceptable grout mix. The FBC ash had the potential to provide strength to the grout while the fly ash enhanced the fluidity of the grout. The addition of 2% cement provided dimensional stability to the hardened grout. Ultimately, nearly 61,000 m<sup>3</sup> of CCP grout were injected into 10.4 ha (26 acres) of the mine. A grout barrier formed at the south boundary of the north lobe to prevent mine water from flowing down the relatively steep dip (9%) into the north lobe, which is the lowest portion of the mine. Investigators used the mine plan to select optimum locations for the injection holes; there was no set hole spacing. Due to the openness of some portions of the mine, grout moved laterally up to 457 m (1500 ft), primarily because of the relatively steep dip of the mine.

Testing of four grout core samples, recovered from the mine 9-10 months after injection, showed a permeability range of  $6.2 \times 10^{-7}$  to  $8.9 \times 10^{-8}$  cm/sec. The hardened grout has proven relatively impervious and, with its dimensional stability, should encapsulate acid-forming materials and greatly reduce future AMD formation.

Injection of CCP grout, as performed during this project, resulted in virtually complete filling of the mine voids, which provided excellent subsidence control. The fact that the hardened grout was found to have significant unconfined compressive strength coupled with a low permeability indicates it will provide good roof support while resisting passage of water, thereby limiting the potential for chemical degradation.

Details of this mine reclamation demonstration can be found in the EPRI final report [28].

# 5 CONCLUSIONS

Utilization of the by-products from the clean coal combustion processes that have developed over the last two decades is progressing, although at a slow rate. Although many different avenues for use of these newly emerging by-products do exist, there are many barriers that need to be overcome. The barriers can be regulatory, economic or technical. This paper has focused on the technical aspects of what has been done to develop the potential reuse applications.

The economic and technical feasibility of using CCT by-products in agriculture and in land reclamation has been investigated in multi-year research projects in several places during the last decade; however, it still is limited by local and regional factors such as the transportation constraints and insufficient support by the regulatory agencies and agricultural "establishments" in each State. Specific land use applications include: (1) soil amendments, (2) erosion control, (3) revegetation, and (4) land reclamation. The use of combinations of organic wastes and CCT by-products appears to be technically feasible for use in agriculture and horticulture. The synergistic waste candidates include: (1) digested sewage sludges, (2) poultry litter, (3) cattle manure, (4) pulp and paper mill wastes, (5) canning wastes, (6) and other food processing wastes.

The use of CCT by-products for stabilization of soil or for waste stabilization has been evolving. The alkaline nature of the CCT material makes it a "natural" for this type of application.

Utilization of CCT by-products to prevent mine subsidence and ameliorate acid mine drainage contamination has been demonstrated at full-scale with positive results. Whether or not this reuse application will continue to develop is dependent on how the US EPA will regulate the reuse of CCTs in underground mines below the groundwater table. This issue was not resolved in the April 2000 regulatory determination.

Overall the future for the reuse of CCT by-products looks promising. As more facilities are placed in service that generate these type of materials there will be more opportunities to match materials with markets.

Getting information to potential end-users of these by-products is critical to the success of getting these materials in new products. The Industrial Minerals Branch of the Office of Minerals Information (formerly the U.S. Bureau of Mines) at the USGS has developed a Geographic Information System (GIS) that can be used to provide information on the availability and proximity of FGD by-products and potential markets, such as wallboard plants, portland cement industries, and AMD problem areas. Hopefully this GIS system can be expanded to include all CCT by-products [41].

# **6** ANNOTATED BIBLIOGRAPHY/REFERENCES

1. *Composition and Leaching of FBC Wastes at the Alliance Test Facility*, EPRI Report: CS-3715, November 1984, 114 pages.

In 1979, EPA tests at the EPRI/Babcock & Wilcox facility in Ohio provided data on the chemical and physical properties of fluidized-bed combustion waste. In 1983 another series of tests was conducted using the latest FBC technology. The results documented in this report, offer a useful comparison with earlier FBC-waste information.

2. Advanced SO<sub>2</sub> Control Solid Waste Management Planning Study, EPRI Report CS-4402, February 1986, 260 pages.

A survey of test facilities and a review of the literature revealed that the characteristics of solid wastes from several advanced SO2 control technologies differ fundamentally from those of conventional coal-fired plants. Those differences may call for modifications in utility waste management and operating approaches.

3. *Advanced SO*<sub>2</sub> *Control By-Products Literature Survey*, EPRI Report CS-5076, April 1987, 336 pages.

A literature survey of solid-waste management systems indicates that currently available information is inadequate to design required waste management systems or to evaluate uses for solid by-products from advanced SO2 control systems. This overview of present practices provides a focus and a starting point for future coal combustion waste management research.

4. *Utilization of Advanced SO*<sub>2</sub> *Control By-Products,* Interim Report, EPRI Report CS-5269, June 1987, 292 pages.

Using results of literature surveys and preliminary market assessments, this report evaluates potential applications for advances SO<sub>2</sub> control by-products. Investigators formed their evaluations by comparing the marketability of these by-products with that of coal ash and wet scrubber sludge.

