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A Review of Agricultural and Other Land Application Uses of Flue Gas Desulfurization Products

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Technical Update, March 2006

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PRODUCT DESCRIPTION

The production of flue gas desulfurization (FGD) products, especially FGD gypsum, is expected to increase substantially over the next ten to twenty years in response to clean air initiatives. There are a large number of agricultural and other land application uses of FGD products that have received previous research and development attention, but only in specific locations of the United States and under limited conditions of crops, climate and soil types. This report discusses current and potential future uses for FGD gypsum and other products in these applications, and provides recommendations for increasing use.

Results and Findings

A thorough review of the research literature identified several beneficial uses for FGD products in agricultural applications. When properly applied, FGD products can be used to favorably modify both the chemical and physical characteristic of soils, resulting in healthier growing environments and increased crop yields. The development of some FGD materials use is technologically advanced while other uses have not yet been initiated or are at the seed stage. The use of FGD gypsum to enhance no-tillage crop production, and the use of FGD materials as nutrient sources (primarily Ca and S), are the most mature applications at present.

Currently less than 200,000 metric tons of FGD gypsum are used annually for agricultural applications. The potential market for this use is very large, possibly as high as or exceeding 10 million metric tons of FGD products. The primary barriers to increased use are clear demonstrations of benefits, acceptance by the end-user, transportation costs, and uncertain regulatory status.

The report highlights several focal points for future research, based on applications with the highest potential for increased use of FGD gypsum. In general, the primary needs are demonstration of the benefits in a variety of geographic regions and soil types, and communication of these benefits to the end-users and regulatory bodies. Specific research areas include: (1) increased crop production by reducing subsurface acidity, (2) enhanced no-tillage crop production, (3) surface applications after tillage for increasing crop production in heavy clay soils, (4) weathering effects during FGD storage, (6) long term impacts to soils and groundwater of FGD applications at recommended agricultural rates, and (7) concentrations and fate of Hg and other trace constituents in FGD materials that are land applied for beneficial uses.

Challenges and Objectives

Land application of FGD product involves placing the product in the terrestrial environment. Beneficial land application implies that the applied FGD product will improve the soil environment. Often, the primary intended benefit is to improve plant growth, but there may be other benefits to soil or water such as reduction of erosion, improved quality of runoff and/or leachate water, or improved internal drainage. The application rate must be sufficient to cause the soil improvement, but not so great as to constitute disposal of the FGD product. Probably the greatest challenge, once the research and technologies have been developed and proven, is to create networks for improved distribution, application, regulatory approval and educational exchanges. This will require a coordinated effort involving the research community, producers (utilities), regulatory agencies, and outreach groups.

Applications, Values, and Use

This report serves as a starting point for further development of agricultural markets for FGD products. The long-term goal is to develop beneficial use programs for FGD gypsum that include agriculture as a component of the overall use strategy. Barriers that often inhibit the use of FGD materials in agriculture are identified and discussed. This information will help utilities make more informed decisions with respect to the use of FGD materials in agricultural applications, and research needs to increase that use. Ideally, use in agriculture will be one component in a strategy that includes other markets, such as wallboard production, that may be sufficient to delay or greatly reduce the scale of new landfill space needs for FGD materials disposal.

EPRI Perspective

Expanding existing markets, and creating new demand, for FGD gypsum is a critical need for the utility industry. Utilities in the United States currently produce almost 11 million metric tons of FGD gypsum, most of which is used in wallboard. However, quantities of FGD gypsum are expected to double or triple as new wet scrubbers with forced oxidation are installed, and some older units are converted to forced oxidation. The increased quantities will likely result in surplus material due to saturation of the wallboard market, at least on a regional level. This report primarily targets use of FGD gypsum in agricultural applications, a largely untapped use with great potential for growth. A companion report (1010384) discusses current and potential uses of FGD gypsum in manufacturing applications, including wallboard.

Approach

The overall goal of this report is to create a document that will move forward the beneficial use of FGD materials to create win-win situations for all involved. A literature review was performed with the following objectives: (1) to provide a comprehensive examination of the benefits that can be obtained from land application of FGD materials, (2) to identify potential markets associated with land application, (3) to discuss barriers to increased land application uses of FGD materials, and (4) to propose research needed to overcome barriers. This report takes a systematic look at the various types of land application uses of FGD materials in terms of the potential FGD volumes that could be utilized, their readiness for the marketplace, description of best management practices and their potential environmental impact.

Keywords

Agriculture	FGD materials markets
FGD gypsum	Land application
FGD products	

ABSTRACT

The use of flue gas desulfurization (FGD) systems to reduce SO_2 emissions from power plants is expected to increase significantly, resulting in a concomitant increase in FGD products. For the purpose of this review, an FGD product is any material produced when SO_2 is captured during or after the combustion of a fuel such as coal, oil, or petroleum coke. The chemical composition of an FGD product is influenced by the type of coal, desulfurization process, and sorbent used in the desulfurization process.

This review takes a systematic look at the various types of land application uses of FGD materials in terms of the potential FGD volumes that could be utilized, their readiness for the marketplace, description of best management practices and their potential environmental impact. The overall goal is to create a document that will move forward the beneficial use of FGD materials to create win-win situations for all involved. Specific objectives of this review are (1) to provide a comprehensive examination of the benefits that can be obtained from land application of FGD materials, (2) to identify potential markets associated with land application, (3) to discuss barriers to increased land application uses of FGD materials, and (4) to propose research needed to overcome barriers.

The properties of the FGD material have a direct impact on potential use in agriculture, and those FGD properties most commonly captured for beneficial purposes are (1) ability to neutralize acid, (2) source of high amounts of soluble calcium and sulfate, (3) source of plant nutrients, and (4) uniform particle size. Land application uses of FGD materials are identified by matching the properties of the FGD material with improvement in some ecosystem function (or functions). For beneficial use, the change in ecosystem function is assumed to be positive.

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

1
INTRODUCTION

1.1 General Background

Combustion of fossil fuels for energy production releases sulfur dioxide (SO_2) at a rate proportional to the sulfur concentration in the fuel. Industrialized nations have adopted flue gas desulfurization (FGD) technology as a means to reduce sulfur dioxide emissions and, thus, their potential impact on the environment. Alcordo and Rechcigl (1995) provided a succinct introduction to the adoption of flue gas desulfurization technology by Japan, the Netherlands, Germany, and the United States. The initial driving force for using FGD technology in the United States was the Clean Air Act of 1970, which set primary ambient air standards for SO_2 and NO_x. The Clean Air Act Amendments of 1990 proposed reductions in SO_2 and NO_x emissions of 10 million Mg and 2 million Mg, respectively, by the year 2000 compared to 1980 levels. Future increases in production of FGD products will be driven by increases in installed electrical generating capacity using FGD processes and in retrofitting older coal-fired generators with FGD equipment (Bruce and Tackett, 2005).

1.2 Types of FGD Products

For the purpose of this review, an FGD product is any material produced when S is captured during the combustion of a fuel such as coal, oil, or petroleum coke. This includes fluidized bed combustion (FBC) ashes where S is captured directly in the furnace as well as products produced when S is removed from the flue gas at some downstream position from the furnace. Karatepe (2000) and Srivastava and Jozewicz (2001) reviewed various FGD processes including their technical advantages/disadvantages and economics. The various FGD technologies can be classified as either regenerable or once-through depending on the fate of the sorbent after it has captured SO_2. In a regenerable process, the spent sorbent is treated to cause release of SO_2 and then the regenerated sorbent is cycled back to the flue gas system to capture more SO_2. In a once-through process, spent sorbent containing SO_2 is disposed of as waste or used as a product. The various once-through processes are generally technically easier to operate or have greater S removal efficiencies than the regenerable processes with the result that the once-through processes have had greater commercial success. This review is primarily concerned with land application of products from various once-through FGD processes.

The once-through FGD technologies can be further classified as wet or dry. A wet process produces a wet slurry waste or product, and the flue gas leaving the absorbing tank is saturated with water. A dry process produces a dry waste or product, and the flue gas leaving the absorber is not saturated.

The chemical composition of any FGD product is influenced by the type of coal, desulfurization process, and sorbent used in the desulfurization process. It is also influenced by the location where fly ash is removed from the flue gas stream. Coal type or rank determines the ranges of S concentration, ash percentage weight, and ash composition. For example, western subbituminous coal averages 0.48% S, 7.9% ash, 1.4% Ca, and 1.0% Fe, but Gulf Coast lignite averages 1.39% S, 23.6% ash, 3.3% Ca, and 2.0% Fe (Pavlish et al., 2003). The S concentration influences the choice of desulfurization process used to meet air quality standards. Ash percentage weight and ash composition directly affect concentrations of trace and other elements in the FGD product if the fly ash is blended with the desulfurization products. There are also specific interactions between elements that influence the composition of FGD products. For example (Sondreal et al., 2004), the Cl content of coal influences the oxidation status of Hg and whether Hg is trapped in the FGD product (for Hg^{2+}) or passes out in the flue gas (for Hg^0). Eastern and midwestern bituminous coals that contain approximately 1000 mg Cl kg^{-1} tend to have higher levels of Hg oxidation with concomitant greater capture of Hg in the FGD product. The reverse is true for western subbituminous and lignite coals that average 100-200 mg Cl kg^{-1}. High concentrations of Ca and other alkaline components of coal ash tend to impede Hg oxidation.

Flue gas desulfurization processes occur at different temperatures that influence the mineralogy of the FGD products. In a comparison of dry FGD processes (Bigham et al., 2005), FGD products from duct injection and spray dryer processes that operate at relatively low temperatures were dominated by portlandite [$Ca(OH)_2$] and hannebachite ($CaSO_3 \cdot 0.5\ H_2O$) but contained no anhydrite ($CaSO_4$). Fluidized bed combustion (FBC) and lime injection multistage burner (LIMB) processes that operate at relatively high temperatures were dominated by anhydrite with no hannebachite and little portlandite.

The chemical composition of FGD products is also dependent on the type of sorbent used. If lime or limestone ($CaCO_3$) is the sorbent, the resulting FGD products are relatively pure $CaSO_3$, relatively pure $CaSO_4$, or a mixture of $CaSO_3$ and $CaSO_4$ with varying amounts of unreacted sorbent. If dolomitic limestone [$CaMg(CO_3)_2$] is the sorbent, various Mg compounds [MgO and $Mg(OH)_2$] will also be present in the product. Some processes include a sodium sulfite sorbent. A wet FGD process using ammonia sorbent produces $(NH_4)_2SO_4$ product. This process is not used widely because of the expense of the sorbent (Karatepe, 2000). A commercial coal gasification plant in North Dakota using an ammonia sorbent system produces fertilizer grade ammonium sulfate (Wallach, 1997).

Wet FGD processes using lime or limestone sorbent are classified according to the extent of calcium sulfite oxidation (Srivastava and Jozewicz, 2001). In a natural oxidation process, the FGD product is a mixture of $CaSO_3$ and $CaSO_4$ and is difficult to dewater. Gypsum scale forms during natural oxidation when the slurry oxidation level (fraction of $CaSO_4$ in the slurry) is greater than 15%. In limestone forced oxidation, air is blown into the reaction tank to force oxidation of $CaSO_3$ to $CaSO_4$. Removal of the gypsum from the slurry decreases the oxidation level in the slurry recycled to the absorber, which minimizes scaling. The gypsum produced in the limestone forced oxidation process is relatively easy to dewater. In limestone inhibited oxidation, sodium thiosulfate or elemental S is added to prevent oxidation of $CaSO_3$ to $CaSO_4$. The waste produced by the limestone inhibited oxidation process is easier to dewater than wastes from the natural oxidation process (Srivastava and Jozewicz, 2001).

Coal-fired boilers produce two basic types of particulate waste products independently of the presence of a flue gas desulfurization system. Bottom ash is coarser and falls to the bottom of the furnace. Fly ash is finer and is carried out of the furnace in the flue gas. Fly ash is removed from the flue gas stream by an electrostatic precipitator (ESP), cyclone, or other device. The trace element composition of any FGD product is influenced strongly by whether the fly ash is removed from the flue gas stream before or after the desulfurization reactions occur. In wet FGD processes, the fly ash is often (usually) removed in the ESP before the SO_2 is removed in the absorber. The wet waste or product from the SO_2 absorber contains little or no fly ash and therefore has relatively low concentrations of trace elements. Because the wet products resulting from the limestone inhibited oxidation and limestone natural oxidation processes are difficult to dewater, fly ash is often added back to these materials to improve handling characteristics.

In dry FGD processes, the desulfurization reactions occur in some part of the boiler (furnace, economizer, duct) usually before the flue gas passes through the ESP, and the mixture of desulfurization reaction products and fly ash is removed in the ESP. Fluidized bed combustion (FBC) systems burn coal in a bed of limestone or dolomite that reacts with the SO_2 released during combustion. The coal and limestone bed is fluidized by blowing air through the bed. The resulting bottom and fly ashes each contain products of the desulfurization reactions. It is not feasible to separate the desulfurization products from the fly ash in an FBC boiler because both products are produced together in the furnace. In spray dryer absorption, a lime slurry is dispersed into the flue gas and reacts with the SO_2. The reaction products undergo drying and are then removed by the ESP or other particulate control device. It is feasible to remove the fly ash from the flue gas stream before it enters the spray dryer absorber.

The desirability of blending fly ash with any FGD product depends primarily on the relative concentrations of various trace elements in the fly ash. It is possible that adding a small amount of fly ash, as is often done to the wet FGD products resulting from the limestone inhibited oxidation and limestone natural oxidation processes, will increase the desirable trace element content of the mixture and improve its potential as a soil amendment. However, adding a larger amount could lead to excessive concentrations of undesirable trace elements in the mixture. The usual goal of blending fly ash with these wet FGD products is to produce a mixture with improved physical handling characteristics and blending is generally done without regard for the chemical composition of the mixture. There may be limited flexibility when blending fly ash with wet FGD product because there is a minimum amount of fly ash that must be added to improve handling characteristics. The greatest flexibility in blending fly ash with FGD product occurs for dry FGD processes where the fly ash is removed from the flue gas stream before the stream enters the desulfurization process. In this case fly ash could be added to the dry FGD product in desired proportions to achieve various trace element compositions. The possible greater expense of blending only a fraction of the fly ash with the dry FGD product, and thus handling the remainder of the fly ash separately, could be offset by having a product with greater potential for land application and reducing the amount of mixture that must be disposed in landfills. Fisher and Franciosi (1997) noted that when fly ash was removed before a flue gas entered a spray dryer system the resulting FGD residue was clean enough to compete with other calcium sources as an amendment for peanuts (*Arachis hypogaea* L.).

1.3 Production of FGD Products

Coal combustion products are generated predominantly by the electric utility industry and account for more than 90% of all fuel combustion wastes produced in the United States. The quantity of coal combustion products created each year in the United States is slightly less than the amount of sand, gravel and crushed stone and more than Portland cement and iron ore. According to the 2004 survey by the American Coal Ash Association (American Coal Ash Association, 2005), more than 111 million Mg (metric tons) of coal combustion products—including fly ash, bottom ash, boiler slag and various FGD products—were produced in the United States. With many electric utilities in the United States in the process of bringing new scrubbers on-line, the amount of FGD product that will be created in the future will greatly increase.

This report focuses specifically on FGD products that have been classified into four different categories by the American Coal Ash Association (American Coal Ash Association, 2005). These types include FGD wet scrubber products, FGD dry scrubber products, FGD gypsum and FGD other. The trend in production of each of these FGD products for 2002-2004 is shown in Figure 1-1.

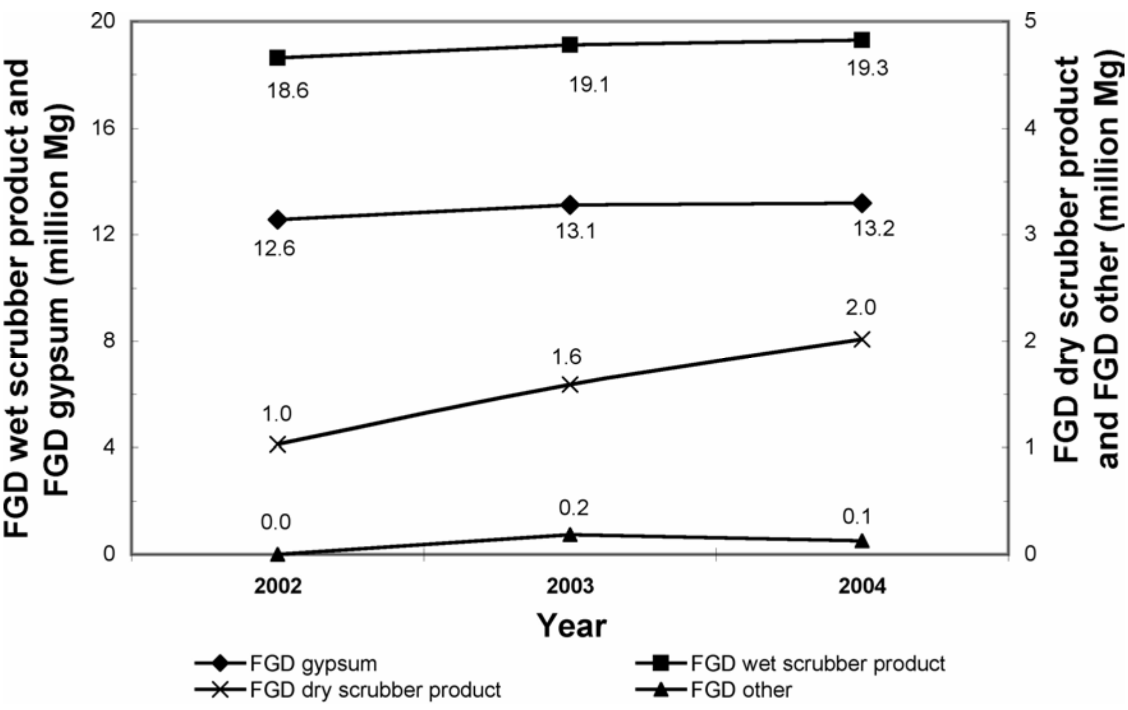


Figure 1-1
Changes in Production of Various Types of FGD Products from 2002-2004 (ACAA, 2005).

For FGD products in 2004, approximately 28.5 million Mg were produced in the United States, but only 9.45 million Mg (33%) were beneficially recycled and utilized. Most of this use involved FGD gypsum for wallboard manufacture and approximately 76% of all FGD gypsum was beneficially used in some way in 2004 (Figure 1-2). Beneficial use of other FGD products has lagged behind that of FGD gypsum. Fortunately, FGD gypsum is the product that has the greatest potential for both increased production and increased use.

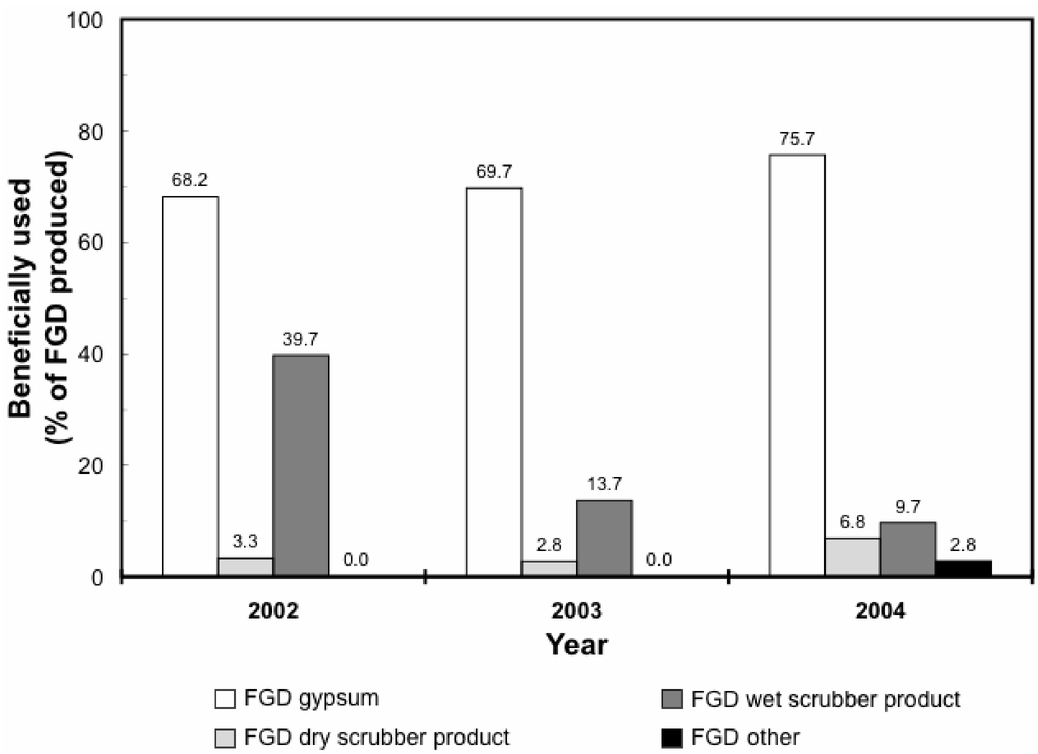


Figure 1-2
Changes in Percentage of Beneficial Use of Various Types of FGD Products from 2002-2004 (ACAA, 2005).

1.4 Definition of Beneficial Land Application Uses of FGD Products

Land application of FGD product involves putting the product on land (i.e. the terrestrial environment). Beneficial land application implies that the applied FGD product will improve the soil environment. Often, the primary intended benefit is to improve plant growth, but there may be other benefits to soil or water such as reduction of erosion, improved quality of runoff and/or leachate water, or improved internal drainage. The application rate must be sufficient to cause the soil improvement, but not so great as to constitute disposal of the FGD product.

For many land application uses of FGD products the appropriate rates can be determined from well-defined principles of soil and agronomic science. Examples include the use of FGD product as a liming agent, as a source of Ca for reclamation of a sodic soil, or as a source of S for plant nutrition. In these examples, application at a rate greater than predicted necessary would constitute disposal and could be harmful, as when overliming with FGD product reduces soil availability of plant nutrients. This is similar to what happens for other types of agricultural inputs, such as nitrogen fertilizer, if applied at excessive rates. For some uses of FGD products, such as to modify a soil physical property, the appropriate rate may be less obvious but still may be approximated. If best estimates are that FGD product should be applied and mixed with soil to constitute 5 to 15% of the soil volume, the uncertainty in the appropriate rate would suggest that a rate as high as 25% of the soil volume might be justified. Then application at a rate to constitute 30% or more of the soil volume would represent disposal. For still other uses, such as FGD product as a component of a synthetic soil mix, there may be no guiding principles as to appropriate rate and the rate may depend on other component(s) in the mix. In these cases the appropriate rates must be determined from specific experiments.

1.5 Potential of FGD Products for Land Application Uses

Land application uses of FGD products are identified by matching the properties of the FGD product with improvement in some ecosystem function (or functions). For beneficial use, the change in ecosystem function is assumed to be positive. For example, an FGD product with a high acid neutralization capacity has the potential to affect the ecosystem function of soil pH and thus beneficially improve the productivity of soils with low pH. In the end, however, all of the properties of the FGD product must be considered to define its use in terms of recommended application rates, environmental impact and economic return.

Some of the properties of FGD products that can be captured for beneficial land application uses are summarized in Table 1-1. There has been little effort, to date, to research and develop these uses and create markets for FGD products. In 2004 the U.S. production of FGD gypsum, which is just one type of FGD product, was 10.8 million Mg (American Coal Ash Association, 2005) and approximately 76% of this gypsum was utilized. However, only 1.4% (or 0.12 million Mg) of this amount was used in agriculture. There is great potential to expand land application uses of FGD products and thus open up valuable new markets. For example, if 10 million Mg of FGD product were produced annually and applied to land at 2 Mg ha^{-1} it would treat only 3.5% of the total cropped land (excluding pasture and rangeland) in the U.S. (Ritchey et al., 2000).

1.6 Need to Develop a Comprehensive Review of FGD Use in Agriculture

Although there is recognition of the potential of using FGD products in agriculture, there is also uncertainty whether this use is sustainable. Currently, there is a general lack of acceptance in the agricultural community for using FGD products. This barrier can only be overcome by sound knowledge that, in some cases, already exists in the scientific and technical literature. Where such knowledge is lacking, research will be needed to provide the information.

This review takes a systematic look at the various types of land application uses of FGD products in terms of the potential FGD volumes that could be utilized, their readiness for the marketplace, description of best management practices and their potential environmental impact. The overall goal is to create a document that will move forward the beneficial use of FGD products to create win-win situations for all involved.

Table 1-1
Beneficial Properties of FGD Materials for Land Application Uses

Property of FGD Product Providing Benefit for Land Application Uses	Description of Benefit
Ability to neutralize acid	Increases soil pH in soils when used as a liming substitute; Neutralizes existing acid and prevents new acid formation from pyrite oxidation at mine sites.
Source of high amounts of soluble calcium and sulfate	Sulfate complexes with subsoil aluminum and reduces its toxicity leading to improved plant root growth; Improves aggregation of soil particles and thus water infiltration and percolation in dispersive soils and improves no-tillage crop production in heavier clay soils; Reclaims sodic soils by replacing exchangeable sodium ions with calcium so that the soil's physical properties (i.e. aeration and water infiltration) are improved; Soluble Ca precipitates P in soils with high concentrations of P improving the quality of water runoff.
Source of plant nutrients	Increases plant growth and harvestable yield by supplying essential plant nutrients; Improves N uptake by increased rooting in the subsoil and overcoming crop S deficiencies.
Uniform particle size	Provides a more suitable medium for plant growth when used in greenhouse and nursery mixes.

1.7 Specific Objectives of This Review

Specific objectives of this review are: (1) to provide a comprehensive examination of existing and new land application uses of FGD products, (2) to identify amounts of FGD products that can be used in these applications, (3) to identify barriers to increased land application, (4) to identify marketing opportunities of FGD products for land application uses, and (5) to propose research needed to overcome limitations and barriers that restrict the expanded use of FGD products for land application uses.

2 BENEFITS OF FGD MATERIALS FOR LAND APPLICATION USES

The primary beneficial function of FGD material when applied to land is to improve one or more soil physical or chemical conditions. Some major benefits of land application of FGD materials include reduction of soil acidity, increasing availability of nutrients to plants and animals, improving soil physical properties, improvement of water quality by reducing P transport, amelioration of sodic soil problems, reclamation of mined lands or degraded industrial sites, and as a component of synthetic/artificial soils for nursery, greenhouse, or sod farm use. When used in a specific environment, an FGD material will likely impact more than one intended soil chemical and physical condition, e.g. amelioration of sodic soil by FGD gypsum involves changes in both soil physical and chemical conditions.

The potential uses of an FGD material depend on its chemical and physical properties. The benefits these properties can provide to a soil must be matched with the need of the soil for that property. For example, an FGD material that is a mixture of gypsum and unreacted lime has different potential beneficial land application uses than a material that is essentially only gypsum or ammonium sulfate. A mixture of gypsum and unreacted lime can be used to treat both Al toxicity (gypsum) and soil acidity (unreacted lime), but a pure gypsum material would only be effective against Al toxicity. The blending of fly ash with an FGD material will also influence its ability to serve as a source for some trace elements such as boron.

The effects of adding an FGD material to a soil will also depend on the characteristics of the soil. In this review the soil used in each study is identified, if known, by series name and classification into subgroup category. For example in a study using a Baltimore soil (Mollic Hapludalf), “Baltimore” is the series name and “Mollic Hapludalf” is the subgroup category. A brief introduction to soil classification and references and links to further information are given in the glossary at the end of the review.

Carlson and Adriano (1993) have reviewed early studies of land application of FGD materials. Dick et al. (2000), Ritchey et al. (2000) and Clark et al. (2001) have discussed benefits and constraints of using the materials for land applications. A more complete review of studies that relate to beneficial land application uses is provided below.

2.1 Reduction of Surface Soil Acidity

There is a close association between soil pH and plant availability of essential plant nutrients (Figure 2-1). Nutrients are generally most available for plant uptake when the soil pH is near neutral. Some nutrients, however, such as Mn and Fe are more available as the soil pH decreases and becomes more acidic. Then there are nutrients such as Mg and Mo that are generally more available as soil pH becomes slightly alkaline.

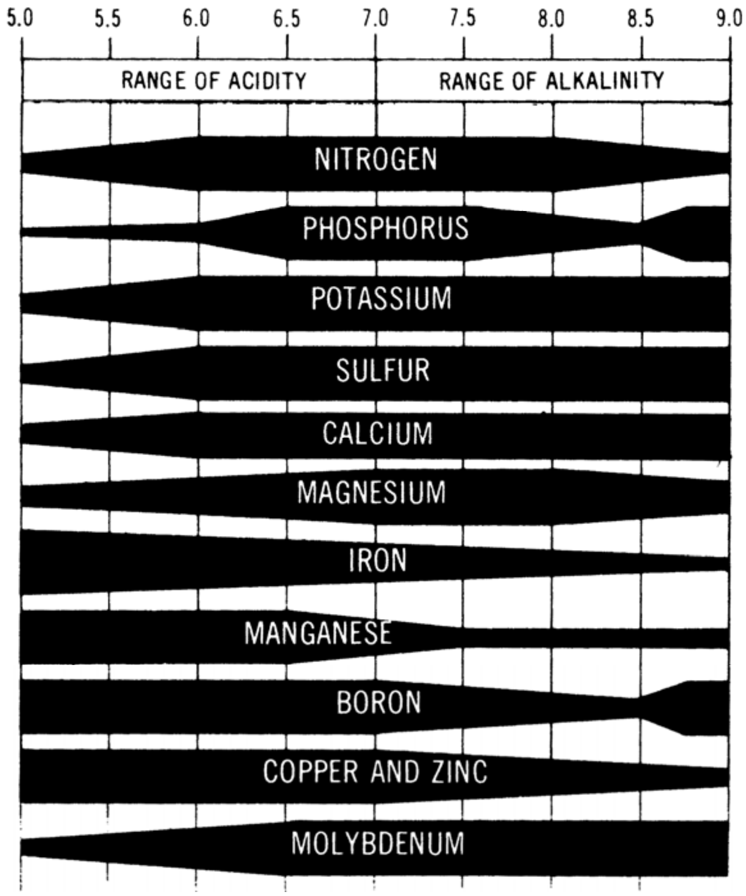


Figure 2-1
Relative Availability of Elements Essential to Plant Growth at Different pH Levels of Mineral Soils.

Basic cations, such as Ca and Mg, are depleted in acid soils because they are replaced on the soil's cation exchange sites with H^+ and Al^{3+} and subsequently leached from soil. If the rate of removal exceeds their formation through natural soil formation processes, the soil will become deficient in these basic cations. Many of the micronutrients (i.e. Fe^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}) are highly soluble at low pH. In acid soils their availability may reach levels that are toxic to plants. In addition, soluble Fe, Al and Mn can interact with other essential plant nutrients such as P and lead to P deficiencies. Overliming a soil will also lead to problems as the high pH precipitates many metals required for plant growth making them extremely unavailable. For example, Fe can become severely deficient in high carbonate soils with high pH. Calcium will also react with phosphate to reduce its availability. Thus, in general, the optimum soil pH for support of good crop productivity is between 6 and 7. However, agricultural plants differ in their ability to tolerate acid soil conditions (Table 2-1).

Table 2-1
Relative Acid Sensitivity of Some Agricultural Plants (Singer and Munns, 2002)

Sensitivity	Plants affected
Highly sensitive	Alfalfa, common bean, peas, red clover, crown vetch, *Leucaena*, spinach, cotton
Sensitive	Cabbage, wheat, soybean, white clover, sorghum
Moderately sensitive	Peanut, potato, oats, rice, rye, corn
Tolerant	Pineapple, tea, coffee, blueberry

A distinction can be made between the use of FGD material to reduce surface soil acidity and increase pH due to its residual lime content and to mitigate toxic levels of Al^{3+} (primarily subsoil Al^{3+}) due to a high content of relatively soluble gypsum. A material that contains both unreacted lime and gypsum could have both effects, but an FGD material of relatively pure gypsum would only mitigate toxic Al^{3+} concentrations.

A number of studies have focused on using the liming potential of FGD materials to reduce surface soil acidity and improve plant growth on agricultural soils and mined lands. In these cases, the ability of the FGD material to neutralize acidity [i.e. hydrogen (H^+) ions] is most important. The illustration below (Figure 2-2) describes how a liming agent, in this case $Ca(OH)_2$, reacts with H and Al ions to remove them from the soil solution and from the soil's cation exchange capacity (CEC) sites, thus improving the soil's fertility and ability to promote good crop growth.

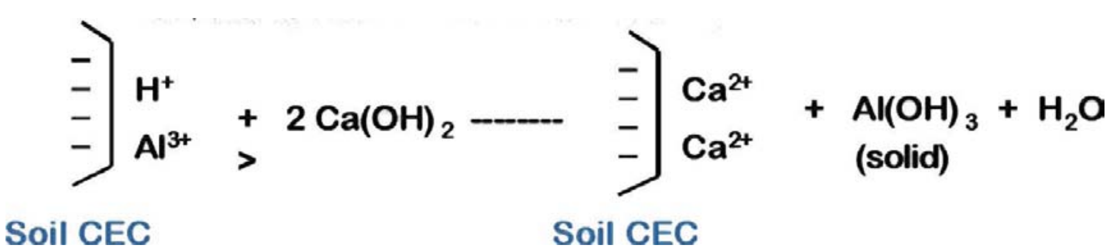


Figure 2-2
Role of Liming Material to Neutralize Soil Acidity. Calcium Ions (Ca^{2+}) Replace H^+ and Al^{3+} on the Soil Cation Exchange (CEC) Sites and the Products Created are Water (H_2O) and Aluminum Oxide [$Al(OH)_3$]. (Illustration Kindly Provided by Dr. Jerry Bigham, The Ohio State University, Columbus, OH.)

Marsh and Grove (1992a) compared an FBC ash with laboratory grade $Ca(OH)_2$ and agricultural lime (i.e. $CaCO_3$) for effectiveness in liming an acid Maury silt loam soil (Typic Paleudalf, pH 4.75) in the greenhouse. The ash was derived from the combustion of petroleum coke with calcitic and dolomitic sorbents. The three materials were applied at rates equivalent to 0.0, 0.33, 0.67, 1.0 and 1.33 times (X) the soil's lime requirement (LR). Soil pH at the 1.0X LR rate was 5.7 for FBC ash versus 5.2 for ag lime and 5.8 for $Ca(OH)_2$. Tobacco (*Nicotiana tabacum* L.) and corn (*Zea mays* L.) grew as well on ash-amended soil as on soil amended with the other materials. For all three materials, growth was best at the 0.33X LR rate and then gradually decreased with increasing liming rate.

In a greenhouse study, Stehouwer et al. (1996) mixed three dry FGD materials with acidic Wooster silt loam soil (Oxyaquic Fragiudalf) at rates up to 28 g kg^{-1}. The materials were limestone injection multistage burners (LIMB) ash and fly ash and bed ash from a pressurized FBC (PFBC) boiler. The LIMB ash was produced using a hydrated lime [$Ca(OH)_2$] sorbent and the two PFBC ashes were derived from a dolomite sorbent. All three FGD products increased soil pH from 4.5 to approximately 7.5. Alfalfa (*Medicago sativa* L.) yields for six harvests were generally increased by FGD ash application except for suppression during the first two harvests at the highest amendment rates. The early yield suppression for alfalfa was strongest for LIMB ash and was attributed to initial high pH (>8). The yield suppression with the PFBC materials was possibly due to high soluble salt concentrations. Tall fescue (*Festuca arundinacea* Schreb.) yield increases by FGD treatments were less than with alfalfa. There were no increases in plant tissue concentrations for any trace elements except B and Mo.

Clark et al. (1997) evaluated three FGD products for effects on individual growth of six forage species on a Lily soil (Typic Hapludult, pH 4.6). The forage species were orchardgrass (*Dactylis glomerata* L.), tall fescue, switchgrass (*Panicum virgatum* L.), eastern gamagrass (*Tripsacum dactyloides* L.), white clover (*Trifolium repens* L.), and alfalfa. Treatments included a high calcium sulfate FGD at rates up to 750 g kg^{-1}, a high calcium sulfate FGD enriched with $Mg(OH)_2$ at rates up to 250 g kg^{-1}, and a high calcium sulfite FGD at rates up to 60 g kg^{-1}. Maximum dry matter yields occurred for the high calcium sulfate FGD at 250 g kg^{-1}, the high calcium sulfate FGD with $Mg(OH)_2$ at 25 g kg^{-1}, and the high calcium sulfite FGD at 30 g kg^{-1}. Beneficial growth responses were greater for the two high calcium sulfate FGDs than for the high calcium sulfite FGD.

Stehouwer et al. (1999) applied magnesium-containing FBC ash at rates up to 2.0 times the lime requirement (2.0X LR) to a Wooster silt loam soil (Oxyaquic Fragiudalf, pH 4.6) and a Coshocton silt loam soil (Aquultic Hapludalf, pH 4.8). The maximum ash rate was 70 Mg ha^{-1} on the Wooster soil and 46 Mg ha^{-1} on the Coshocton soil. Ash was a 40:60 (w/w) mixture of bed ash and cyclone ash from a pressurized FBC boiler using dolomitic limestone sorbent. Soil pH within the depth of incorporation (0-10 cm) was increased to near 7.0 for at least two years after ash application. Corn grain yields were generally not affected by FBC ash during three years except for a slight decrease on the Wooster soil during the first (dry summer) year. Alfalfa yields were increased on both soils for all three years. The yield increase was steepest for FBC ash applied at 0.5X LR, but yields generally continued to increase with increasing ash rate up to 2.0X LR. Surface application of the magnesium-containing ash affected subsoil chemistry primarily through downward movement of Mg and SO_4. In the Wooster soil, which had relatively high exchangeable Ca in the subsoil, downward movement of Mg and Al decreased subsoil Ca and increased subsoil Al. In the Coshocton soil, which had relatively high exchangeable Al in the subsoil, downward movement of Mg and SO_4 decreased subsoil Al and increased subsoil Mg.

In a greenhouse study, Wright et al. (1998) added four coal combustion products at rates up to 80 g kg^{-1} to soil from the A horizon of a Baltimore soil (Mollic Hapludalf) or a Hagerstown soil (Typic Hapludalf). The coal combustion products were bed ash and fly ash from a fluidized bed combustion furnace, a mixed FGD material (calcium sulfite, calcium sulfate, calcium oxide, and fly ash), and a high gypsum FGD material. On the Baltimore soil, all products, except the FGD gypsum, increased soil pH from 5.4 to as high as 9.0 for bed ash. The FGD gypsum caused a slight decrease in soil pH. Fly ash increased yield of annual ryegrass (*Lolium multiflorum* Lam.) on both soils. The mixed and high gypsum FGD materials increased ryegrass yield on Baltimore soil but were not detrimental on Hagerstown soil. Bed ash at 40 or 80 g kg^{-1} decreased germination and yield on both soils by causing high alkalinity, high soluble salt conditions.

Punshon et al. (2001) applied FGD material to the surface of an Orangeburg soil (Typic Kandiudult) in outdoor mesocosms at rates up to 222 Mg ha^{-1}. The dry FGD material was produced using a hydrated lime sorbent and included fly ash as a component. Surface soil pH increased from 5.5 for untreated control to 8.1 for the highest rate of FGD material. The applications did not affect germination of corn, soybean [*Glycine max* (L.) Merr.], radish (*Raphanus sativa* L.), or cotton (*Gossypium hirsutum* L.), and all rates stimulated aboveground biomass of these species. A rate of 56 Mg ha^{-1} was considered optimum for beneficial effects on crop growth without detrimental effects on soil or leachate quality.

Chen et al. (2001) applied several types of FGD products at rates up to 2.0 times the soil's lime requirement (2.0X LR) in a field study on Wooster silt loam soil. The FGD products contained calcium sulfate, calcium hydroxide, fly ash, and either vermiculite or perlite. The highest FGD application rate was equivalent to 75.2 Mg ha^{-1}. In the second year after treatment, alfalfa yields for the 1.0X LR rate of FGD material were approximately 7 to 8 times greater than for the untreated control and 30% greater than the commercial ag-lime treatment. No soil contamination problems were observed even at the 2.0X LR rate of material.

In a greenhouse study, growth of Northern red oak (*Quercus rubra* L.) was increased significantly when FGD material derived from a dolomitic lime sorbent was surface applied or mixed within the A horizon of an acid forest soil (Rayne silt loam; Typic Hapludult, pH 4.4) (Crews and Dick, 1998). The FGD material was applied at rates up to 2.5 times the lime requirement (2.5X LR), where the lime requirement was 7.26 Mg ha^{-1}. The increase in growth compared to the untreated control was greatest (75%) for FGD material applied at the 1.5X LR rate. Four months after treatment, sulfur concentration in the soil leachate increased from less than 10 mg L^{-1} for control soil to 234 mg L^{-1} for soil treated at 2.5X LR.

2.2 Amelioration of Problems Associated with Subsoil Acidity

Various trials have involved application of pure or fairly pure FGD gypsum to ameliorate subsoil acidity. Plant root growth into the subsoil is increased, which allows plants to obtain water and nutrients from a larger volume of soil. This potentially increases plant yield. Shainberg et al. (1989), Sumner (1993), and Levy and Sumner (1998) provide detailed reviews of use of gypsum in agriculture to mitigate subsoil acidity and improve soil physical conditions.

The solubility of gypsum is about 200 times that of lime ($CaCO_3$) making it an ideal material to ameliorate subsurface toxic Al^{3+} concentrations brought about by low pH (i.e. subsurface soil acidity). The impact of the added gypsum is especially great if combined with application of limestone. Figure 2-3 shows corn root density in a soil treated either with limestone alone or with a combination of limestone and gypsum. The combination treatment is much more effective in promoting root growth. The mass of roots is not only greater but extends deeper into the soil. This allows the corn plant to explore more of the soil volume for plant nutrients and increases the amount of soil water that is available as roots explore deeper into the soil profile. The beneficial effect of the gypsum is due to complexation of the Al^{3+} with SO_4^{2-} (Figure 2-3). This reduces the impact of the Al, which strongly inhibits root growth, even though the pH of the soil has not changed. The potential result of increased nutrient and water uptake by the crop is to increase overall crop yield.

Gypsum source generally has little effect on the soil changes induced by gypsum application. Mined gypsum and various by-product gypsums from flue gas desulfurization, phosphorus fertilizer production, titanium dioxide production, or other chemical processes are equally effective when applied to soil as long as the gypsums are fairly pure. There is some evidence, however, that by-product gypsums may actually dissolve faster than mined gypsum and thus impart their benefit more quickly to the soil (Alcordo and Rechcigl, 1995). In this review, we include information from papers or reports that show the effects of gypsum application regardless of the gypsum source.

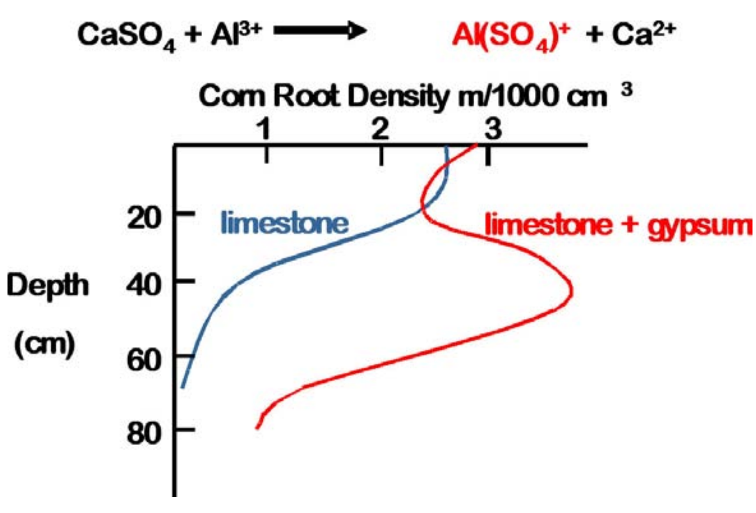


Figure 2-3
Role of Gypsum in the Amelioration of Soils Containing High Concentrations of Subsoil Toxic Al^{3+} Due to Acidic Conditions. (Illustration Kindly Provided by Dr. Jerry Bigham, The Ohio State University, Columbus, OH and Adopted from Farina and Channon, 1988b.)