5. Evaluation of TCLP Test for Utility Wastes, EPRI Report CS-5355, August 1987, 104 pages.

EPA has proposed a new method to determine waste toxicity. To evaluate this method, EPRI has conducted an extensive physical and chemical characterization of a wide range of coal combustion waste samples. This study examined 43 utility wastes to compare the performance of the new and the old tests.

Annotated Bibliography/References

6. *Calcium Spray Dryer Waste Management Design Guide*, EPRI Report CS-5312, September 1987, 616 pages.

This report presents guidelines for designing and operating waste management subsystems, including waste transfer, storage, and disposal, associated with calcium spray drying. Conceptual designs for both new and retrofitted systems showed levelized costs of \$14 to \$18/t of disposed waste as compared to \$9/t for conventional fly ash and \$12/t for scrubber sludge disposal.

7. Sampling and Analytic Protocol for Advanced SO<sub>2</sub> Control By-Products, EPRI Report CS-5625, February 1988, 380 pages.

The EPRI effort to develop waste management design guidelines includes the physical and chemical characterizations of wastes produced by advanced clean coal technologies. Methodology and quality assurance procedures developed here can ensure the accuracy of chemical, physical, and engineering data.

8. Laboratory Characterization of Advanced SO<sub>2</sub> Control By-Products: Spray Dryer Wastes, EPRI Report CS-5782, May 1988, 240 pages.

An extensive laboratory investigation studied wastes collected from seven US spray dryer units. The data provide important physical and chemical characteristics and engineering properties of waste for evaluating waste disposal and reuse options. The analysis included the EPA extraction procedure and TCLP tests.

9. Laboratory Characterization of Advanced SO<sub>2</sub> Control By-Products: Furnace Sorbent Injection Wastes, EPRI Report CS-5783, May 1988, 192 pages.

An extensive laboratory investigation studied wastes collected from three limestone and two lime injection processes. The data provide important physical and chemical characteristics and engineering properties of waste for evaluating waste disposal and reuse options. The analysis included the EPA extraction procedure and TCLP tests.

10. Advanced SO<sub>2</sub> Control By-Product Utilization, Laboratory Evaluation, EPRI Report CS-6044, September 1988, 356 pages.

Dry wastes from  $SO_2$  control processes have high potential for marketing as road base, soil and sludge stabilization materials, and grout products. This report decscribes the technical and economic feasibility and performance of samples from five  $SO_2$  technologies and identifies those with the most promise for offsetting utility waste disposal costs.

11. Atmospheric Fluidized-Bed Combustion Waste Management Design Guide, EPRI Report CS-6053, December 1988, 704 pages.

Addressing such issues as waste transfer, storage, pretreatment, conditioning, transport, and disposal, these technical guidelines can help utilities design and operate waste management systems for the by-products of atmospheric fluidized-bed combustion (AFBC). The report

includes conceptual designs for calculating the economic impact of such systems on AFBC economics.

12. Furnace Sorbent Injection Waste Management Design Guide, EPRI Report GS-6382, June 1989, 720 pages.

Addressing such issues as waste transfer, storage, pretreatment, conditioning, transport, and disposal, these technical guidelines can help utilities design and operate waste management systems for the by-products of furnace sorbent injection systems. The report includes conceptual designs for calculating the economic impact of such systems overall process economics.

13. Sodium Injection Waste Management Design Guide, EPRI Report GS-6486, September 1989, 685 pages.

Addressing such issues as waste transfer, storage, pretreatment, conditioning, transport, and disposal, these technical guidelines can help utilities design and operate waste management systems for the by-products of sodium injection systems. The report includes conceptual designs for calculating the economic impact of such systems overall process economics.

14. Laboratory Characterization of Advanced SO<sub>2</sub> Control By-Products: Dry Sodium and Calcium In-duct Injection Wastes, EPRI Report GS-6622, December 1989, 240 pages.

An extensive laboratory investigation studied wastes collected from both sodium and calcium based in-duct injection processes. The data provide important physical and chemical characteristics and engineering properties of waste for evaluating waste disposal and reuse options. The analysis included the EPA extraction procedure and TCLP tests.

15. Commercialization Potential of AFBC Concrete: Part 2, Mechanistic Basis for Cementing Action, EPRI Report GS-7122, January 1991, 132 pages.

This report explores the mechanism by which binding occurs in AFBC concretes and focuses on their potential commercialization. Testing was done on six fly ashes and three AFBC residues from three different plants. The report documents chemical characterization and microstructural analysis at ten different curing stages.

16. Properties of Pressurized Fluidized-Bet Combustion Ashes, EPRI Report TR-101209, January 1993, 140 pages.

This report presents laboratory data on the rheological, electrical, and chemical properties of ashes at high temperature and pressure from three PFBC plants.

17. Laboratory Characterization of Atmospheric Fluidized-Bed Combustion By-Products, EPRI Report TR-105527, Sep 1995, 300 pages.

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