Feldhake and Ritchey (1996) used a simplified approach to investigate the effects of FGD gypsum on subsoil acidity by growing plants in the subsoil only (pH 3.8 in 0.01 M $CaCl_2$) from a Lily soil (Typic Hapludult). They leached the subsoil with two rates of a saturated aqueous solution of a high gypsum FGD product. The quantities of gypsum in the leaching solutions were equivalent to surface applications of 5 and 25 Mg ha^{-1} if all the gypsum dissolved. Increases in water use and root growth of orchardgrass were correlated with decreases in soil aluminum saturation (35% or 62% decreases) resulting from the leaching treatments.

In a column leaching experiment, Wendell and Ritchey (1996) added FGD materials (containing very little fly ash) to a mixture of the A and B horizons of a Porters silt loam soil (Typic Dystrudept). A high gypsum material at rates up to 100 g kg^{-1} and a primarily calcium sulfite FGD material at rates up to 20 g kg^{-1} were either incorporated into the soil or added to the soil surface. Treated soil columns were leached by 90 cm of water equivalent to one year of local rainfall. Amount of Al leached varied with type of FGD material, rate, and method of application. Total amount of Al leached varied from 0.10 mmol for untreated control to 2.61 mmol for 10 g kg^{-1} of high gypsum FGD material incorporated into the soil. Application of FGD products decreased leachate pH but increased bulk soil pH. Root lengths of sudangrass [*Sorghum bicolor* (L.) Moench] grown four days in the leached soils were up to 3.1 times the control length for high gypsum material and 4.4 times the control length for calcium sulfite FGD material.

Gypsum (not from FGD) was applied at 10 Mg ha^{-1} to a Normandien clay loam soil (Plinthic Paleudult, subsoil pH < 4.55) that also received 15 Mg ha^{-1} of dolomitic lime (Farina and Channon, 1988a; Farina and Channon, 1988b). Various deep tillage treatments were also combined with the standard lime application. Average corn grain yield for three years was significantly greater for the gypsum + lime treatment (7301 kg ha^{-1}) than for lime alone (6158 kg ha^{-1}). Yield for the gypsum + lime treatment was also significantly greater than 7 of 9 treatments (yields of 6100 to 7210 kg ha^{-1}) combining deep tillage with lime. Gypsum application produced a marked increase in rooting density between 0.40 and 0.60 m soil depth, but also caused decreased rooting between 0.20 and 0.40 m.

Marsh and Grove (1992b) applied FBC ash or agricultural lime to an acid Trappist silt loam soil (Typic Hapludult, pH 4.2) at rates equivalent to 0.0, 0.5, 1.0, and 1.5 times the soil lime requirement (LR) of 6.72 Mg ha^{-1}. This study did not involve gypsum application but it is included here because the focus was on subsoil chemistry and rooting. After 15 months, soil pH in the 0-15 cm depth was increased to at least 6.5 by the higher rates of FBC ash compared to 5.4 for ag-lime. There were no “self-liming” effects at lower depths due to sulfate replacing Al-bound hydroxyl ions. Calculated soil solution Al^{3+} activity in the 15-30 cm depth was lower for ag-lime than for the higher rates of FBC ash. Both liming materials reduced exchangeable Al^{3+} in the 0-15 and 15-30 cm depths but not at greater depths. Soybean yields were increased by both materials up to the 1.0X LR rate. Yields were strongly correlated with root length density in the 15-30 cm depth soil layer.

The effects of applying FGD materials on distribution of exchangeable cations (Ca, Mg, K) and several trace elements were studied in three soil profiles of varying texture in Georgia (Kukier et al., 2001). A relatively pure FGD gypsum was applied singly and in a 1:1 mixture with fly ash at rates up to 20 Mg ha^{-1}. Downward movement of Ca into the subsoil depended on soil texture and rate of FGD material. After 13 months, increases in exchangeable Ca were noted to 60 cm depth in a sandy soil, and to lesser depths in two soils with greater clay content, as a result of FGD applications.

Stout and Priddy (1996) evaluated effects of two FGD gypsum products and also commercially available agricultural gypsum on yields of alfalfa. The gypsums were applied to a Rayne soil (Typic Hapludult with strongly acid subsoil) at rates up to 18 Mg ha^{-1}. Yields were increased by as much as 21% for agricultural gypsum and 14% for FGD gypsum. In the subsoil, gypsum treatments decreased soluble Al and increased Ca content and the Ca:Al ratio.

A pasture restoration study on a Gilpin silt loam soil (Typic Hapludult) in West Virginia used FGD gypsum at rates up to 32 Mg ha^{-1} in combination with dolomitic limestone (Ritchey and Snuffer, 2002). Forage yields of mixed orchardgrass and tall fescue pasture were monitored during two-year establishment and two-year production stages. Use of 16 Mg ha^{-1} FGD gypsum plus limestone increased yields by 42% during establishment and 11% during production compared to dolomitic limestone alone. About 8% of the mean 790 kg ha^{-1}yield increase was attributed to acidity-neutralizing effects of the FGD gypsum. After six years, there was little effect of gypsum applications on yield (Ritchey et al., 2004).

Nitrogen use efficiency may increase as a result of improved root development in the subsoil following gypsum application. Souza and Ritchey (1986), as cited in Shainberg et al. (1989), found that total N uptake by corn in Brazil increased from 91 to 135 kg ha^{-1} following gypsum application at 6 Mg ha^{-1}. As nitrogen fertilizer becomes more expensive due to increased energy costs, such improvements in nitrogen use efficiency would be extremely beneficial in terms of overall farm economics as well as the economics of gypsum application.

2.3 FGD Materials as a Source of Plant Nutrients

Plants require at least 17 chemical elements for growth. Those elements needed in large concentrations (from 1 to 450 g kg^{-1} of dry matter) are called macronutrients and those needed in smaller concentrations (from 0.1 to 100 mg kg^{-1} of dry matter) are called micronutrients. The sources of various plant nutrients for plants are shown in Table 2-2. Sulfur is the nutrient that is most naturally associated with FGD materials. That is because S is a major component of FGD materials. Because scrubbers effectively remove S from the flue gases, the concentrations of S in the atmosphere have decreased significantly with time. For many years, crops received more than enough S from rainfall but monitoring of S levels, deposited by rainfall onto soil, has revealed significant decreases of S inputs. In 1971 there were about 34 lbs of S $acre^{-1}$ deposited and this decreased to about 19 lbs S $acre^{-1}$ in 2002 (Figure 2-4). This and other decreases in S inputs to our soils make S fertilizer additions to crops more and more economical as crops, especially forages, respond with increased yields to S fertilizer inputs.

Table 2-2
Essential Plant Nutrients – Their Chemical Symbol and Source for Plant Uptake.

Nutrient	Symbol	Source
Macronutrients:		
Hydrogen	H	Water
Carbon	C	Air
Oxygen	O	Air
Nitrogen	N	Soil organic matter, air
Potassium	K	Soil parent material
Calcium	Ca	Soil parent material
Magnesium	Mg	Soil parent material
Phosphorus	P	Soil parent material
Sulfur	S	Soil organic matter, atmospheric deposition
Micronutrients:		
Chlorine	Cl	Soil parent material
Iron	Fe	Soil parent material
Boron	B	Soil parent material
Manganese	Mn	Soil parent material
Zinc	Zn	Soil parent material
Copper	Cu	Soil parent material
Nickel	Ni	Soil parent material
Molybdenum	Mo	Soil parent material

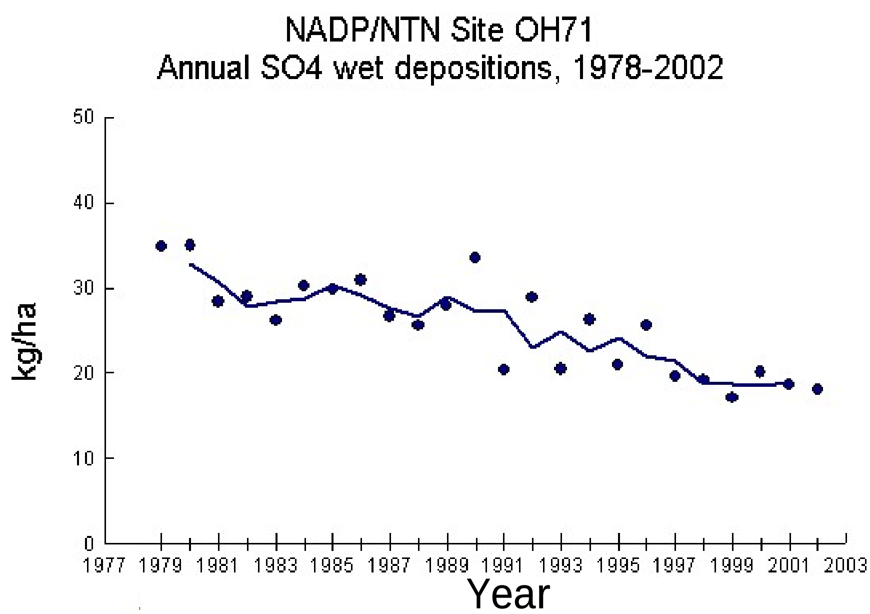


Figure 2-4
Amount of S Deposited by Rainfall Onto Soil Each Year at Wooster, OH From 1979 to 2002.

Overall, there have been relatively few research studies focusing on FGD materials as a source of specific plant nutrients even though FGD products can be an excellent source of plant nutrients. The specific nutrients supplied will depend on the composition of the product. The macronutrients will usually be Ca and S, but may also be Mg, N, or K. Use of FGD material at rates sufficient to reduce soil acidity will also provide Ca and S sufficient to improve plant nutrition or even provide excess Ca and S. FGD material may also serve as a source of micronutrients such as B and Mo. Adding a small amount of fly ash to FGD material as a mixture will increase the supply of micronutrients. It is likely that most applications of FGD material will have some direct or indirect effect on plant nutrition.

Calcium sulfate, as FGD gypsum, can benefit crops such as sweet potatoes, peanuts, roses, blueberries, and Irish potatoes that are grown at low soil pH and require high amounts of soluble Ca for production of fruit or tubers (Ritchey et al., 1998). For these crops, it is desirable to maintain a low soil pH and gypsum is the ideal Ca and S fertilizer source as it supplies the required nutrients without changing the soil pH.

A particularly promising research topic is the effect of FGD gypsum on improving crop N use efficiency when applied to mitigate subsoil acidity/Al toxicity. Research in Brazil showed increased N recovery by corn and wheat due to increased rooting in the subsoil following gypsum application (Ritchey, 1995a). There has been little study of this particular benefit of gypsum application. Increases in N use efficiency from FGD gypsum application might be obtainable on extensive areas of cropped Ultisols in the southeastern United States. As fertilizer N becomes more expensive due to increased energy costs, increases in N use efficiency will become more valuable. Although the research in Brazil was involved with removing impediments to subsoil rooting caused by acidity/Al toxicity, increases in N use efficiency might also be possible on many poorly drained soils if gypsum application improved internal drainage and rooting into the subsoil.

Sloan et al. (1999) evaluated an FGD material as a source of S, B, and Mo for alfalfa. The material was a mixture of two-thirds fly ash and one-third scrubber product and contained 55.8 g kg^{-1} S, 824 mg kg^{-1} B, and 7.4 mg kg^{-1} Mo. The ratio of $CaSO_4$ to $CaSO_3$ in the scrubber product was approximately 2 to 1. The material was applied at rates of 0, 0.46, and 3.75 Mg ha^{-1} immediately prior to seeding alfalfa on a Renova silt loam soil (Typic Hapludalf), which is considered marginally deficient in B and S for optimal alfalfa production. FGD material applications did not affect alfalfa yields but did increase shoot concentrations of B and S in the second harvest cutting, and of B, S, and Mo in the third cutting.

Chen et al. (2005) tested two FGD materials (vermiculite FGD material and perlite FGD material) and commercial gypsum as S sources for alfalfa and soybean. The FGD materials contained calcium sulfite, calcium sulfate, unused lime [$Ca(OH)_2$], fly ash, and either vermiculite or perlite. Sulfur concentrations (g kg^{-1}) were 67.1 for the vermiculite material, 66.4 for the perlite material, and 161 for gypsum. In one experiment the FGD materials and gypsum were applied for three years (2000-2002) at rates equivalent to 0, 16, and 67 kg S ha^{-1} to a Wooster silt loam soil (Oxyaquic Fragiudalf). Alfalfa was seeded in 2000. Cumulative alfalfa yields for three years were increased significantly for both FGD products and gypsum at the 16 kg S ha^{-1} rate. There was no yield increase at the 67 kg S ha^{-1} rate. In a second experiment, the S amendments were applied at rates equivalent to 0, 8, 16, and 24 kg S ha^{-1} to established alfalfa stands on five different soil types in Ohio. Vermiculite FGD material was applied for one year and the other two materials were applied for two consecutive years. Mean alfalfa yields for the five soil types were increased by approximately 5.0% in 2001 and 6.0% in 2002 by S amendments. The soybean yield trials were conducted on different sites in 2000 and 2001. In 2000, the S amendments were applied to Wooster silt loam soil at rates of 0, 16, and 67 kg S ha^{-1}. The S amendments increased soybean yields by 3.3% to 11.6% compared to the control yield of 2670 kg ha^{-1}. In 2001, the vermiculite material and gypsum were applied to a Brookston silty clay loam soil (Typic Argiaquoll) in Clark County at rates of 0, 5.6, and 17 kg S ha^{-1}. The S applications had little effect on soybean yields (-0.4% to 0.8%) compared to the control yield of 3360 kg S ha^{-1}. The lack of yield response on this site was attributed to a higher amount of atmospheric S deposition and greater soil organic matter (31.5 g kg^{-1}) that released more S for crop growth. In general, the FGD products and gypsum produced similar yield increases of alfalfa and soybeans and were good S sources for improving crop growth on Ohio soils.

A liquid FGD solution containing ammonium sulfite was used as an N source for barley (*Hordeum vulgare* L.) and annual ryegrass in Denmark (Gissel-Nielsen and Bertelsen, 1989). The solution contained 9.5% ammonium-N, 24.0% sulfite, 11.2% sulfate, and 0.38% fly ash and was applied to give N rates of 60 or 120 kg N ha^{-1}. Plant yields using the FGD solution as N source were generally similar to those obtained using a calcium-ammonium nitrate N source. There were some short-term yield depressions attributed to sulfite toxicity if the FGD solution was applied to the growing plants instead of the soil.

Land applications of FGD material may improve the selenium (Se) nutrition of livestock. The desirable Se concentration in cereals and forages for livestock feed is between 0.05 and 2.0 mg kg^{-1}. There are broad areas in both the eastern and western United States where forage crops have Se concentrations too low (<0.1 mg kg^{-1}) to meet animal nutritional requirements (Gissel-Nielsen et al., 1984). An FGD material containing a small amount of fly ash could significantly improve the quality of the forage crops subsequently fed to animals by increasing the level of Se in the forage. FGD gypsum, however, should be avoided if the beneficial use is related to improving Se content in forages. This is because gypsum contains a high concentration of S, which competes with Se, and is taken up the plant instead of Se.

Conversely, in areas where Se levels are too high and result in concentrations in the forage that are toxic, application of gypsum would be an ideal solution to this problem. Arthur et al. (1993) found that gypsum amendments reduced Se uptake by alfalfa growing on a coal fly ash landfill. In this study, the reduction of Se uptake by alfalfa was considered a benefit because alfalfa on the untreated landfill contained Se concentrations approaching toxic levels if fed to animals.

2.4 Improvement of Soil Physical Properties

FGD gypsum serves both as a fertilizer (discussed in the section above) and as a soil conditioner. When used as a fertilizer source of essential plant nutrients, particularly for Ca and S, application rates are generally in the range of 200 to 1,200 kg ha^{-1}. At higher rates of 2,000 to 4,000 kg ha^{-1}, it is used to remedy soil texture and to improve aeration and drainage problems in heavy (high clay) soils where it flocculates small particles into larger aggregates. The first usage is an annual one needed to replace minerals continuously lost from the site when a crop is harvested or due to water leaching the nutrient below the root zone. The second usage is repeated every few years to develop and maintain good soil structure and is described in more detail below.

Soil structure is defined as the arrangement of primary mineral particles and organic substances into larger units known as aggregates with their inter-aggregate pore system (Horn et al., 1995). Soil structure has been shown to influence a wide variety of soil processes including water and chemical transport, soil aeration and thermal regime, erosion by wind and water, soil response to mechanical stress, seed germination, and root penetration (Dexter, 1988; Kay, 1990; Horn et al., 1995).

Soils with high sodium and magnesium contents have poor structure because the sodium and magnesium tend to hydrate and disperse soil particles. When soil particles are dispersed instead of being bound together into aggregates, these dispersed particles get into soil pores, clogging them so that water and air cannot enter. Surface addition of FGD gypsum adds a large amount of soluble Ca at the place where water and air infiltration is most apt to be controlled, i.e. at the interface between the soil surface and the atmosphere above the soil. This Ca, in contrast to Na^+ and Mg^{2+}, remains unhydrated and binds clay particles together instead of keeping them in a dispersed state (Figure 2-5). Other FGD materials, in addition to gypsum, can improve infiltration and reduce erosion by influencing clay dispersion although gypsum is considered most effective.

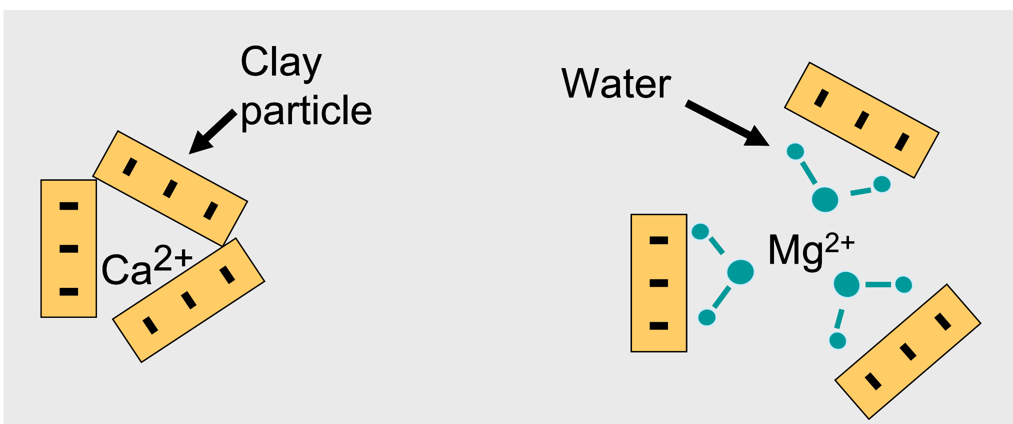


Figure 2-5
Soil Dispersion is Mainly Caused by Highly Hydrated Na^+ and Mg^{2+} Attracted to the Surfaces of Clay Particles. In Contrast, Ca^{2+} Remains Unhydrated and Binds Clay Particles Together into Aggregates. (Illustration Kindly Provided by Dr. Jerry Bigham, The Ohio State University, Columbus, OH.)

Soil crusting is the destruction of surface soil structure by raindrop impact, resulting in a surface layer enriched with individual soil particles and micro-aggregates. Surface sealing reduces water infiltration and gaseous exchange with the atmosphere. The benefit of applying gypsum to soil is that the calcium is mobilized by dissolution of gypsum and replaces sodium and/or magnesium on the soil cation exchange complex, thus promoting flocculation and structure development in these highly dispersed soils (Oster, 1982; Shainberg et al., 1989). Gypsum has been shown to improve infiltration of water into soil (Norton, 1995; Norton and Dontsova, 1998; Zhang et. al., 1998).

Hardsetting soils have a surface layer that slumps into a hard, structureless mass during drying. Slumping causes an increase in bulk density without application of the external load that is usually associated with soil compaction. It is difficult to cultivate a hardsetting soil until it is rewetted, and seedling emergence in the hard soil is reduced. The problem of hardsetting soils is primarily recognized in Australia, but soils in many other areas of the world, such as some Alfisols in the United States, have properties conducive to hardsetting. Gypsum applications have improved soil structure and plant yield on some but not all hardsetting soils (Mullins et al., 1990).

Gypsum applications may improve water relations on the weathered Ultisols common in the southeastern United States. Limitations to water infiltration and storage often represent major impediments to optimum agricultural use of Ultisols (West et al., 1998). Miller (1987) evaluated surface applications of phosphogypsum (5 Mg ha^{-1}) for effects on infiltration, runoff, and soil loss on three sandy Georgia Ultisols. Soil from the Ap horizon of the Cecil and Wedowee soils (both Typic Kanhapludults) and the Worsham soil (Typic Endoaquult) received simulated rainfall at 50 mm h^{-1} intensity. Rainfall was applied to dry soil for one 60 min event and then 24 h later was reapplied to wet soil in three events of 30 min each. Phosphogypsum treatment doubled the final infiltration rate of the Cecil and Wedowee soils, but had little influence on the final rate for the Worsham soil, which was highly dispersible. Compared to the untreated control, phosphogypsum increased cumulative infiltration from 44 mm to 80 mm for Cecil soil, from 18 mm to 49 mm for Wedowee soil, and from 16 mm to 28 mm for Worsham soil. On Cecil soil, phosphogypsum reduced soil loss (kg ha^{-1}) from 266 to 96 for the dry soil rainfall event but had no significant effect on soil loss for the three wet soil events. On the Wedowee and Worsham soils, phosphogypsum significantly reduced soil loss during all rainfall events and reduced total soil loss by 50%.

Surface application of FBC bottom ash may aid in controlling erosion on agricultural land and construction sites with swelling soils. Reichert and Norton (1994) evaluated water infiltration and erosion for five soils amended with FBC bottom ash at 5 Mg ha^{-1}. The soils were Grey clay soil (Udic Chromoustert) and Irving clay soil (Typic Pellustert) from Australia, Heiden soil (Udic Haplustert) from Texas, Hoytville soil (Mollic Epiaqualf) from Ohio, and Pierre soil (Aridic Leptic Haplustert) from South Dakota. These soils are characterized by swelling clays and, except for the Hoytville soil, belong to the order Vertisols. Soils were subjected to simulated rainfall of 110 mm h^{-1} for 90 min. For the unamended soils, steady state water infiltration rates were low at 1.8 to 5.8 mm h^{-1}, total soil losses were 220 to 1998 g m^{-2}, and total water losses were 78 to 112 mm. Surface application of FBC bottom ash increased infiltration rates 3.6 to 5.0-fold, reduced soil losses by 1.5 to 3.9-fold, and reduced water losses by 1.1 to 2.0-fold.

The effects of the phosphogypsum or FBC ash application on infiltration and erosion, described above, were attributed to increased electrolytes (i.e. salts) in the runoff. These reduced soil swelling and clay dispersion. This, in turn, led to reduced surface sealing and crusting caused by clay dispersion and then reduced surface water runoff and erosion.

FGD gypsum may improve other subsoil properties and reduce physical resistance to root growth. Root penetration into the subsoil is restricted by hard subsurface layers in many highly weathered soils (Sumner, 1993). Radcliffe et al. (1986) evaluated gypsum effects on subsoil mechanical properties in several experiments on an Appling coarse sandy loam (Typic Kanhapludult). They applied gypsum (not from FGD gypsum) at rates of 10 or 35 Mg ha^{-1}. Gypsum treatments reduced the cone penetrometer index, which is a measure of resistance to root penetration, at soil depths up to 70 cm. In one experiment gypsum also increased the percentage of large water-stable aggregates. These changes in physical properties were not seen on gypsum-treated plots that were fallow (non-vegetated). The authors concluded that the improvements in subsoil mechanical properties were the result of increased root activity due to improvements in subsoil chemistry (amelioration of Al effects) by gypsum.

2.5 Reduction of P and N Concentrations in Surface Water Runoff

Human activities often result in the addition of excessive amounts of plant nutrients (primarily P, N, and C) to streams and lakes. Runoff from agricultural fields, field lots, urban lawns, and golf courses is one source of these nutrients. These nutrients are a powerful source in stimulating algal growth in a process called eutrophication when they are introduced into surface waters. The excessive growth, or “blooms”, of algae promoted by these nutrients can lead to oxygen depletion and resultant fish kills.

Applications of FGD materials have the potential to reduce P and N runoff from soils, thus bringing about improved environmental quality. However, there must be a balance between reducing P in runoff without overly reducing the P available for plant growth. Water-extractable P was reduced an average of 71% for eight soils equilibrated with an FBC ash at 10 g kg^{-1} soil and 48% for soils equilibrated with an FGD material at the same rate. Soil test P measured by the Mehlich-III procedure was only reduced 8 to 13% (Stout et al., 1998). In another study, dissolved P in simulated runoff was reduced 20% by treatment with FBC ash and 43% by FGD material in measurements on grassed soils. A high application rate of FGD material reduced total P in runoff by 35%. On bare soils there was no effect of FBC ash or FGD material on dissolved P in runoff because P loss was controlled by erosion of particulate P (Stout et al., 2000). In a greenhouse study with three soils, FGD gypsum at 22.4 Mg/ha decreased water-extractable soil P 38 to 57% but had little effect on Mehlich-III soil P. After three growth cycles and harvests, yield of perennial ryegrass (*Lolium perenne* L.) was not affected by FGD treatment. This confirmed that treatment of high P soils with FGD gypsum decreases water-extractable P but does not decrease plant production (Stout et al., 2003).

Brauer et al. (2005) evaluated applications of gypsum not from FGD, alum, and a waste paper product, applied alone or in combinations, for reducing soil test P on a Zulch fine sandy loam soil (Thermic Udertic Paleustalf). Soil test P was measured as Bray-1 P and as dissolved reactive P (DRP) using distilled water as extractant. The initial soil had Bray-1 P approaching 4000 mg kg^{-1} in the top 6.5 cm and dissolved reactive P exceeding 35 mg kg^{-1} down to 30 cm depth. None of the amendment treatments was effective in reducing Bray-1 P. Among amendment treatments, only gypsum at 5 Mg ha^{-1} was effective in reducing DRP. A single application of gypsum at 5 Mg ha^{-1} reduced DRP after five months, but three annual applications at 1.5 Mg ha^{-1} did not reduce DRP. The amount of Ca added by the high rate of gypsum approached the Bray-1 P values, which indicated that reduction in DRP was associated with addition of Ca in amounts similar to Bray-1 P values.

Cox et al. (2005) measured P runoff from two drainage basins (3.6 and 4.2 ha areas) in Australia as affected by gypsum application. The basins had improved pasture vegetation and were grazed by cattle that were free to move between the two basins. Gypsum was applied at 15 Mg ha^{-1} to the larger basin. Runoff P was measured in major storm events from 1998 to 2000 as overland flow and as flow along the interface between the B and C soil horizons. For overland flow, total P (mg L^{-1}) was reduced from 0.88 to 0.57 and molybdate reactive P (mg L^{-1}) was decreased from 0.71 to 0.41 by gypsum treatment. For B-C interface flow, total P was decreased from 0.44 to 0.39 and molybdate reactive P was reduced from 0.26 to 0.16 by gypsum amendment. These were not considered to be substantial changes.

The effects of FGD gypsum application on N leaching were studied in a column experiment using a Candler fine sand soil (Lamellic Quartzipsamment, pH 7.0), which is a soil used in citrus production in Florida (Alva et al., 1998a). Nitrogen was applied as calcium nitrate or ammonium nitrate at 180 kg N ha^{-1}. FGD gypsum rates were equivalent to 0, 4.5 (low rate), or 9.0 (high rate) Mg ha^{-1}. Columns were leached with water equivalent to 5 cm of rainfall for 13 events, or a total of 65 cm of rainfall. Leaching of nitrate applied as ammonium nitrate was reduced by 22% for the low gypsum rate compared to the treatment without gypsum, but there was no reduction for the high gypsum rate. Gypsum application did not affect leaching of nitrate from the calcium nitrate source. Total recovery of applied N was 62 to 67% for calcium nitrate and 69 to 78% for ammonium nitrate.

In summary, there have been relatively few studies of the effects of gypsum on P runoff. Results of small scale laboratory or greenhouse studies generally show more promise for gypsum to reduce P runoff than results from larger scale field or drainage basin studies. Some of this difference may be due to greater variability and weaker control of conditions in field studies than in laboratory or greenhouse studies. More field studies are particularly needed to further examine the potential for gypsum to reduce P runoff.

2.6 Remediation of Sodic Soils

A sodic soil contains enough exchangeable sodium (Na) to cause impaired crop production and soil structure. Too much Na causes dispersion of soils and an extremely poor soil structure and overall plant growth environment. The sodium adsorption ratio (SAR) is a measurement of the degree of sodicity of soil and the equation used to calculate the SAR is shown below:

$$SAR = \frac{[Na^{+}]}{\sqrt{0.5 \cdot \left(\left[Ca^{2+}\right] + \left[Mg^{2+}\right] \right)}}$$

The concentrations of the Na^+, Ca^{++} and Mg^{++} cations are expressed in meq L^{-1} (milliequivalents per liter) in the soil saturation extract. A saturation extract of a soil that has a SAR value of at least 13 is considered to be a sodic soil. Sodic soils are noted for their dispersivity in water caused by the exchangeable Na^+ (Alcordo and Rechcigl, 1993). In water of low salt concentration, aggregates from sodic soils imbibe water and deflocculate into individual particles that clog soil pores. The plugging of soil pores causes reduced infiltration at the soil surface and reduced hydraulic conductivity within the bulk soil.

Application of FGD gypsum can remediate sodic soils by displacing Na and providing solutes that increase the electrolyte concentration in the soil. These effects reduce clay dispersion (i.e. increase clay flocculation), which increases infiltration rate and hydraulic conductivity. Gypsum has the advantage of being more than 200 times more soluble than the calcium carbonate in agricultural lime so that Ca can dissolve and leach to the subsoil quickly, but not as soluble as calcium chloride ($CaCl_2$) that dissolves so quickly that it is quickly lost from the soil profile (Shainberg et al., 1989). The moderate rate of gypsum dissolution serves to maintain the soil solution electrolyte concentration at a level that prevents dispersion and decreases in hydraulic conductivity. Impure FGD gypsums that contain substantial unreacted limestone or other sorbent will also increase soil pH when surface applied, providing additional benefit. However, the increase in pH can sometimes enhance rather than reduce clay dispersion (Miller et al., 1990; Miller, 1995).

In a study conducted by Lebron et al. (2002), three sodic soils were mixed with different amounts of gypsum (source not specified), packed into columns and leached under saturated conditions for a period of time between 1 and 3 mo. Saturated hydraulic conductivity (K_{sat}) was measured and soil thin sections were analyzed using scanning electron microscopy (SEM) and image analysis to measure the size and shape of the aggregates and the pores. These properties were then correlated with soil chemical and physical parameters. The size of the aggregates correlated closely with the exchangeable Na percentage (ESP), bulk density, pore size, and K_{sat}. There was no significant relationship between pore size and texture, indicating that transport models using particle-size distribution to infer porosity may not be successful in predicting water transport in soils under reclamation. The linear relationship between aggregate size and pore size indicates that the pore space is determined by the packing of the aggregates not the individual particles. These findings have implications not only for water transport but for modeling hydraulic properties, in general, for sodic soils being reclaimed using gypsum.

Miller and Scifres (1988) measured infiltration on a nonsodic Greenville soil (Thermic Rhodic Kandiudult) under simulated rainfall conditions as affected by surface applications of sodium nitrate (0.6 Mg ha^{-1}) and gypsum (5 Mg ha^{-1}). Gypsum was by-product phosphogypsum from the phosphate fertilizer industry. For a 60 min infiltration run starting with a dry soil, infiltration rate (cm h^{-1}) was significantly lower for treatment with sodium nitrate alone (0.90) compared to untreated soil (3.56) or gypsum treatment alone (4.67). Simultaneous application of sodium nitrate and gypsum gave an infiltration rate (4.71) similar to gypsum alone. Application of gypsum after sodium nitrate produced an intermediate infiltration rate (3.45). Similar results were obtained for three 30 min infiltration runs starting with wet soil. These results showed that gypsum applications could mitigate decreases in infiltration rates caused by applications of Na-containing fertilizers or wastewaters. This latter effect is also especially important in irrigated agriculture where Na in the irrigation water can cause problems.

Amezketa et al. (2005) measured infiltration and leaching on a sodic soil (Typic Xerofluvent) in Spain after treatment with FGD gypsum, lacto-gypsum, mined gypsum, or sulfuric acid. Infiltration was measured in soil columns leached with canal water (electrical conductivity = 0.38 dS m^{-1}) using a constant hydraulic head of 3 cm. In an initial experiment on soil crusting, all amendments were surface applied at equivalent rates of 5 Mg pure-gypsum ha^{-1}. Final infiltration rates (mm h^{-1}) were 0 for unamended control, 9 for lacto-gypsum, 15 to 17 for FGD gypsum and mined gypsum, and 21 for sulfuric acid. In an experiment simulating sodic soil reclamation, all gypsums were soil-incorporated but sulfuric acid was surface applied. The rates of application were based on the amount needed to reduce exchangeable sodium percentage to one or less. Infiltration rates (mm h^{-1}) were 0 for control, 8 to 9 for all gypsums, and 17 for sulfuric acid. Reductions in electrical conductivity, sodium concentration, and sodium adsorption ratio in the leachates were fastest for the sulfuric acid amendment. The three gypsum materials produced similar rates of change in the leachates and were equally effective for reclaiming the sodic soil.

Chun et al. (2001) and Sakai et al. (2004) used wet or semi-dry FGD materials at rates up to 23.1 Mg ha^{-1} on a sodic soil (mollisol) in China. In one experiment, soil pH decreased from 9.0 to 7.7, exchangeable sodium percentage (ESP) decreased from 22% to 4.8%, and total four-year corn yield increased from 430 to 8480 kg/ha when FGD was applied at 23.1 Mg ha^{-1}.

In the United States and Canada, the areas of sodic soils requiring remediation are potentially large, but these soils are considered to be of low quality and value. Until there is pressure to bring these soils into production, there is little incentive for their remediation. Thus, published studies of the use of FGD gypsum for improving sodic soils in the United States or Canada are almost entirely lacking.

2.7 No-Tillage Crop Production on Clay Soils

No-tillage, or zero till technology, is defined as the planting of crops directly into the residues of the previous year's crop without any tillage at all. No-tillage technologies are well advanced and have been adopted by an increasing number of farmers in the world, including in the United States. About 6.8 million hectares of land in the United States was no-tilled in the year 1990 and by 2004 it had increased to about 25.2 million hectares (http://www.ctic.purdue.edu/ctic/CRM2004/1990-2004data.pdf). No-tillage offers a large number of benefits such as less soil erosion, increased C sequestration, increased crop yields and better profits, less labor, less time consumption, reduction in the wear and tear of equipment, better water quality, less soil compaction, better habitat for wildlife, and improved soil tilth.

However, expansion of no-tillage crop production systems onto clay soils has been a slow process because clay soils used in no-tillage crop production often become compacted and exhibit poor aeration and water infiltration properties. Somewhat poorly drained or poorly drained soils with seasonal high water tables can only be no-tilled with careful management (Ohio Cooperative Extension Service, 1990). Currently these soils produce optimum yields under no-till only if they are systematically drained and crops are rotated. In Ohio alone, approximately 57% (5.9 million acres) of the soils used for cropland have a natural drainage limitation (Ohio State University Extension, 1995). This is cropland that is not widely no-tilled but could be if surface and internal drainage were improved. Gypsum can increase water penetration and improve internal soil drainage because it dissolves quickly and releases electrolytes that aggregate soil clay particles, i.e. gypsum releases calcium which replaces exchangeable magnesium and sodium that naturally tend to disperse soil clays (Shainberg et al., 1989). Therefore, applications of FGD-gypsum could significantly increase the amount of land suitable for no-tillage, including soils where tile drainage is needed for good crop performance (Perszewski, 2006). At the same time, this potential agricultural use could absorb a large volume of FGD product each year. In fact, this is probably the single most important new market for FGD gypsum in agriculture, and one that is slowly expanding but requiring much additional research and demonstration to become widely accepted.

Because of work by scientists at the USDA-ARS National Soil Erosion Laboratory at Purdue University and work done in Ohio by Ag Spectrum (DeWitt, IA) and by The Ohio State University, there is developing an increasing awareness among farmers of the benefits of applying gypsum to no-tillage soils (Ramsier and Norton, 2006). The benefits seem especially noticeable when gypsum and no-tillage are applied to heavier soils (i.e. soils with a substantial amount of clay in them) where no-tillage has traditionally not been practiced. Currently, studies are being conducted in Ohio to document the potential yield benefits of applying FGD gypsum to no-tillage fields located on heavier, clay soils. This work is ongoing and results are preliminary. The results to date suggest there is an interaction between tillage and FGD gypsum application, with better results occurring when the FGD gypsum is surface applied to the no-tillage soil than when applied to soil that is subsequently plowed and tilled.

When no-tillage is continuously practiced, major changes in soil organic matter quantity and quality occur (Dick et al., 1991). The amount of carbon stored in the top 20 cm of a no-tillage soil under continuous corn was 6.0 Mg/ha (2.7 tons/ac) greater than in plow tillage plots. Organic matter accumulated in the surface 7.5-cm soil layer at levels 3 to 6 times higher than when the soil was tilled each year (Dick and Durkalski, 1997). Thus, one additional benefit of this FGD gypsum use is that expanded no-tillage crop production represents increased concentrations of C in the soil. This not only improves the quality of the soil by increasing water retention, metal chelation, buffering activity, plant nutrient storage, microbial activity, and cation exchange capacity (Dick and McCoy, 1993) but also provides the best and most efficient way to sequester C in the soil, thus counteracting the trend towards increased CO_2 levels in the atmosphere that are presumably linked to global warming.

2.8 Synthetic Soils and Mixes

A synthetic soil may be defined as a plant growth medium created by the blending of two or more materials to have specific desirable physical, chemical, and/or biological characteristics for supporting plant growth. The uses of synthetic soils or mixes include urban landscape restoration, commercial plant nurseries, and sod farms. Schlossberg et al. (2004) noted that the risk of accumulating excessive amounts of regulated metals (or other chemicals) at a site producing or using synthetic soil is reduced when the soil is exported with the final plant product, as occurs for container-grown horticultural plants or turfgrass sod.

The use of FGD materials in synthetic soils and mixes will require co-utilization with some other material because FGD materials are not suitable plant growth media in pure form. Co-utilization involves blending, mixing, or co-composting two or more materials to produce a product with specific properties for use in agricultural production, soil reclamation, or other market need (Korcak, 1998). There has been relatively little research on co-utilization of coal combustion materials. For example, Bilski et al. (1995) emphasized that there has been voluminous research on fly ash and sewage sludge alone but very little research on fly ash and sewage sludge together as a compost mixture. Schumann and Sumner (1999) evaluated mixtures of fly ashes (not from FGD processes) with sewage sludge or poultry manure for growth of corn. There do not appear to be any studies using FGD gypsum in composting, but one experiment has used wallboard gypsum (Clean Washington Center, 1997 as cited in Korcak et al., 2000). Chipped (<1 cm diam.) gypsum wallboard was mixed with sewage sludge and yard waste at rates of 0, 12.5, 25, and 37.5 percent gypsum by volume. There were no detrimental effects on compost quality or radish seed germination at the 37.5% gypsum rate. Composts produced with the higher gypsum contents were drier and had lower concentrations of plant nutrients except for calcium, sulfur, and nitrate. At the 37.5% gypsum rate, the finished compost contained up to 57% gypsum on a dry weight basis. Composts produced with the two highest gypsum rates contained numerous white specks of gypsum but compost from the 12.5% gypsum rate had no noticeable gypsum specks.

Most research on the use of coal combustion by-products in synthetic soils/mixes has used fly ash or bottom ash (but not FBC ash) instead of FGD by-products. Franciosi (1997) described the use of a compost containing fly ash as a container medium for ornamental woody plants. Bearce et al. (1997) used bottom ash at rates up to 100% by volume in potting mixes for growing peperomias (*Peperomia viridis* L.), poinsettias (*Euphorbia pulcherrima* Willd. ex Klotzsch), and Easter lilies (*Lilium longiflorum* Thumb.).

Bhumbla et al. (1997) prepared semi-synthetic soils for growing apples on a reclaimed coal surface mine. The four soils were constructed from various proportions of minesoil, FBC ash, and sewage sludge and were spread to 120 cm depth over regraded spoil material. The volumetric ratios of soil:FBC ash in the constructed soils varied from 3:1 to 1:3. The control treatment was limed and fertilized topsoil. Growth of Golden Delicious and Gala apple varieties was more vigorous and healthier on the constructed soils than on the control topsoil. Foliar concentrations of N, P, and Ca were greater in apples on the constructed soils. Concentrations of Mn, which at high concentrations causes internal bark necrosis in apples, were much lower on the constructed soils than on the control topsoil.

Ritchey et al. (1998) reviewed co-utilization of coal combustion products but described little research with FGD materials as components of synthetic soils. They discussed a synthetic soil amendment produced by mixing lime kiln dust or cement kiln dust with municipal sewage sludge in a pasteurization process developed by the N-Viro Corporation. In test trials, an FBC ash or a dry FGD material were substituted for the kiln dust. The mixture of sludge and FGD by-product developed increases in pH and temperature that served to stabilize the sludge. Substitution of the FBC ash or dry FGD material gave a synthetic product (N-Viro soil) that was rated superior to the product derived with kiln dust on the basis of granularity, odor control, and general appearance.

Logan and Harrison (1995) and Logan and Burnham (1995) described additional details of the N-Viro process for alkaline stabilization of municipal sewage sludge. Logan and Harrison (1995) discussed physical characteristics of 28 different N-Viro materials including three that used FBC bed ash as a component. In general, the N-Viro soils have the physical characteristics of medium to fine textured, porous soils with granular, stable aggregates and nonplastic consistency. The physical properties of the N-Viro soils appeared to have no limitations for the use of the materials as soil substitutes. The high initial pH and soluble salts are chemical characteristics that would limit the use of N-Viro soils. The 28 N-Viro soils had a mean pH of 11.9 and mean electrical conductivity of 9 dS m^{-1}.

Norton et al. (1998) prepared synthetic soil mixes in the laboratory by co-blending an organic rich industrial sludge with ash from an atmospheric circulating FBC boiler. The aerobically digested sludge was from a pharmaceutical fermentation process and contained 12% solids. Sludge was mixed with either bottom ash or fly ash at rates of 1:1, 1.5:1, 2:1, 2.5:1, or 3:1 (sludge volume/ash weight). The synthetic soils were characterized in the laboratory, but no data on plant growth in the soils was given.

Hermsmeyer et al. (2002) described physical properties of a fine-granular saline aluminum recycling by-product (ALRP) as a soil substitute for covering potash mining residue mounds in Germany. The residue mounds are primarily rock salt (NaCl) and produce briny runoff. Mixing FGD material with the ALRP produced a soil substitute that had lower salt content and erodibility factor K but greater water-holding capacity than the ALRP alone. The mix was proposed as a soil substitute for covering residue mounds even on steep slopes.

Bardhan (2005) prepared a large variety of synthetic soils using varied proportions of bottom ash, FGD gypsum, peat, and several composts from biosolids, cow manure, and yard waste. The bottom ash was from a pressurized FBC boiler. The composts were used individually or combined into several mixed composts. Plant growth in several of the synthetic mixes was generally better than growth in two different commercial potting mixes. Wheat (*Triticum aestivum* L.) and marigold (*Tagetes patula*) grew best in synthetic soils containing 30 to 35% bottom ash, 20 to 25% gypsum, 30 to 35% mixed compost, and 10 to 15% peat. Tomato (*Lycopersicon esculentum* L.) grew best in a soil containing 50% bottom ash and 50% cow manure compost, but also grew well in mixes containing 20 to 40% bottom ash, 20 to 40% gypsum, and 40% mixed compost.

In summary, the production of synthetic soils/mixes using wastes or by-products is a relatively new endeavor and there have been some trials using FGD materials as components of the mixes. There is an unlimited potential for using FGD materials in the diverse mixes needed to satisfy a variety of growing conditions. Many of the specific mixes will probably be low-volume uses for FGD materials, but the aggregate volume of required FGD material may be significant.

2.9 Horticultural Uses

Some horticultural uses for FGD materials are as a component of mixes or soils for plants grown in containers or nursery beds and as soil amendments for orchards and turfgrass. The former use was discussed in the previous section on synthetic soils and mixes. This section will describe studies of FGD materials as soil amendments for orchards and turfgrass.

Korcak (1993) reviewed several older studies of FGD material application to orchards. In one study, bed ash from an FBC system was surface applied to an established apple orchard at rates up to 112 Mg ha^{-1}. The material formed a porous cap that suppressed weed growth for up to four years. Cumulative yields during six years were increased for three of four cultivar/rootstock combinations. After 12 years, surface soil pH was about 7.6, indicating a long-lasting effect of the application.

In a greenhouse study, Alva (1994) applied FGD gypsum alone or with chicken manure to a Myakka sand soil (Aeric Alaquod, pH 5.8) at rates equivalent to 4.48 Mg ha^{-1} for each material. Growth of citrus seedlings from two different rootstocks was increased significantly by both amendment treatments. In a combined application of FGD gypsum, chicken manure, and fly ash with each material at 8.96 Mg ha^{-1}, seedlings of both rootstocks had significantly decreased growth. The reason for the growth decrease was not known, but it may have been related to P nutrition. Seedlings had significantly lower foliar P concentrations, as much as 60% lower for one rootstock, when grown on the combined treatment compared to the unamended control.

Korcak (1997) applied FBC ash as a surface mulch to two established apple orchards on Beltsville soil (Typic Fragiudult). The ash was applied once at a rate of 269 Mg ha^{-1} and was either supplemented or not supplemented with annual recommended fertilizer applications. A peletized gypsum treatment equivalent to the gypsum content of the FBC ash treatment was applied as a third treatment. After four years, there were no significant treatment effects on leaf dry weight or leaf surface area. There were no indications of a buildup of heavy metals in fruit, bark, or wood. Soil Ca at 30 and 40 cm depths was greater for both FBC ash treatments than for the gypsum or untreated control treatments.

There appear to be no published studies of FGD materials as amendments for turfgrass soils. There was no mention of FGD materials in a review of soil mixtures and amendments for turfgrass (Waddington, 1992). Fly ash, but not from an FGD system, was used in a turfgrass experiment in South Carolina (Adriano et al., 2002). Schlossberg et al. (2004) used bottom ash in several combinations with fly ash, compost, and biosolids as the growth media for hybrid bermudagrass (*Cynodon dactylon* (L.) Pers. x C. *transvaalensis* Burtt-Davy) in Georgia, but the bottom ash was apparently not from an FBC boiler. Korcak (unpublished data, 1996) as cited in Korcak et al. (2000) compared pulverized wallboard gypsum to agricultural gypsum when applied to established tall fescue (*Festuca arundinacea* Schreber) fields on a Cordova silt loam (Typic Argiaquoll, pH 5.7). Four to six months after surface application at 2.23 Mg ha^{-1}, neither gypsum affected turfgrass biomass. Waddington (1992) stated that gypsum is unlikely to produce lasting beneficial physical effects on turfgrass soils. Application of FGD gypsum, however, seems a promising treatment to mitigate subsoil acidity in urban or other soils affected by construction activities. Unless precautions are taken, reshaping the landscape during construction may expose an acidic subsoil that inhibits growth of turfgrass or other ornamental plants. Carrow et al. (2001) and Carrow and Duncan (1998) described the practical use of FGD gypsum to ameliorate acidity or sodicity in turfgrass culture.

2.10 Mineland Reclamation

Applications of FGD materials will enhance reclamation of mined areas affected by soil acidity or sodicity. In the eastern United States, abandoned coal surface mines or coal waste disposal areas in need of revegetation are usually plagued by acidity. Such sites are benefited by amendment with an FGD material containing unreacted lime or limestone sorbent. In the western United States, abandoned bentonite mines suffer from high exchangeable sodium and low hydraulic conductivity similar to other sodic soils (Schuman et al., 2000). Bentonite clays are used in drilling muds (for oil and gas exploration), foundry castings, processing of taconite (iron) ore, environmental sealants for landfills and sewage lagoons, and many products such as cat litter, face creams, and laxatives. There are many thousands of hectares of abandoned bentonite mines in Wyoming, Montana, and South Dakota. Coal mine spoils in the western United States may also be sodic (Sandoval and Gould, 1978; Sencindiver and Ammons, 2000). Even when sodic coal spoils are reclaimed by covering with a layer of nonsodic topsoil, the topsoil may become sodic with time due to upward migration of sodium.

In a greenhouse/laboratory study, Brown et al. (1997) evaluated two pressurized FBC fly ashes for effects on plant growth in an acid coal spoil and hydraulic conductivity in a sodic coal spoil. Karhula ash was produced in a circulating PFBC unit burning low-sulfur subbituminous coal with limestone sorbent. Tidd ash was produced in a bubbling PFBC unit burning high-sulfur bituminous coal with dolomitic sorbent. In the first part (acid coal spoil) of the study, the fly ashes or ag-lime were added to the acid spoil (pH 3.5) at two rates dependent on acid-base accounting using either total sulfur level or pyritic sulfur level. Yield of Garrison meadow foxtail grass (*Alopecurus protensis* cult. Garrison) was zero in unamended soil but significant for soil amended with either ash, than for ag-lime. In the second part (sodic coal spoil) of the study, Karhula ash was added at rates of 0, 10, 25, and 50 wt% to a sodic clayey spoil (sodium adsorption ratio = 42.6). Hydraulic conductivity (in units of 10^{-8} cm s^{-1}) increased from 0.0 for unamended spoil to 1.2 for the 25 wt% ash amendment and to 1.6 for 50 wt% ash amendment.

In another greenhouse study, von Willert and Stehouwer (2003) added compost, calcium carbonate, and gypsum to an acidic coal spoil (pH 2.5) in Pennsylvania. Gypsum (not from FGD) was used alone and in various combinations with calcium carbonate and compost. The gypsum rate was 22.3 g kg^{-1} to supply sufficient Ca^{2+} equivalents equal to the total extractable acidity of the spoil. Gypsum application did not increase the yield of birdsfoot trefoil and tall fescue or cause large reductions in extractable Al in the topsoil or the subsoil.

Stehouwer and Dick (1997) tested an FGD product from an atmospheric FBC boiler as a substitute for topsoil to reclaim an abandoned coal surface mine with pH 3.5 to 4.5. The FBC material was applied at 280 Mg ha^{-1} with or without yard waste compost at 112 Mg ha^{-1}. The topsoil treatment included 112 Mg ha^{-1} agriculture limestone applied to the spoil surface, deposition of a 20 cm layer of topsoil, and then an additional 45 Mg ha^{-1} limestone applied to the topsoil layer. After one year, soil surface pH was near or slightly above neutral for all three treatments. Plant biomass yield (Mg ha^{-1}) was greater on the topsoil treatment (4.3) than on the FGD treatments (1.7-1.8). After four years, soil pH for all treatments was still near neutral at the soil surface, but decreased significantly as depth increased. Plant yields (1.0-1.4 Mg ha^{-1}) did not differ significantly by treatment (Houser, 1999).

The use of a wet FGD material to reclaim an abandoned coal refuse pile (pH 2.3) at Rehoboth, Ohio was described in the section (2.1) on reduction of surface soil acidity (Stehouwer and Mafi, 1997). The FGD material was applied at rates of 672, 1120, and 1568 Mg ha^{-1} with or without yard waste compost at 112 Mg ha^{-1}. Agricultural lime treatments at 179 Mg ha^{-1} were also applied with or without compost and supplied alkalinity equivalent to the 1120 Mg ha^{-1} rate of FGD material. Soil pH at 15 cm depth was increased to 7.0 by FGD material at 1120 Mg ha^{-1} (with or without compost). After one year soil pH for that FGD material rate declined to 5.1 with compost and to 3.4 without compost. Yields of a grass-legume mixture after one year were greater for the FGD treatments (560 or 880 kg ha^{-1}) than the agricultural lime treatments (270 or 310 kg ha^{-1}). This study, however, clearly showed that high application rates of FGD materials can also introduce B in sufficient amounts to inhibit plant growth. It is extremely important that sufficient lime be applied with the FGD material to keep the concentrations of plant available B below inhibitory levels. In addition, the spreading of the FGD material must be uniform to prevent burnout spots from developing that, under conditions of drought stress, can rapidly expand and lead to eventual reclamation failure.

Kost et al. (1997) applied two FGD materials to an acidic minesoil (pH 3.4) in Noble County, Ohio. The FGD materials were a calcium sulfite material mixed with fly ash and applied at 600 Mg ha^{-1} and an FGD gypsum enriched with 4% $Mg(OH)_2$ and applied at 280 Mg ha^{-1}. Aerobically digested sewage sludge at 100 Mg ha^{-1} was applied alone and in combination with each FGD material. A sixth treatment involved covering the minesoil with silty clay borrow soil to 30 cm depth. After one year soil pH (0-10 cm depth) was 6.5 or greater for all treatments except sewage sludge used alone (pH 4.6). Soil pH at the surface remained stable through the fifth year. After two years herbaceous ground cover (primarily grasses/legumes) yield was greater for calcium sulfite material with (3380 kg ha^{-1}) or without (2630 kg ha^{-1}) sewage sludge than for most other treatments (range 1840 to 2170 kg ha^{-1}). After five years there were no significant yield differences among the six treatments, with yields ranging from 2490 kg ha^{-1} for borrow soil to 3410 kg ha^{-1} for calcium sulfite FGD without sewage sludge.

Some larger scale coal reclamation demonstration projects have used FGD materials. In Clay County, Indiana, the Chinook site was a barren, 50 ha area covered by coal processing wastes from a surface mining operation (Branam et al., 2005). The site was reclaimed by covering it with a synthetic soil mix at a rate of 270 to 335 Mg ha^{-1} and then incorporating the mix into the coal waste to a depth of 20 cm. The mix was composed of FBC ash from an institutional boiler and spent fermentation cake from a pharmaceutical company. The treated site was seeded with grasses. Vadose water from a lysimeter at 0.45 m depth remained acidic during a two year monitoring period. After four years a vegetative cover appeared to be established.

Schuman and Meining (1993) demonstrated that gypsum application would improve soil conditions in bentonite mine reclamation. They applied commercial (not FGD) gypsum at 56 Mg ha^{-1} to an abandoned bentonite mine that had been previously reclaimed using a wood chips amendment. Gypsum reduced the exchangeable sodium percentage and increased water storage to 60 cm depth in the reclaimed soil.

These greenhouse and field trials have shown the benefit of amending acidic coal soils with FGD materials. For some extremely acidic spoils, amendment with FGD materials may not provide a permanent solution to the soil acidity. There has been only one study using gypsum to amend bentonite spoils.

2.11 Matching FGD Material to Land Application Use

The optimum benefit from using a FGD material for a particular land application use will only occur if the appropriate material is used. The previous sections on various uses often identify an FGD product associated with a particular use. Table 2-3 summarizes the appropriate FGD materials that would generally be recommended for each land application use discussed in this chapter.

Table 2-3
Matching FGD Land Application Use to Appropriate FGD Material.

FGD Land Application Use	Best FGD Material to Use
(1) Reduction of surface soil acidity	Wet FGD sludge with excess sorbent; FBC ash, spray dryer ash
(2) Ameliorate subsoil acidity	FGD gypsum with or without some limestone
(3) Sources of plant nutrients	Depends on specific nutrient. Gypsum is a good source of Ca and S. Mixtures containing some fly ash are good sources of trace elements (e.g. B, Mo, Se).
(4) Improve soil physical properties	FGD gypsum, FBC bottom ash
(5) Reduce P and N runoff	FGD gypsum, wet FGD sludge, spray dryer ash, FBC ash
(6) Remediate sodic soils	FGD gypsum
(7) No-tillage on clay soils	FGD gypsum
(8) Synthetic soils and mixes	Depends on specific use of mix and plant growth requirements
(9) Horticultural uses	Depends on particular use. Gypsum, wet FGD sludge, spray dryer ash, and FBC ash are all potential materials for use in horticultural applications.
(10) Mineland reclamation	Wet FGD sludge with excess sorbent, spray dryer ash, and FBC ash for acidic coal minesoils; FGD gypsum for bentonite minesoils

3
POTENTIAL MARKETS ASSOCIATED WITH LAND APPLICATION USES

Many producers of FGD materials are facing increased disposal costs and are, therefore, interested in alternatives to landfilling. However, it is important that the alternative uses provide enough benefit to the end user to be economically viable. At the same time, the use must not result in negative environmental impacts. The proper balance, as for many other agricultural inputs, is in having knowledge of best management practices. In this case the best management practices will involve use of FGD materials.

Research has shown that beneficial agricultural and land application uses of FGD materials exist and important opportunities have been identified. Our increasing knowledge about the properties of these materials is allowing us to tailor the design and use of them in agriculture. In some cases, agricultural uses will be economically competitive with disposal methods.

3.1 Potential Use Amounts

The market for agricultural and land application uses of FGD materials is in its infancy and it is almost impossible to make predictions of how the market will develop. Numerous examples could be provided in the business world of products that still failed after millions of dollars of marketing research had predicted otherwise. However, as has been done for compost, we can make guesstimates of the most likely FGD material products or uses in relative terms.

In 2005, 1.1 million Mg of gypsum were used for agricultural applications out of a total domestic consumption of 37.9 million Mg (US Geological Survey, 2006). The percentage of gypsum used for agriculture in 2005 that was derived from FGD gypsum was not reported. In 2004, only 0.12 million Mg of FGD gypsum were used in agriculture (American Coal Ash Association, 2005). This indicates a potential increase from 0.12 million to 1.1 million Mg in amount of FGD gypsum that could be used in agriculture.

Cooperband (2000) listed the potential market sizes for various compost uses. Similarly, estimates can be made to provide some insight into the potential relative market sizes of various FGD material uses (Table 3-1).

Table 3-1
Potential Amounts of FGD Materials Used in Agriculture and Other Land Applications

Use	Volume
Liming agent	Large
Treatment to overcome problems associated with subsoil acidity	Large if combined with traditional liming of surface soils
No-tillage soil conditioner	Large
Source of plant nutrients, especially S and Ca	Moderate, but linking use to improved N use efficiency would enhance acceptance and amounts used
Component of synthetic soil mix for nursery and greenhouse use	Moderate
Reduce P runoff	Small
Sodic soil reclamation	Small
Horticultural soil conditioner	Small
Mineland reclamation	Small overall but could be large for some localized situations.

The potential market sizes are large for use of FGD material as a liming agent, to treat soils with problems associated with subsoil acidity, and for improving the overall productivity of no-tillage agriculture on heavier clay soils. Moderate amounts of FGD material could be used as sources of plant nutrients, especially S and Ca, and as a component of soil mixes in horticultural and nursery industries. Small amounts will probably be used to treat soils with high P levels to improve water runoff quality, to reclaim sodic soils, for horticultural uses and for mineland reclamation. Smaller volume uses do not imply these uses should not be seriously considered by a producer of FGD material. For example, there may be either an active or abandoned surface coal mine site where FGD material would be an ideal material to be used in the overall reclamation process. There may also be areas in the United States where a producer of FGD material is located close to sodic soils that could be reclaimed using FGD materials and brought into agricultural production. In many instances, the treatment costs can be discounted because of avoided landfilling costs.

Other uses listed as small or moderate volume uses may be limited because of lack of research and demonstration of the benefits associated with the identified use. Use of FGD materials as a component of synthetic soil mixes or as a horticultural amendment could be easily expanded if the benefits were recognized. For example, the author of this review (WA Dick) currently is working with scientists from Israel in using FGD bed ash for the commercial production of various plants (primarily flowers). The end users have been extremely happy with the results they have obtained and use is expanding. The bed ash replaces volcanic ash material that must be mined from politically sensitive areas. Replicated research trials are beginning to document the benefits, but the key to use in Israel has been a close cooperation among all of the parties involved (i.e. producer, end user, researcher, regulatory personnel), high land values that encourage extensive management practices, and political uncertainties making consistent access to volcanic ash uncertain. To return to the problem of reclaiming sodic soils, the technology of using gypsum for such a purpose is well known in the United States and around the world. However the investments associated with purchase, transport and application of the FGD gypsum are generally higher than the value of the land after reclamation has been completed.

A major potential use of FGD materials in agriculture will be for FGD gypsum to ameliorate problems associated with subsoil acidity such as Al toxicity. Most studies of this type discussed earlier were performed on soils of the order Ultisols, which often have high amounts of exchangeable Al in the subsoil (West et al., 1998). There are 55 million ha of Ultisols in ten eastern and southern states, but not all of these soils are used for cropland. Miller and Sumner (1997) estimated that 4.5 million metric tons of gypsum could be used annually on cropland in nine southeastern states if 25% of the 16.2 million ha of cropland were treated with an average of 1.12 metric ton per year. They did not state what fraction of the cropland occurs on Ultisols, but the fraction is presumably large. Forestry is another important use for Ultisols. Forests on Ultisols would also probably benefit from gypsum application, or at least application of an FGD material having residual lime content (Crews and Dick, 1998), but the economics of application would almost certainly be less favorable than for cropland. However, if a quality FGD material were available in an area where forest plantations exist, its application to the forest soils would increase forest productivity and provide a beneficial use outlet of the FGD material for the producer.

Blount soils (Aeric Epiaqualfs) are also often acidic below the plow layer (i.e. below about 20 cm depth). This acid subsoil restricts root growth and ultimately crop production even though roots of corn in other soils commonly extend much deeper than 20 cm in search of water and nutrients. Blount soils total more than 2.5 million acres in the upper region of the corn belt and there are many other soils east of the Mississippi River with properties similar to Blount soil. The Ohio State University has conducted preliminary studies of the use of FGD gypsum on a Blount soil in Ohio during the past two years. These studies will lead to a better understanding of the benefits obtained by applying FGD gypsum and the appropriate application rates. Currently, The Ohio State University is recommending FGD gypsum application rates of 1-2 tons every other year if applied to no-tillage and more often in tillage soils. At these application rates, the potential amount of FGD gypsum that could be used to improve overall soil quality and crop productivity would range from 1.25 (one ton acre^{-1} rate every other year) to 2.5 million tons (two tons acre^{-1} rate every other year) every year. This calculation is for Blount soil only, but could be extended to other related soil types.

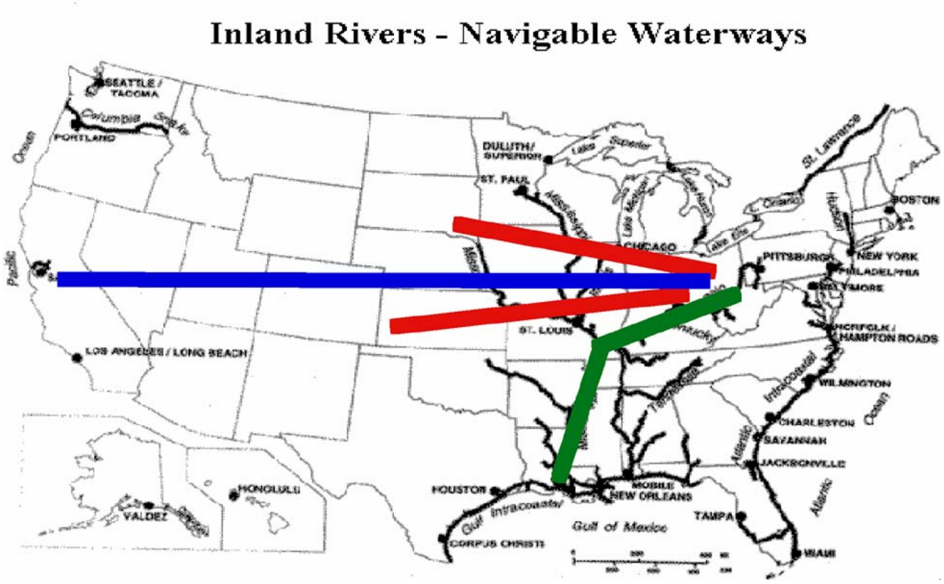
The potential use of FGD materials in synthetic soils and mixes is also likely to increase. Craul (1999) noted that the use of topsoil substitutes in urban landscape restoration projects should increase because borrow topsoil is not available and many cities have potentially large restoration projects. The topsoil substitutes could be formulated to contain a component of FGD material. There are probably a variety of uses for synthetic soils in plant nurseries. For example, harvesting ornamental woody plants with an attached ball of soil from nurseries removes 450 to 560 Mg of top soil per hectare during each harvest (Gouin, 1998). This soil must be replaced with a synthetic soil containing FGD material to maintain nursery productivity.

The issue of transportation costs understandably arises whenever potentially large volume uses of FGD products are proposed. The price that a farmer is willing to pay for a farm input is generally fixed within a rather narrow range. If FGD product pricing is greatly impacted by transportation costs, then the market space will be relatively restricted to that area within a 30-50 mile radius of a producing utility. Ag Spectrum (DeWitt, IA) has probably the greatest experience in marketing FGD gypsum of any company in the United States. The 30- to 50-mile radius is generally considered a limit if trucks are the primary means of transporting FGD gypsum (Cliff Ramsier, personal communication). However, rail and barge transportation costs are much less than trucking. Assuming that a 50-mile radius is the limit, material storage sites located at 100-mile intervals along a rail line or barge route could be set up for moving the FGD gypsum from the utility to the farmer.

A map illustrating the various routes from Ohio to markets outside of Ohio is shown in Figure 3-1, along with estimated retail prices of the FGD gypsum required to make it competitive with alternative agricultural inputs. It must be noted, however, that FGD products are not only found in Ohio but are dispersed across the United States. The availability of FGD product to farmers will be controlled by the relative access to transportation options such as trucks, rail lines or barges.

The potential value for FGD for land application uses includes the market value of the material that is replaced by the FGD material and the avoided cost of landfilling or other disposal of the FGD material. The prices listed at the bottom of Figure 3-1 are the prices that farmers would likely be willing to pay after FGD has been loaded on a truck at the rail/barge location located within 50 miles of their farming operation. The farmer would pay additional freight and spreading costs in the field. These prices are estimates and various local factors would affect the prices on a local basis. The factors would include alternative supplies such as drywall recycling operations, local FGD-generating facilities, and perceived needs by farmers relating to their specific farming situation. The actual market values will undoubtedly change with time as experience is gained by marketers and as farmers gain confidence in the value of using FGD products in agriculture to enhance their farming operations.

If producers of FGD gypsum were to trade the transportation of the gypsum to agricultural areas and provide the verification and aggregation of C credits from farmers’ fields, the farmers would likely accept the FGD gypsum in trade for the C and possibly NOx credits they would generate (Ramsier and Norton, 2006). Since many generators are already in the transportation business, arranging back hauls with trucks, rail or barges would be a relatively simple, low-cost, in-house activity.



Delivery Routes	Description of Routes	Estimated Retail Prices Based on Cost Per Short Ton Offloaded at Site
	Rail tipper routes to mid-western corn belt sites.	Values range from $10.00 east to $18.00 west
	Rail route to San Joaquin Valley.	Value, $26.00
	River barge routes to delta agriculture.	Value, $8.00 Ohio River to $12.00 lower Mississippi

Figure 3-1
Estimated Rail and Barge Routes and Transportation Costs of Moving FGD Gypsum to Markets Outside of Ohio.

3.2 Addendum

During the writing of this review, it became apparent that transportation costs were a major impediment to many agricultural uses. However, it was also noted that barge transportation costs are probably the least expensive and for FGD material producers located on navigational rivers, barges offer an attractive way of moving material to the market. If these producers are located on the Mississippi River or on rivers that eventually flow into the Mississippi River and the Gulf of Mexico, then a potential use of FGD materials is noted below. This is not an agricultural use and that is why it is identified as an addendum.

The restoration of wetlands that have been lost in the Mississippi River delta region south of New Orleans could potentially use large volumes of FGD material. The annual loss of wetlands from subsidence is variously reported as 6,500 to 11,000 ha. Wetland loss was a contributing factor to the severity of hurricane Katrina's effects on New Orleans, and any scenario for rebuilding and protecting New Orleans from future storms involves protecting the storm-buffering wetland system as well as building bigger levees around the city. Wetland subsidence is due to a combination of factors that have altered wetland hydrology including levees that prevent the river from depositing its sediment load into the wetlands. In the absence of changes to restore the original hydrology, mitigation of subsidence can be achieved by applying fill material to the wetlands (Nussbaum, 2004). Initial expenditures for freshwater diversion into the wetlands, grass plantings and dredged fill material have been estimated to be $1.9 billion (Nussbaum, 2004) with a substantial portion of this cost being associated with fill material. The usual source of fill material is dredgings from waterways, but FGD material could be used as well. The FGD materials, if properly treated (for example augmented with a small amount of lime), set up like a poor quality concrete and could be stable enough to serve as fill in wetland restoration. The FGD materials could also be used to help reconstruct the levees. Using a barge transport cost (Anonymous 2002) of 1.0 cent/ton-mile (1.1 cent/Mg-mile), 1 Mg of FGD material could be transported 1000 miles for $11.00 or 2000 miles for $22.00. Power plants on the upper Mississippi and Ohio Rivers would lie within the 2000 mile range and the $22.00/Mg cost for transport to the Mississippi delta could be less than the landfill disposal cost.

4
BARRIERS TO INCREASED FGD LAND APPLICATION USES

4.1 Perception of the End User

Before any large volume use of FGD materials will occur, it is crucial that the potential end user be educated to the potential benefits that can be achieved by such use. The market value associated with any specific use will then be determined by a host of factors. In most cases, increased profit will be a major stimulant to increased use and this will have to come about because of increased crop/nursery/greenhouse yields, decreased input costs, or some other economic incentive that is provided to the end user. An example of some other incentive would be approval of a nutrient management plan, submitted by a farmer to the National Resources Conservation Service of the United States Department of Agriculture, that uses FGD material to reduce nutrient (particularly P) runoff concentrations. Research, demonstrations and personal experiences will be extremely important to document the benefits, in terms of increased profits and/or other benefits associated with FGD materials use.

Whenever a new technology or product is introduced, there are three types of response groups. There are the early adopters, the majority users and the tailing users. It is important to identify people that are willing to work with FGD materials as early adopters. These people provide access to field sites and field data, become important sources of information to neighbors and at farm meetings, and legitimize the use of FGD materials in agriculture. The majority users will follow the lead of the early adopters if they become convinced that the risks involved are less than the benefits obtained. The tailing users may never fully embrace the new technology or product but they will not serve as an impediment to others in the use of the new technology or product.

The land grant system of agricultural research is ideal for development and testing of new technologies. The land grant system provides an extensive network of university personnel, agricultural consultants and agricultural industry people that work closely together. A new product or technology may be perceived as a threat to an existing technology or product and the best way to break down this barrier is through research that is then used as a basis for extension activities. In addition, information that is published in farm magazines or related publications is widely circulated within the agricultural community and farmers tend to have a high level of acceptance of the information that is distributed in this way. Appendix B includes a recent article that targets both the producer and potential end users of FGD materials (Ramsier and Norton, 2006).

4.2 Cost

The relationship between costs and benefits, or the cost/benefit ratio, will always be an important consideration for increasing FGD land application use or even for sustaining current uses. There are several different scenarios for using FGD materials that have different inherent cost/benefit ratios. The costs associated with using an FGD product include the costs of purchasing the material, transporting it from the site of generation to the site of use, and (usually) spreading it on the land.

For an FGD material that will be used in lieu of some other material, the main consideration is the relative effectiveness of the two materials. The combined cost of purchasing, transportation, and spreading must be similar to that associated with the material being replaced. Even if transportation and spreading costs were greater for the FGD product, these increased costs might be offset by reduced purchase costs (or no purchase costs) for the FGD product. Examples include the use of FGD materials in place of ag-lime for routine soil liming or use of FGD gypsum versus conventional gypsum as a source of calcium for peanut fruiting. Another example is the use of synthetic soil mixes containing FGD materials in place of conventional soil mixes by nurseries. If research shows the FGD materials perform similarly in comparison to the product that is routinely used, and the combined cost of purchasing, transport and use are similar, then the FGD material has a chance to become accepted by the nursery industry. What would be most needed at this point would be effective education and marketing.

If an FGD material will be used to provide some additional improvement to soil or plants and will not replace some existing material, then purchase, transportation, and spreading costs become even more important. Even if the FGD material has no purchase cost (free), the user may not want to pay transportation and spreading costs unless the benefit is well defined and documented. This highlights the importance of research and demonstration results that define clearly the benefit(s) to be gained by using the FGD material.

Currently, most FGD gypsum and other FGD materials are produced in the eastern United States. Potential beneficial use markets that are located in the western United States may never become economically viable for FGD materials produced in the eastern United States. Transportation costs can be reduced if using railcars or even barges if the source and markets for the material are near a navigable waterway or rail line. Generalized shipping rates (cents per ton-mile) are 0.97 for barge, 2.53 for rail, and 5.35 for truck transport (Anonymous, 2002). If an FGD material was valued at $5.35 per ton, it could be shipped 551 miles by barge, 211 miles by rail, but only 100 miles by truck before the shipping costs exceeded its value. With current fuel prices, trucking becomes even less attractive for transporting FGD material.

4.3 Lack of Consistent Product or Product Creation

Utilities are in the business of providing energy and not producing FGD material for resale. As a result, attention is not always given towards the quality of the end product, often to the detriment of potential beneficial uses of the FGD material.

Changes in sources of materials and plant operating procedures will affect the properties of FGD materials and their possible suitability for a particular use. Korcak (1993) listed boiler efficiency, source of coal, and type of sorbent as factors that will influence the characteristics of bed ash from FBC systems. If the bed material is recycled to increase the utilization of CaO, the result may be lowered CaO content but increased gypsum and ash content. The increase in ash content may lead to increased trace element concentrations.

Characterization of an FGD material, in terms of measuring various physical and chemical properties of the material, is conducted to help make predictions of the potential impacts on crop production and soil properties after land application. One basic goal of such characterization is to predict how the material will influence overall soil quality. Sims and Pierzynski (2000) discussed the soil quality concept in relation to land application of industrial by-products. The concept of soil quality is that any particular soil performs a variety of beneficial functions such as plant production, erosion protection, groundwater protection, surface water protection, air quality protection, and food quality protection. Each soil property (physical, chemical, or biological) has a range of values that is optimal for a particular beneficial function. The optimal range for one function may or may not coincide with the optimal range for a different function. For example, the range of soil pH for optimum production of most crops might be 6.3 – 7.0 because this range of pH will allow good growth of a large diversity of useful plants. Application of a material that changed soil pH out of this range would be seen as causing a decline in soil quality unless there were overriding improvements in other soil functions. Thus the concept of soil quality cannot be applied without reference to intended use. Any particular user of a soil will generally value one use more than other uses, such as plant production more than erosion protection, groundwater protection, etc. Even within a particular use, such as plant production, the optimal range for a soil property will vary with the particular crop plant. If it is desired to grow an acid-loving crop such as strawberries, a change in soil pH from the general optimum soil quality range of 6.3 – 7.0 would be necessary and desirable. Thus characterization of an FGD material for potential beneficial use will often result in different recommendation of use because of competing functions of soil quality after land application.

Fundamental physical and chemical properties such as particle size distribution, mineralogy, and chemical composition will all affect the potential impacts (both positive and negative) that occur when FGD materials are land applied. Physical and chemical properties of various FGD materials have been published. Armesto and Merino (1999) described properties of circulating FBC and pressurized FBC ashes. Kost et al. (2005) characterized a diversity of dry FGD materials from spray dryer, duct injection, and both atmospheric and pressurized FBC systems. Hower et al. (1997) presented chemical properties of some wet FGD materials. A total chemical analysis provides a baseline on possible changes in soil element concentrations after land application. If a specific element is present only in low concentrations in a material, land application probably will not increase the soil concentration of the element but might decrease the concentration by dilution.

Studies on mineralogical characterization of FGD materials include Zhou and Dayal (1990), Hower et al. (1997), Gomes et al. (1998), Laperche and Bigham (2002), Wang et al. (2004), and Bigham et al. (2005) The mineralogy of a specific FGD material is strongly influenced by the particular FGD process that in turn influences reaction temperatures and type of sorbent material.

For many beneficial uses of FGD materials, measurement of pH, calcium carbonate equivalency (CCE) and electrical conductivity are extremely important in addition to measurement of metals concentrations. This is because these properties have a great influence on many responses such as crop responses and heavy metal uptake. The CCE should be measured even if FGD material is not being used as a liming agent. Schumann and Sumner (1999) noted poor maize growth due to overliming when a fly ash with 54% CCE was applied at the same high rate (80 Mg ha^{-1}) as various other fly ashes having lower CCE. Table 4-1 provides information on pH, CCE and available lime on a variety of dry FGD materials. Generally, the wet FGD materials will have much lower values for pH and CCE than dry FGD materials and pure FGD gypsum has no CCE.

Once the use of a particular FGD material has been shown to provide benefit, and a market has been identified, the end user or broker that is marketing the FGD material will only continue to use the product if the material provided remains the same as that initially evaluated. If a change in the chemical and physical properties of the FGD materials occurs, and it negatively affects the end use, the user will lose faith in the product. Any material with changed properties will probably need some research done on it to determine the potential impact on end use before it can be marketed. However, as more research is done and more experience is gained in use of FGD materials, it will be easier to take existing information and make extrapolations from this information to the new material being considered. Once an end use is identified and a market has been created, however, the producer of the FGD material should make every effort to provide a consistent product over as long a time as economically possible.

4.4 Regulatory Issues

Dockter and Jagiella (2005) described the evolution of federal regulations controlling the management of coal combustion by-products (CCBs). The principal federal law that regulates hazardous and solid wastes is the Resource Conservation and Recovery Act (RCRA). Subtitle C of RCRA regulates wastes that are both “solid” and “hazardous.” Wastes that are not considered hazardous are regulated under Subtitle D, which passes regulation to the states as solid wastes. The original draft of RCRA did not specify whether CCBs were to be regulated under Subtitle C as hazardous wastes or under Subtitle D as solid wastes. The Solid Waste Disposal Act amendments to RCRA in 1980 temporarily excluded CCBs from regulation under Subtitle C. This meant that CCBs fell under Subtitle D to be regulated under state law as solid wastes. The U.S. Environmental Protection Agency (EPA) issued a report to Congress in 1988 stating that CCBs should remain permanently under Subtitle D. This position was reaffirmed by the EPA in1993 for fly ash, bottom ash, boiler slag, and FGD material. The most recent ruling by EPA in 2000 also states that FBC wastes, co-managed wastes, and wastes from coal combustion by non-utilities, petroleum coke combustion, co-burning of coal and fuel, and oil and natural gas combustion would continue to fall under Subtitle D and be regulated by the states.

Table 4-1
Paste pH, Calcium Carbonate Equivalence (CCE), and Available Lime for Dry FGD Products (Kost et al., 2005).

		pH	
FGD Process†	No. of Samples	Mean	Range
Spray Dryer	13	12.3	11.83 – 12.5
Duct Injection	7	12.2	12.0 - 12.5
LIMB	12	12.3	12.1 – 12.5
FBC bed	6	12.2	11.2 – 12.6
FBC cyclone	10	11.8	9.9 – 12.6
Other	6	8.9	5.2 - 12.5
		Calcium carbonate equivalent, %	
		Mean	Range
Spray Dryer	13	65.2	41.6 – 97.7
Duct Injection	8	52.3	27.1 – 71.6
LIMB	12	50.9	19.7 – 85.8
FBC bed	6	62.0	39.5 – 75.2
FBC cyclone	10	47.6	11.8 – 72.4
Other	7	24.8	-1.0 – 61.1
		Available lime %	
		Mean	Range
Spray Dryer	9	9.0	0.8 – 24.1
Duct Injection	4	25.5	3.6 – 33.5
LIMB	3	17.9	12.3 – 29.0
FBC bed	3	23.1	2.6 – 38.4
FBC cyclone	4	12.4	2.3 – 19.0
Other	2	9.0	1.8 – 16.2

†LIMB, lime injection multistage burner; FBC bed, fluidized bed combustion bed ash; FBC cyclone, fluidized bed combustion cyclone ash

The regulatory climate is currently somewhat antagonistic or noncommittal to FGD land application use because most states (39) do not have specific laws authorizing FGD land application. Fifteen states allow individual proposals for land application use but even if proposals are approved readily such a system tends to inhibit rather than promote FGD land application. A summary of state regulations related to FGD materials use is provided by the

National Energy Technical Laboratory web site (http://www.netl.doe.gov/technologies/coalpower/ewr/coal_utilization_byproducts/states/select_state.html).

All states except California, Washington, Rhode Island, and Tennessee designate FGD materials as exempt from regulation as hazardous wastes. Those four states require FGD materials to be tested (chemical analysis) before being exempted as hazardous wastes. Most states regulate FGD materials as solid wastes, industrial solid wastes, or special wastes. New Jersey, Oklahoma, and Utah exempt coal combustion by-products as solid wastes under certain uses or conditions. Thirty-two states do not have laws or permit by rule arrangements specifically authorizing reuse of FGD materials. Several states (Indiana, Texas, Utah, Wisconsin, and New York) that have laws authorizing reuse of FGD materials generally specify construction (road building) or other engineering uses instead of land application uses. Fifteen states evaluate proposals for reuse on a case-by-case basis.

States that have laws authorizing land application uses are Pennsylvania, Michigan, Illinois, Virginia, North Carolina, Missouri, Maryland, West Virginia, and Nebraska. Ohio and Oklahoma lack specific laws for reuse but do permit land application under other administrative arrangements. The specific language describing reuse varies by state but is generally as a soil substitute, additive or nutrient additive, conditioner, or amendment. Pennsylvania, Illinois, Virginia, and Maryland include mine reclamation as a reuse. Virginia appears to have one of the broadest definitions for reuse as a soil nutrient or other agricultural use. Maryland includes reuse as a soil improver or conditioner.

Uncertain regulatory oversight is a major barrier to increased beneficial land application uses of FGD materials. It is considered too risky to get into the business of marketing FGD materials if these materials have not been approved by the appropriate regulatory or oversight agencies. It is important to note the use of FGD materials should not be treated any differently than other agricultural inputs. Many agricultural inputs (e.g. pesticides and fertilizers) can offer tremendous benefits for crop production, but can also lead to impaired environmental quality if not used properly. What is greatly needed for increasing FGD material land application uses is the development of clearly defined permitted uses that are approved by rule. Oversight and/or penalties should only be extended if there is a violation of the permitted use. The number of permitted uses can be increased and existing uses can be modified or no longer permitted based on sound scientific research. It is not possible, however, with any agricultural input, to legislate rules that result in use that is 100% safe. There will always be people that overapply N fertilizers, misuse pesticides, or overapply FGD materials. However, appropriate use of penalties for these types of actions will greatly limit such misuse.

Table 4-2
Summary of Potential Areas of Agronomic and Environmental Concerns Related to FGD Materials Use in Agriculture and Other Land Applications.

Concerns	Elements in FGD material
Toxic elements	B, Se, Mn, As, Mo
Overfertilization	N, Ca
Creation of conditions leading to plant nutrient deficiencies	Ca, Mg
Soil salinity	Na, Cl, S, Ca
Soil alkalinity	Na
Poor soil structure	Na, Mg

4.5 Environmental Concerns

Some potential problems associated with any type of by-product that is applied to land include enrichment of soils with potentially toxic elements, overfertilization with plant nutrients, creation of conditions leading to plant nutrient deficiencies, development of soil salinity, development of soil alkalinity, and development of poor soil structure (Barker et al., 2000) (Table 4-2). Soils receiving FGD materials may exhibit Al, B, or sulfite toxicities, excess accumulations of Ca and S, Ca imbalances leading to Mg or P deficiencies, and soil salinity (Clark et al., 2001). The severity of these potential problems generally increases as FGD material rate increases.

Boron (B) toxicity is common in plants grown in fly ash (without any FGD material present) that has not been weathered and leached. Toxicity should be suspected any time unweathered fly ash is a component of an FGD planting medium. This includes FBC fly ash, wet FGD sludge mixed with fly ash for better handling characteristics, and dry FGD residue when the desulfurization reaction products and fly ash are removed together in the electrostatic precipitator. Ransome and Dowdy (1987) applied FGD material at rates up to 40 Mg ha^{-1} to a B deficient Hubbard loamy sand soil (Entic Hapludoll). The FGD was from a low S, high ash subbituminous coal and had a high B concentration (4100 mg kg^{-1}). In the first year, soybean had foliar B concentrations of 482 to 644 mg kg^{-1} on treated plots compared to 68 mg kg^{-1} for untreated control, and bean yield was strongly depressed at the 40 Mg ha^{-1} rate. By the third year, foliar B was still slightly elevated (69 to 75 mg kg^{-1} on treated plots compared to 57 mg kg^{-1} for untreated control), but yields were increased for all FGD material rates. Clark et al. (1999) tested three FBC ashes, six high $CaSO_3$

FGD materials, and three high $CaSO_4$ FGD materials as individual amendments for growth of maize in an acidic Porters series soil (typic dystrudept, pH 4.22). Plant shoots developed potentially toxic B concentrations (> 200 mg kg^{-1}) in soil amended with one FBC, two $CaSO_3$ FGD materials, or one $CaSO_4$ FGD material. These materials had relatively high (99 to 175 mg kg^{-1}) B concentrations. In another study, soybean shoots had B concentrations exceeding 200 mg kg^{-1} in a soil amended with FGD material at 167 or 222 Mg ha^{-1}. The FGD material was a low-grade gypsum product mixed with fly ash (Punshon et al., 2001). Finally, northern red oak leaves showed symptoms of B toxicity when grown in soil amended with FGD material at rates of 14.5 or 18.1 Mg ha^{-1}, but not at 10.9 Mg ha^{-1} or less (Crews and Dick, 1998). The highest leaf concentration of B was 230 mg kg^{-1} in FGD-treated soil versus 90 mg kg^{-1} in unamended soil. The dry FGD material was a mixture of fly ash and desulfurization reaction products and contained B at a concentration of 369 mg kg^{-1} FGD.

Boron need not be a problem if FGD material is allowed to weather and the B is leached from the material before it is applied to the soil. Alternatively, applying FGD material in the fall of the year in a humid climate may provide sufficient time for the B to be leached so that concentrations are reduced below inhibitory levels. This is an example where proper management and education can make a big difference in how successful a beneficial use program becomes.

Trace elements other than B may also have elevated concentrations in plants grown on FGD-amended soil. In ryegrass (Wright et al., 1998), concentrations of Se were increased on soil amended with FBC fly ash, concentrations of As were increased on soil amended with wet FGD sludge, and concentrations of Mo were increased on soil amended with either FBC bed ash, FBC fly ash, or wet FGD sludge. Only Se on soil amended with FBC fly ash was elevated enough to be a concern for livestock diets. Several crop plants (corn, soybean, radish, cotton) also had elevated concentrations of As, Mo, and Se on soil amended with a mixture of dry FGD material and fly ash (Punshon et al., 2001). In these cases, the levels observed were below those generally considered to be of concern for ecological or human health.

Applications of sulfite-containing FGD material to soil may reduce plant growth by sulfite toxicity. Ritchey et al. (1995b) demonstrated that calcium sulfite added to acid soils decomposes to generate sulfur dioxide and presented evidence that sulfur dioxide is the primary toxic agent to plants. They found that soil pH strongly influenced the toxicity of calcium sulfite to plants. Root growth in the presence of $CaSO_3$ was best if the soil pH was greater than 6. Also, root growth at pH less than 6 (e.g. pH 4.6) in the presence of $CaSO_3$ improved with time due to depletion of $CaSO_3$ by oxidation to $CaSO_4$. In another study, short-term decreases in forage yields were attributed to sulfite toxicity when a liquid ammonium sulfite FGD was added to soil or sprayed onto the plants (Gissel-Nielsen and Bertelsen, 1989). Thus, the severity of sulfite toxicity depends on soil pH. However, under natural environmental conditions and at rates recommended for agricultural use, the sulfite is rapidly oxidized to sulfate and problems do not occur. Field studies are being initiated in Ohio (in 2006), using sulfite-based FGD materials, to provide field-based information to demonstrate the ability of these materials to provide agricultural benefit.

Farina and Channon (1988b) observed a decrease in corn rooting density in some subsoil layers following gypsum application. The rooting decrease was correlated with high levels of exchangeable sulfate but they were not sure if the decrease was caused directly by the sulfate or some other factor (N or B nutrition) affected by the sulfate. Sulfur concentrations (Stout and Priddy, 1996) in alfalfa approached potentially toxic levels for grazing animals for alfalfa grown on soil amended with FGD gypsum at 9 or 18 Mg ha^{-1}.

Applications of FGD material may cause Mg deficiencies resulting from increased leaching of Mg. The increase in leaching is due to competitive exchange of Mg by Ca. In a laboratory experiment (Alva et al., 1998b), FGD gypsum was applied at rates equivalent to 4.5 or 9.0 Mg ha^{-1} to columns packed with soil from the top 15-cm of a Candler fine sand soil (Lamellic Quartzipsamment). Leaching of Mg and K was increased strongly by the FGD treatments. Miller and Scifres (1988) noted strong decreases in exchangeable Mg following infiltration measurements when phosphogypsum was applied at 5 Mg ha^{-1} to soil from the Ap horizon of a Greenville soil (Thermic Rhodic Kandiudult). Field experiments have also identified Mg problems resulting from FGD application. In Georgia, application of a high gypsum FGD material alone or with fly ash at rates up to 20 Mg ha^{-1} caused potential Mg deficiency to 60 cm depth in a sandy soil and decreased exchangeable Mg in the upper 20 cm of two soils with greater clay content (Kukier et al., 2001). In West Virginia, FGD gypsum applied to Gilpin silt loam soil at rates up to 32 Mg ha^{-1} decreased soil and plant Mg concentrations (Ritchey and Snuffer, 2002).

Soil amendment with FGD gypsum or other gypsum often results in increased plant Mn concentrations (Ritchey et al., 1995). Orchardgrass grown in soil leached with gypsum solution equivalent to a 25 Mg ha^{-1} gypsum application had 570 mg Mn kg^{-1} compared to 208 mg Mn kg^{-1} for the control treatment. Foliar Mn in corn increased from 49 mg kg^{-1} on unamended soil to 87 mg kg^{-1} on soil amended with calcium sulfate at 6 Mg ha^{-1}. Some of the increase is attributable to increased Mn levels in subsoil. Other increases in plant Mn were noted by Shainberg et al. (1989), who stated that the increased Mn levels had not produced decreases in plant yields.

There are a variety of leaching tests that attempt to predict the solubilization and movement of chemical constituents from a matrix such as soil. Sorini (1997) reviewed the characteristics of these tests and their possible use for characterizing coal combustion by-products. Most tests have limitations in terms of simulating the disposal environment of coal combustion by-products. Also, most tests are not representative of the conditions following land application of an FGD material where the FGD material represents a small fraction of the total soil volume. Characterization of a material must be based on more than a single leaching procedure and must include chemical, physical, and mineralogical measurements.

4.6 Mercury (Hg) Issues

Because of the heightened concern and interest regarding Hg and the environment, a separate section has been devoted to this topic.

Mercury in the environment is a concern because of its impact on human and ecological health. Coal-fired utility boilers in the United States emit an estimated 40 to 52 tons of Hg yearly. Approximately 40% of the Hg entering a power plant in the coal is captured and 60% is emitted (Pavlish et al., 2003). Adoption of new technology to provide enhanced removal of Hg from flue gas will likely result in increased Hg concentrations in FGD materials. This will increase concerns regarding the safety of land application of FGD materials. The primary safety issues regarding Hg and land application of FGD materials are Hg volatilization from the FGD materials, Hg uptake into plant tissue, and the extent of Hg leaching. In general, studies have indicated that Hg in FGD materials is not easily removed by leaching or volatilization (see paragraphs below). Plant uptake information into agricultural crops growing on soils treated with FGD products needs to be evaluated.

Pavlish et al. (2003) gave a detailed review of Hg control issues and options for coal-fired power plants. Mercury concentrations (mg kg^{-1}) in utility coals by region and coal rank were 0.049 for western bituminous, 0.068 for western subbituminous, 0.09 for both Fort Union lignite and interior bituminous, 0.119 for Gulf Coast lignite, and 0.126 for Appalachian bituminous. Essentially no Hg is removed in the furnace or bottom ash of wall-fired and tangentially fired pulverized coal boilers so that all Hg in the coal enters the particulate control device. Percent Hg emission from the boiler for four cyclone-fired units was 66% and for four FBC boilers was 79%.

Wet scrubbers remove about 90% of the oxidized gaseous mercury (Hg^{2+}) entering with the flue gas but none of the elemental mercury (Hg^0) (Pavlish et al., 2003). The percentage of total Hg removed across particulate control devices and scrubbers combined is influenced by coal chlorine (Cl) content, which determines the oxidation status of the Hg leaving the particulate control device and entering the scrubber. For wet scrubbers following a cold-side electrostatic precipitator (CS-ESP), percent of total Hg removed by the scrubber alone increased from 30% to 60% as coal Cl content increased from 50 to 1000 mg kg^{-1}. For wet scrubbers following a hot-side ESP (HS-ESP), percent of total Hg removed by the scrubber alone increased from 20% to 50% as coal Cl content increased from 200 to 1000 mg kg^{-1}.

The average percent of total Hg removed by a wet scrubber combined with a fabric filter was 88%, with 58% removed by the filter and 77% of the remaining Hg entering the scrubber in oxidized form (Pavlish et al., 2003). The average percent of total Hg removed by a wet scrubber combined with a CS-ESP was 49%, with 27% removed by the CS-ESP and 53% of the remaining Hg entering the scrubber in oxidized form. A wet scrubber combined with a HS-ESP removed an average of 26% of total Hg, with only 4% removed by the HS-ESP and only 34% of the remaining Hg entering the scrubber in oxidized form. Thus, both the fly ashes and FGD products from wet scrubbers coupled with fabric filter or CS-ESP will have potentially greater Hg contents than for wet scrubbers coupled with HS-ESP if factors such as coal Hg content and mass of FGD products are similar among the three systems.

Spray dryers remove about 90% of the oxidized gaseous mercury entering with the flue gas, and spray dryers coupled with a fabric filter also remove a significant fraction of the elemental Hg

(Hg^0) for coal Cl contents above 200 mg kg^{-1} (Pavlish et al., 2003). The average percent of total Hg removed by a spray dryer combined with a fabric filter was 38% (range from 0% to 99%). The percent of total Hg removal was very low for coal Cl contents below 100 mg kg^{-1} and very high for Cl contents above 900 mg kg^{-1}. The average percent of total Hg removed by a spray dryer combined with an ESP was 18% at three test sites and showed no relationship with coal Cl content.

Fluidized bed combustion (FBC) boilers combined with fabric filters removed the highest average percent of total Hg (86%) with a range from 66% to 99% (Pavlish et al., 2003). The high removal rates are believed to be partly due to Hg capture on relatively high carbon content of the fly ash.

Schroeder and Kairies (2005) reported Hg concentrations in FGD gypsum samples from four power plants varied from 0.143 to 1.17 mg kg^{-1}. Mercury concentrations were not decreased by drying samples from 30% to 25% moisture (by wt.) or by leaching samples with dilute acid for 200 hours from an initial pH 8 to final pH 2.5. When aqueous slurries of an FGD gypsum containing approximately 200 mg Hg kg^{-1} were heated at temperatures up to 94 ^{o}C for equilibration times exceeding 6 hours, less than 0.5% of the Hg was released into solution. In settling experiments the Hg was always concentrated in the top-most, slower-settling layer of the gypsum. For example, Hg concentrations (mg kg^{-1}) in top layer/bottom layer for three settling trials were 3.56/0.072, 2.90/0.180, and 13.0/0.70.

Aljoe et al. (2004) listed Hg concentrations in various FGD materials derived from full-scale field testing of a proprietary liquid reagent to enhance Hg capture in coal-fired power plants with wet FGD systems. The field tests in two plants were described by Nolan et al. (2004). Concentrations varied from 0.016 mg kg^{-1} for CS-ESP ash to 0.055 mg kg^{-1} for FGD gypsum to 38 mg kg^{-1} for wet FGD fines. They suggested that use of particle separation techniques and separate disposal of the fines portion may be necessary for beneficial use of FGD gypsum. Using only the larger gypsum particles will significantly reduce the risk of Hg exposure. The high Hg concentration value for FGD fines is similar to that for the slowly-settling fraction of gypsum found by Schroeder and Kairies (2005).

There are no specific federal regulations concerning land application of FGD material. Heavy metal concentrations were measured in samples of FGD gypsum and natural gypsum (Dontsova et al., 2005). The Hg concentrations in both gypsum materials were less than the detection level of 0.26 mg kg^{-1}. This is quite low compared to the regulation level of 17 mg kg^{-1} (Part 503 regulations for land application of biosolids). Hower et al. (2005) noted that Hg concentrations (mg kg^{-1}) in FGD materials from Kentucky power plants were greater for wet sulfite systems (0.463) than for forced-oxidation gypsum systems (0.176).

If Hg in the FGD material does not leach out of the FGD material into the environment, there is a reduced risk of exposure. However, mobility of Hg has been identified as a concern for beneficial use of the FGD material. Aljoe et al. (2004) reported Hg concentrations in leachates from various coal combustion by-products including fly ashes, bottom ashes, FGD sludges, and spray dryer ashes. The analysis used the TCLP (Toxicity Characteristic Leaching Procedure) as the measurement method under different pHs. Mercury concentrations in all by-product leachates were less than the 1 ug L^{-1} detection limit. This is below the drinking water standard of 2 ug L^{-1}. They also described groundwater monitoring at an active wet FGD disposal area. Their preliminary testing on two quarterly sample dates indicated that Hg concentrations were below the 1.0 ug L^{-1} detection limit for all six monitoring wells and two seepage sites.

There appear to be few specific studies on Hg leaching from field-applied FGD material. In a study of mineland reclamation, using 280 Mg ha^{-1} of FGD material from a fluidized bed combustion burner, Hg concentrations in surface water and groundwater samples were below detection limits and Hg measurements were discontinued (Dick et al., 1999). Leaching of Hg from FGD material will be affected by the chemical, biological, and physical environment where the material is applied. The change in the chemical form of Hg also needs to be considered because the organic form of Hg has higher toxicity than the inorganic form. Specifically, methyl Hg will form when the inorganic form of Hg enters an anoxic environment such as sediments or wetland areas. Therefore, a study of fate and transport of Hg from the field-applied FGD material is needed if the total potential health effect of Hg is to be understood.

Xin et al. (2005) evaluated factors affecting Hg release from coal combustion products including 13 fly ashes and 8 FGD materials. The materials were collected from 10 power plants burning a variety of coals and using a variety of pollution controls. Mercury concentrations in the FGD materials varied from 0.053 to 0.846 mg kg^{-1}. Leachates prepared using the Synthetic Precipitation Leaching Procedure (SPLP) had Hg concentrations varying from non-detectable to 13.0 ng L^{-1}. Total Hg concentration in an FGD sludge (0.673 mg kg^{-1}) was greater than in the fly ash (0.103 mg kg^{-1}) from the same bituminous-coal burning plant. Leachable Hg for this FGD sludge was 2.3 ng L^{-1} versus non-detectable for the baseline fly ash. The effects of post-combustion NO_x controls on Hg concentrations in FGD gypsum (limestone forced oxidation) were evaluated by collecting samples with the NO_x control system turned on and off. NO_x control used selective catalytic reduction (SCR). Total Hg concentration was lower in FGD gypsum with SCR on than with SCR off (0.053 vs. 0.128 mg kg^{-1}). In the laboratory, FGD materials emitted a greater flux of Hg to the atmosphere when wet than when dry. A bituminous-derived FGD sludge had a Hg emission rate (ng m^{-2} h^{-1} at 25 ^{o}C in dark) of 68.7 when wet (35 wt% water content) and 3.0 when dry. In the field, unstabilized FGD materials derived from lignite coal had a low (0.8 ng m^{-2} h^{-1}) Hg emission rate. Scrubber sludge mixed with fly ash or pyrite had greater Hg emission rates (11.2 and 10.9 ng m^{-2} h^{-1}). An emission rate of Hg of 11.2 ng m^{-2} h^{-1} is equivalent to 0.98 g ha^{-1} yr^{-1}.

Hassett et al. (2004) measured Hg vapor release at ambient and near ambient (37 ^{o}C) temperatures from six fly ash samples including a mixed sample that was a mixture of fly ash and FGD material. Total Hg concentrations in the samples varied from 0.112 mg kg^{-1} for the mixed sample to a maximum of 0.736 mg kg^{-1} for the other samples. Mercury vapor release (pg Hg g^{-1} sample for 174 days) at ambient temperature was greater for the mixed sample (2.400) than for the other fly ash samples (range 0.119 to 1.013) even though the mixed sample had a lower total Hg concentration. These results agreed with an earlier study showing that the bulk of the Hg in the mixed sample thermally desorbed at a lower temperature (250 ^{o}C) than the Hg in the other samples (above 300 ^{o}C).

4.7 The Texas Example

Buckley et al. (2005) discussed developments in Texas that led to a progressive approach for the utilization of coal combustion products (CCPs). The percentage of coal ash, primarily fly ash, utilized in Texas increased from 15% in 1992 to 60%-70% in 2003. Most of the ash was used in the construction and transportation industries, and there was no mention of use in agricultural land applications. Texas has been less successful in promoting use of FGD materials than of ordinary fly ash.

Three actions were taken that led to increased coal ash use in Texas that are also applicable to increased use of FGD materials for land applications. First was the development of a coal ash utilization group consisting of power utilities, ash marketers, environmental consultants, and university personnel to promote the use of coal combustion products and remove barriers prohibiting utilization. It was perceived that a state environmental department was less likely to take the initiative to facilitate CCP utilization without the effort of an industry-sponsored group to bring the opportunity of CCP utilization to the attention of the agency. Second was the adoption of governmental rules establishing criteria for use of CCPs and omitting utilized CCPs from the definition of solid waste. Interestingly, one criterion requires that a CCP meets or exceeds raw material specifications without treatment or reclamation. This criterion may impede the use of FGD gypsum for wallboard in Texas if chlorides would need to be removed to make the gypsum wallboard-ready, but it would not affect possible land application uses of the gypsum. Third was passing legislation that prevents unauthorized discharges to state waters and thus provides a ready avenue of enforcement if CCPs are used improperly. Other actions were taken specific to the utilization of CCPs in construction and transportation that are not applicable to agricultural land application uses.

The above example from Texas strongly suggests a regular meeting of all interested and involved parties in a state would go far to identifying the most important barriers to increased FGD materials use and how to overcome these barriers. As various states become more familiar with rules that promote proper and safe use of FGD materials, these states become a resource for other states facing similar issues.

5
RESEARCH TO OVERCOME BARRIERS

There are a large number of potential agricultural and other land application uses of FGD products. Several of these have received previous research attention, but only in specific locations of the United States and under limited conditions of crops, climate and soil types. It is not necessary, or even possible, to study the efficacy and potential environmental impacts of FGD materials for agricultural use under every potential combination of climate, soil type, crop and application rate. However, as FGD materials markets develop, it will be important to have information available to answer questions by customers and other interested parties. The more studies that are done, and the more information and experience that is generated by these studies, the higher the level of comfort will be for FGD materials use.

Some uses of FGD materials in agriculture have potential to consume large amounts of materials while others will be used in much more limited amounts. The development of some FGD materials use is technologically advanced while other uses have not yet been initiated or are at the seed stage. Some uses are already accepted by the marketplace, and others are only now being introduced into research projects. Research is needed that spans the range of small seed grants to large demonstrations.

Research support could come from a variety of sources including the industrial producers, farm commodity groups, government and universities. There is currently intense interest in developing next generation, coal-fired electricity generating plants that have zero gaseous emission. Even these plants will create products that have potential benefits for agriculture. Far-sighted thinking is needed to plan beneficial uses of products generated by these plants at the beginning of such projects rather than at the end.

Table 5-1 provides a list of 20 research projects that relate to potential beneficial uses of FGD materials. Not all are of equal importance and some projects may yield results that create new products. Other projects involve refinements of existing technologies that will lead to markets in new areas and on new crops or soil types. Taken together, all of the projects have the potential to lead to the beneficial reuse of a large percentage of the current and future FGD products generated.

Background information related to some proposed research projects and the existing state of knowledge has been provided in Chapters 1-4 of this review. What follows is the identification and brief description of each of the 20 potential research projects.

Table 5-1
Research and Demonstrations to Enhance Agricultural and Land Application Uses of FGD Materials

Research That Can Impact Large Potential Volume Use

(1) Reduction of the effects of subsurface acidity on crop production

(2) Use of FGD gypsum to enhance no-tillage crop production

(3) Surface applications of FGD gypsum after tillage on heavy clay soils

(4) Weathering effects during FGD storage

(5) Demonstration sites planned in association with each research project

(6) Long term impacts of FGD applications at recommended agricultural rates

(7) Concentrations and fates of Hg and other elements in FGD materials that are land applied for beneficial uses

Research That Can Impact Moderate Potential Volume Use

(8) Expanded S and N fertility work for crops

(9) Application of FGD materials to forest plantations to improve tree production

(10) Development of synthetic soils and mixes for use in the nursery and greenhouse industries

(11) Use of calcium sulfite-based FGD materials

(12) Reclamation of sodic or saline soils

Research That Can Impact Small Potential Volume Use

(13) Use as a soil amendment on road right of ways

(14) Reductions of P concentrations in surface water runoff

(15) Improving soil quality in urban and industrial areas

(16) Cover for landfills and for supporting the establishment of vegetation when landfills are closed

(17) Co-mingling sulfite FGD materials with coal refuse and coal wash waste

(18) Use as an co-amendment during composting of organic materials (i.e. manures, food wastes, leaves, grass clippings, etc.)

(19) Use of FGD materials for mineland reclamation and for improving final cover

(20) Enhanced production of sod at sod farms

The first seven research projects identified in Table 5-1 are those that are felt to have the greatest potential to impact the marketplace in terms of the volumes of FGD products that could be used. The research projects listed as 8-12 in Table 5-1 have moderate potential for consuming volumes of FGD products and research projects 13-20 are those that will probably consume the smallest amounts of FGD products.

(1) <u>Reduction of the effects of subsurface acidity on crop productivity</u>. Because of the greater solubility of FGD gypsum compared to other commonly applied soil amendments, the Ca and sulfate can readily move downward into the soil profile with percolating rain water. When the Ca and sulfate reach an acidic soil subsurface layer, the Ca will displace the exchangeable Al, Mn and Fe. This will stimulate the downward movement of the Al cations that inhibit root development and growth. In addition, the sulfate can form complexes with Al and make it unavailable for plant uptake. Both mechanisms result in an improved soil environment for crop root development in acid subsoils. The increased crop rooting increases the volume of soil that is exploited by the plant for uptake of water and essential nutrients leading to increased nutrient use efficiency and better crop yields. Research is needed to document root growth, nutrient uptake and crop yields in replicated field trials with and without FGD gypsum application.

(2) <u>Use of FGD gypsum to enhance no-tillage crop production</u>. This work is currently occurring to a limited extent by researchers at The Ohio State University and Ag Spectrum Company (DeWitt, IA). The potential amount of FGD gypsum that could be used to enhance no-tillage crop production is huge, but university recommendations are totally nonexistent and, in some cases, university extension personnel are even hostile to use of FGD gypsum as a soil amendment. We do not have a good understanding of the soil types that best respond to FGD gypsum applications, the relative efficacy of large rates every few years versus small annual rates, the crops that respond best, and the long-term impacts of FGD gypsum use on soil properties. No-tillage is becoming a major crop production practice in many parts of the United States and research sites need to be strategically located in states where no-tillage is commonly practiced. The economics of FGD gypsum use (i.e. crop yields, nutrient use, reduced inputs if FGD gypsum allows a farmer to do no-tillage that before was not practical, etc.) need to be carefully documented.

(3) <u>Surface applications of FGD gypsum after tillage on heavy clay soils</u>. While most of the research to date in the corn belt of the United States has been conducted on no-till soils, there is testimonial support that surface applications of gypsum after final tillage also have benefit in maintaining good soil aeration, improved water infiltration and greater crop yields. At the 2005 National No-Till Conference (Cincinnati, OH), a farmer conversed with the lead author of this report and communicated his positive experiences of using gypsum on tilled fields. The results were only evident if the gypsum was surface applied and not mixed into the soil at time of tillage. These types of leads need to have follow-up research to determine whether such benefits really exist.

(4) <u>Weathering effects during FGD storage</u>. Besides the agricultural field research that is required, there are other practical issues in FGD materials handling that will need to be

investigated. If all applications are made within a narrow window of time, it may not be possible to deliver the material to the farmer at the time it is requested. Could FGD materials be stored at locations such as farmer cooperatives? Should storage be required for FGD materials that have elevated levels of B or sulfites? How do the properties of FGD materials change when stored in the open? Does storage reduce the value of the FGD materials? The answers to some of these questions can be arrived at using common sense. However, regulatory agencies generally do not like to see materials they consider solid wastes stored in open, public places. Research to document the environmental safety of FGD materials that are stored prior to use may be important to achieve regulatory approval.

(5) <u>Demonstration sites planned in association with each research project</u>. Careful visual documentation should be included as part of the research plan for every research site. Researchers are skilled in making many different types of observations and measurements. What is often most convincing to a new user is data plus a site visit or pictures that clearly show treatment differences.

(6) <u>Long-term impacts of FGD applications at recommended agricultural rates</u>. The nay-sayers often raise the question of long-term impacts to inhibit a new technology. There are certainly enough examples of unforeseen impacts of a new technology to warrant some of these types of questions. Research should be conducted that seeks out sites in the United States where FGD materials have been applied for many years to determine whether changes occurred that warrant caution, above and beyond that currently imposed for FGD land application uses. This would include measuring soil, water and plant quality at such sites.

(7) <u>Concentrations and fates of Hg and other elements in FGD materials that are land applied for beneficial uses</u>. The one issue that could potentially derail FGD materials use in agriculture is Hg. As more and more Hg is removed from the flue gases, it will be imperative that we understand the fate of Hg in the environment, and how to reduce its levels in the FGD product. There is evidence that some rather simple steps can be taken at the utility producing the FGD product to reduce Hg in the material that is marketed for agricultural use. Probably the easiest solution is to separate the fines, where recent research suggests much of the Hg resides, before removing the rest of the FGD material and making it available to the agricultural market. Like any product, it will be important that the levels of all elements of concern, such as Hg, are monitored and remain at levels that are acceptable for the intended use. The only guidelines currently available for determining whether a material should be allowed for land application are the 503 regulations established for biosolids. Although some scientists maintain that these regulations are not appropriate for any materials other than biosolids, they are generally restrictive enough that even if availability of elements in FGD materials is greater than that in biosolids, the built-in margin of safety is sufficient to provide protection to the public until such regulations can be reviewed and new ones written that are specific for FGD materials use.

(8) <u>Expanded S and N fertility work for crops</u>. Sulfur deficiencies in crops are increasingly being reported, especially for forage crops. FGD materials are excellent sources of S and fertility work is needed to reassess the importance of S nutrition to provide optimum yields for a wide variety

of crops and in many different locations. Crops grown on soils that are sandy, low in organic matter and in more humid areas are most likely to be deficient in S and would benefit from use of FGD materials as a S fertilizer. FGD materials alone, or in combination with a small amount of coal ash, provide other nutrients that can increase crop yields. Little systematic research has been done that relates application rates of FGD materials to increased uptake of nutrients. FGD materials may be particularly effective in supplying inexpensive amounts of trace nutrients to crops. Agronomists have long held the idea that optimum N use efficiency cannot be achieved if other nutrients are also limiting. Research at The Ohio State University has shown that a significant N by S interaction occurs when corn is grown on a Wooster silt loam soil (Typic Fragiudalf) (Chen, Kost and Dick - manuscript in preparation). Sulfur additions, as FGD materials, increased the N use efficiency and, along with high fertilizer N costs, this becomes an attractive incentive for farmers to apply FGD materials on their soils.

(9) <u>Application of FGD materials to forest plantations to improve tree production</u>. Trees are a “crop” that requires many years to reach maturity. Any increase in growth can have a tremendous impact on the bottom profit line. Research conducted in Ohio indicates that a treatment of FGD materials onto forest soils can increase the soil pH and improve overall nutrient availability. For some tree species, it is important that the pH adjustment be rather small as optimum pH for growth is lower than for agronomic crops. FGD materials with low acid neutralization potential would be ideal. Research is needed to determine the best ways to apply the FGD materials to the trees, to document growth improvements and to determine the optimum rates and frequency of FGD materials applications.

(10) <u>Development of synthetic soils and mixes for use in the nursery and greenhouse industries</u>. There is a need for increased research on use of FGD materials as components of synthetic soils. Production of synthetic soils is a way to overcome any limitations for plant growth regarding both FGD materials and the other components of a synthetic soil. The proper mix of FGD materials and other components may ameliorate limitations for plant growth that the individual materials possess. Production of synthetic soils by proper blending of the components (i.e. organic matter, sand, bed ash, fertilizer, etc.) may result in several grades of materials. Some mixes of lower quality may be used for nursery plant production and in landscaping. Others may be of higher quality for more specialty crops and where there are human food chain concerns.

(11) <u>Use of calcium sulfite based FGD materials</u>. A major unanswered question is whether Ca-sulfite can be used as an agricultural amendment. Unlike gypsum, which has a history of use in agriculture and a rapidly developing research base, there is little information on agricultural uses of Ca-sulfite. A few studies have shown short-term sulfite toxicity when sulfite-containing FGD materials were used as soil amendments. Rates of conversion of the S in the FGD from Ca-sulfite to Ca-sulfate, under natural environmental conditions and at recommended agricultural amendment rates, need to be determined. Also, erosion of large amounts of newly applied Ca-sulfite into ponds and streams could, theoretically, remove most of the biologically available oxygen and cause fish kills or other water quality problems. This is because oxidation of sulfite to sulfate has a high oxygen demand. Finally, research is needed to determine the best way to store FGD Ca-sulfite to allow for natural occurrence of the oxidation of sulfite to sulfate before

field application. This may be an issue whose importance decreases with time as most new scrubbers force the oxidation of the sulfite to sulfate and produce high quality gypsum.

(12) Reclamation of sodic and saline soils. Gypsum is a well-known amendment for reclamation of sodic and saline soils. Gypsum has been used extensively in reclamation of sodic soils with infiltration problems. It is well known that application of gypsum to sodic soils improves the soil physical conditions by promoting flocculation, enhancing aggregate stability and increasing the infiltration rate. These observations have little scientific documentation or quantification support regarding the actual assembling of the soil particles at the aggregate level. There is also little work that compares efficacy of FGD gypsum with mined gypsum. There probably is little doubt that the two gypsum sources will work equally well. However, if the cost of gypsum to the user is decreased because of a program developed with a utility to help defray transportation or application costs, the areas of sodic and saline soils that become available for economic remediation are expanded. Research is needed to expand the use of FGD gypsum to soils that traditionally have been marginal in terms of cost effectiveness of remediation. Also, research where high value crops are grown in areas where land is relatively unavailable because of urban and industrial pressures could open up new markets for the FGD gypsum.

(13) Use as a soil amendment on road right-of-ways. The federal highway bill has set aside millions (billions?) of dollars for new road and to upgrade and repair existing roads. States are also involved in highway construction. Often the soils in the right-of-ways are of very poor quality and vegetation establishment is not very successful. Research that could be used to help highway departments write guidelines that specify FGD materials for use in vegetation establishment on highway right-of-ways could be an important outlet for some producers of FGD materials.

(14) Reduction of P concentrations in surface water runoff. Livestock owners and operators are becoming familiar with the National Pollutant Discharge Elimination System (NPDES). This system is being revised to address nonpoint source discharges. If approved, the system would require the implementation of a comprehensive nutrient management plan (CNMP) to address the nutrient, sediment, or pathogen discharges. Research is being done in multiple states to investigate materials that may be effective, when land applied, to reduce P concentrations in surface water runoff. There is evidence that FGD materials can be effective in this type of application. The benefits, both in terms of improved water quality and economics compared to other proposed materials, need to be documented at sites across the United States.

(15) Improving soil quality in urban and industrial areas. There is a need for a general examination of the value of FGD gypsum for improving urban hydrology. Many cities have combined storm/sanitary sewer systems, and significant decreases in receiving water quality often occur during large storms when the large flows must be discharged without treatment. Even in cities with separate storm and sanitary sewers, downstream flooding may be reduced by reducing storm runoff. Storm runoff from urban soils will be reduced by optimizing infiltration and hydraulic conductivity. FGD gypsum applications have been shown to increase infiltration and reduce runoff on dispersive soils. Gypsum applications will also ameliorate subsoil acidity

and promote deeper rooting that extracts water from a larger soil volume. The increased soil volume can be recharged during storms. The urban soil landscape consists of an amalgam of soils with diverse physical and chemical characteristics. Instead of studying the specific response of each soil type to gypsum application, the goal would be to identify soils to which gypsum should not be applied. Then gypsum would be applied to all the remaining soil types. The FGD gypsum would hopefully be available from a nearby power plant to help minimize transportation costs. Another facet of optimizing urban hydrology would involve the construction of living roofs (rooftop planters) that store storm water and remove it by plant transpiration. The living roofs would be constructed from synthetic soils including FGD materials as components.

(16) <u>Cover for landfills and for supporting the establishment of vegetation when landfills are closed</u>. Landfills seem to have an enormous need for daily cover and for final cover when a portion of a landfill is closed. Effective and inexpensive cover material is not always available. Cover that incorporates large amounts of FGD materials in appropriate ways could be beneficial to landfill owners and provide an outlet for FGD materials. This could be done on site on landfills owned and operated by utilities. While some efforts have been made in this regard, additional work is needed to prove the concept and to allow utilities to write this use of FGD materials into their ash and FGD disposal plans.

(17) <u>Co-mingling sulfite FGD materials with coal refuse and coal wash waste</u>. FGD materials that contain high concentrations of sulfite could be mixed with coal mine spoil or coal wash refuse to prevent oxidation of the pyrite and thus inhibit acid generation. Several coal preparation plants are currently using this technology but little research information is available to document the success of these operations.

(18) <u>Use as a co-amendment during composting of organic materials (i.e. manures, food wastes, leaves, grass clippings, etc.)</u>. Because mushrooms have no chlorophyll, they must get all their nutrients from organic matter in their growing medium. The most commonly used medium is compost that has been scientifically formulated from various materials such as straw, corn cobs, cotton seed and cocoa seed hulls, gypsum and nitrogen supplements. FGD gypsum could be used as a replacement for mined gypsum in this use in those locations where mushroom production is occurring. Additional work to develop composts that are derived from mixes of organic matter and FGD materials could create value-added products that could be sold for use by homeowners, landscapers, or anyone requiring a source of compost to support plant growth. Research is needed to determine how various FGD materials and their ratios in the compost feedstock impact the quality of the final product.

(19) <u>Use of FGD materials for mineland reclamation and for improving final cover</u>. Surface mines are required to store topsoil that is removed when the mine is first opened and then use this stored material as final cover when the site is reclaimed. During the process of restoring the mine site to an approximate original contour, the soils can become extremely compacted by the traffic of heavy equipment. When the topsoil is placed over the graded material, it is often of insufficient depth to allow for proper rooting of plants. The roots are restricted from entering the regraded materials because of poor physical and chemical conditions. Application of FGD

materials into the final lift of regraded spoil prior to topsoil replacement could enhance overall reclamation success and provide a means of beneficially using FGD materials. FGD material that has acid neutralization abilities could be used to mix with the stored topsoil to improve soil quality.

(20) Enhanced production of sod at sod farms. Sod growth for urban markets has expanded rapidly in the United States. Sod farms require fields that are uniform with little slope and that can quickly establish good quality sod. Then the soil must be free of stones and be easily cut so that harvesting of the sod can be easily accomplished. FGD materials could be mixed into soil at sod farms to prepare a good quality bed for sod establishment. As the sod is harvested and soil is removed, the FGD material could be replaced on a regular basis. A small amount of FGD material, such as FGD gypsum, that is transported with the sod could also benefit the soil properties where the sod is placed. Fly ash has been used in this way, but no research has been done to incorporate FGD materials into production of sod.

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A
TERMINOLOGY

A.1 Glossary

Bulk density – The mass of dry soil per unit bulk volume of soil. The value is expressed as megagrams per cubic meter (Mg m^{-3}).

Calcium carbonate equivalency (CCE) – The content of carbonate in a liming material calculated as if all of the carbonate is in the form of $CaCO_3$. The value for pure $CaCO_3$ is 100. For example, pure CaO has a molecular weight of 56 grams per mole and pure $CaCO_3$ has a molecular weight of 100 grams per mole. Therefore CaO is 1.78 times more reactive (178% CCE) compared to pure calcium carbonate (100/56 = 1.78).

Dolomitic limestone – Limestone is composed primarily of calcite ($CaCO_3$). If dolomite ($CaCO_3{\cdot}MgCO_3$) is present in appreciable quantities, it is called a dolomitic limestone.

Electrical conductivity (EC) – Ability of an electric current to pass through water or a water extract of soil. Commonly used to estimate the soluble salt content in solution.

Electrolyte – A substance that dissociates into free ions when dissolved in a solvent.

Erodibility factor K – One of the factors for the universal soil loss equation. This equation predicts, *A*, the average annual soil loss in mass per unit area per year, and is defined as, $A = RKLSCP$. Here *R* is the rainfall factor, *K* is the soil erodibility factor, *L* is the length of slope, *S* is the percent slope, *C* is the cropping and management factor, and *P* is the conservation practice factor. *K* is a measure of the susceptibility of the soil to erosion.

Exchangeable cation – A positively charged ion, such as Na^+ or Ca^{2+}, on the surface of any surface-active material (such as clay or organic matter). This cation is interchangeable with other positively charged ions in soil solution.

Exchangeable sodium – Sodium ions (Na^+) on the surface of soil clay or organic matter that are interchangeable with other positively charged ions in soil solution.

Hardsetting soils – Following wetting, soils exhibit transient but only slowly reversible cementation and/or induration throughout significant fractions of the profile. This restricts seedling emergence and root penetration.

Hydraulic conductivity – A measure of the capability of a medium to transmit water or another fluid. Unlike the infiltration rate, it is not necessarily downward movement.

Hydraulic head – A measure of the amount of energy possessed by groundwater or soil water. Water flows from points of higher to lower hydraulic head.

Infiltration rate – A soil characteristic determining or describing the maximum rate at which water can enter the soil. The volume of water entering a specified cross-sectional area of soil per unit time.

Internal drainage – The downward movement of soil water by percolation through the soil.

Leachate – Liquids that have percolated through a soil and contain substances in solution or suspension.

Lime requirement – The mass of agricultural limestone or the equivalent of other liming material required to increase the pH of the soil to a desired value under field conditions.

Liming agent – A material such as calcium carbonate that neutralizes soil acidity.

Overliming – Application of a liming agent to a soil in excess of the lime requirement that causes an excessive increase in soil pH and reduced availability of some plant nutrients.

Phosphorus, water-extractable soil P – Soil phosphorus measured in a distilled water extract of the soil.

Phosphorus, soil test P – Phosphorus extracted by one of various methods that are supposed to mimic the ability of plants to absorb the phosphorus from the soil. Examples are the Mehlich III test and the Bray-1 test.

Phosphorus, dissolved reactive P – Same as water-extractable P.

Saline soil – A nonsodic soil containing sufficient soluble salt to adversely affect the growth of most crop plants. The lower limit of electrical conductivity for a saturation extract of such soils is conventionally set at 4 dS m^{-1}(at 25 °C).

Saturation extract – The solution extracted from a mixture of soil and water at the condition when all pores between the soil particles are filled with water.

"Self-liming" effects – By adding gypsum to a highly weathered soil, ligand exchange takes place between the added sulfate and OH groups on sesquioxide surfaces and the alkalinity produced precipitates some Al in soil.

Sodic soil – A soil containing sufficient exchangeable sodium to adversely affect crop production and soil structure under most conditions of soil and plant type. The sodium adsorption ratio of the saturation extract is at least 13.

Sodium adsorption ratio (SAR) – A relationship between soluble sodium and soluble divalent cations that can be used to predict the exchangeable sodium fraction of soil equilibrated with a given solution.

$$SAR = \frac{[sodium]}{[0.5 \cdot (calcium + magnesium)]^{1/2}}$$

where the cation concentrations are in millimoles of charge per liter ($mmol_c\ L^{-1}$).

Soil acidity – Generally, pH value of soil solution. A soil with a pH value <7.0 is acid soil.

Soil sodicity – See sodic soil.

Sorbent – In a flue gas desulfurization process, the solid material that binds and reacts with sulfur dioxide to cause removal of sulfur dioxide from the flue gas stream.

Synthetic soil mix – The material used as a plant growth medium for horticultural or other practices. Traditionally consists of proportions of peat moss, compost, perlite and vermiculite. Recycled material has been tried as components of these mixes.

A.2 Soil Classification and Descriptions

Soils differ widely in their chemical, physical and biological properties. These differences have a major impact on the potential beneficial uses of FGD materials and environmental impacts. Therefore, it seemed appropriate to provide a brief primer on how soils are classified in the United States.

Soils in the United States are classified into 12 major groups called soil orders. Each order has at least one defining characteristic. Examples of orders mentioned in this review are entisols, inceptisols, alfisols, ultisols, vertisols, mollisols, and spodosols. When a soil name is mentioned in the review, it is followed by a two-word (or sometimes three-word) descriptor called the subgroup category. The subgroup category provides information about the soil's characteristics.

For example, for a Baltimore soil (Mollic Hapludalf), "mollic hapludalf" is the subgroup category. The term "hapludalf" is composed of a root part and two prefixes. The root "alf" indicates that the soil is a member of the alfisols order. The prefix "ud" indicates type (humid) of moisture regime and the prefix "hapl" indicates type (simple or minimum) of soil horizon development. The modifier "mollic" indicates that this soil has some characteristics similar to the mollisols order but not strong enough to be classified as a mollisol.

By becoming familiar with the subgroup categories, it is possible to discern some knowledge of any soil without having specific knowledge of that particular soil. Additional information on soil classification is provided in the Soil Science Society of America's "Glossary of Soil Science Terms" (http://www.soils.org/sssagloss/) and the textbook by Buol et al. (2003).

Some brief definitions of the soil orders and individual soils mentioned in this review are provided below. Additional information on soil names is available at the USDA-NRCS Soil Survey Division's "Soil Series Name Search Query Facility" (http://ortho.ftw.nrcs.usda.gov/cgi-bin/osd/osdnamequery.cgi). Typing a soil name into the query facility provides a link to an official description of that soil.

Entisols – recently formed soils that have little or no horizon development. Example is a soil developing in floodplain deposits.

Candler fine sand (*lamellic Quartzipsamment*) – Entisol (*ent*) developing in sand (*psamm*) having high quartz content (*quartz*)

Inceptisols – soils that have more horizon development than in entisols but not enough to qualify for inclusion in other more developed soil orders. Common in areas of glacial deposits that are only a few thousand years old.

Porters silt loam (*Typic Dystrudept*) – Moist (*ud*) inceptisol (*ept*) that has low base saturation (*dystr*). Base saturation is less than 60%.

Alfisols – soils that developed under forest cover and have an accumulation of clay in the subsoil and good fertility (calcium, magnesium, potassium status) for crop production. Good fertility results from high base saturation.

Hagerstown soil and Renova silt loam are *Typic Hapludalfs* – Moist (*ud*) alfisols (*alf*) that have the minimum (*hapl*) horizon development common to alfisols. They have typical (*typic*) characteristics of the group.

Baltimore soil (*Mollic Hapludalf*) - Moist (*ud*) alfisol (*alf*) that has the minimum (*hapl*) horizon development common to alfisols. It also has some similarities to a mollisol (*mollic*).

Coshocton silt loam (*Aquultic Hapludalf*) – Moist (*ud*) alfisol (*alf*) that has the minimum (*hapl*) horizon development common to alfisols. It has evidence of wetness (*aqu*) and also has some similarities to an ultisol (*ultic*).

Wooster silt loam (*Oxyaquic Fragiudalf*) – Moist (*ud*) alfisol (*alf*) that has a hard subsurface pan called a fragipan (*frag*). The fragipan is brittle when moist and very hard when dry. The soil is sometimes water saturated (*aquic*) but when saturated the water is oxygenated (*oxy*).

Maury silt loam (*Typic Paleudalf*) – Moist (*ud*) alfisol (*alf*) that has old or excessive (*pale*) horizon development.

Hoytville soil (*Mollic Epiaqualf*) – Wet (*aqu*) alfisol (*alf*) that has a perched (*epi*) water table. A perched water table is a saturated layer of soil that is separated from any underlying saturated layers by an unsaturated layer. This means the perched water table is not in contact with the ground water. The soil also has some similarities to a mollisol (*mollic*).

Blount soil (*Aeric Epiaqualf*) – Wet (*aqu*) alfisol (*alf*) that has a perched (*epi*) water table. A perched water table is a saturated layer of soil that is separated from any underlying saturated layers by an unsaturated layer. This means the perched water table is not in contact with the ground water. The soil has somewhat better drainage (*aeric*) than the typical epiaqualf.

Zulch fine sandy loam *(Thermic Udertic Paleustalf*) – Dry (*ust*) alfisol (*alf*) that has old or excessive (*pale*) horizon development. It occurs in a relatively warm (*thermic*) environment and also has some similarities to a moist vertisol (*udertic*).

Ultisols – soils that developed under forest cover and have an accumulation of clay in the subsoil but poor fertility (calcium, magnesium, potassium status) for crop production. Poor fertility results from low base saturation.

Gilpin silt loam, Lily soil, Rayne silt loam, and Trappist silt loam are *Typic Hapludults* – Moist (*ud*) ultisols (*ult*) that have the minimum (*hapl*) horizon development common to ultisols. They have typical (*typic*) characteristics of the group.

Appling coarse sandy loam, Cecil soil, and Wedowee soil are *Typic Kanhapludults*. Moist (*ud*) ultisols (*ult*) that have the minimum (*hapl*) horizon development common to ultisols. The accumulation of clay in the subsoil is called a kandic horizon (*kan*) and has clay with relatively low cation exchange capacity.

Greenville soil (*Thermic Rhodic Kandiudult*) – Moist (*ud*) ultisol (*ult*). The accumulation of clay in the subsoil is called a kandic horizon (*kand*) and has clay with relatively low cation exchange capacity. The soil occurs in a relatively warm (*thermic*) environment and has dark red color (*rhodic*).

Worsham soil (*Typic Endoaquult*) – Wet (*aqu*) ultisol (*ult*) that has a ground water (*endo*) table. The water table is in contact with the groundwater.

Mollisols – soils that developed under grass cover and have a dark, fertile surface horizon and good fertility in the subsoil. Examples are the highly productive soils that once supported prairie and are now the Corn Belt in the United States.

Brookston silty clay loam and Cordova silt loam are *Typic Argiaquolls* – Wet (*aqu*) mollisols (*oll*) that have an accumulation of clay called an argillic (*argi*) horizon in the subsoil.

Hubbard loamy sand (*Entic Hapludoll*) – Moist (*ud*) mollisol (*oll*) that has the minimum (*hapl*) horizon development common to mollisols. The soil has some similarities to an entisol (*entic*).

Vertisols – dark, clayey soils that shrink and swell upon wetting and drying. Large cracks form during shrinking, and surface soil material falls into the cracks.

Heiden soil (*Udic Haplustert*) – Dry (*ust*) vertisol (*ert*) that has the minimum (*hapl*) horizon development recognized in a vertisol. The moisture regime approaches or is similar to that of a moist (*udic*) climate.

Pierre soil (*Aridic Leptic Haplustert*) – Dry (*ust*) vertisol (*ert*) that has the minimum (*hapl*) horizon development for a vertisol. It is thinner (*leptic*) than the typical haplustert. The soil has some similarities to an aridisol (*aridic*).

Spodosols – soils that generally develop under forest cover and have an accumulation of humus, aluminum, and sometimes iron in a dark-colored horizon in the subsoil.

Myakka sand *(Aeric Alaquod*) – Wet (*aqu*) spodosol (*od*) that has high aluminum (*al*) but low iron in the subsoil. The soil has better aeration (*aeric*) than most wet spodosols.

B
REPRINT

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A WIN/WIN SOLUTION FOR FGD-GYPSUM:

RESEARCHERS DISCOVER BENEFICIAL APPLICATIONS FOR BY-PRODUCT IN AGRICULTURE

By Cliff Ramsier and Darrell Norton

In an ironic twist, an attractive new market for the coal ash industry has developed as a result of agricultural research conducted by the USDA and related universities. With winds of change sweeping every industry, including agriculture, research conducted since 1995 at The Ohio State University and the USDA-ARS National Soil Erosion Research Lab at Purdue University have uncovered some viable new reasons for using FGD-Gypsum as a regular part of production agriculture. While some farmers already use gypsum to increase soil nutrients, prevent surface sealing, and detoxify soils, widespread use of gypsum would provide the coal ash industry with a huge market for an under-used by-product with challenging disposal issues.

Current production of FGD-gypsum is consumed by an expanding construction industry for both wall board and cement. This doesn't include the sulfite materials that, for the most part, are landfilled. In the next seven to ten years, an additional 15 to 17 million tons of these FGD materials will be generated with little hope of use in the construction industry. Other uses will be necessary to reduce pressures on current and future landfills.

Agriculture to the rescue! Recent research work has centered on FGD-gypsum or calcium sulfite and to a much lesser extent on fly ash. Researchers have found three agronomically valuable functions of these materials. First, and most obvious, is the fertilizer value of these materials. Both calcium and sulfur are essential minerals required for plant growth and development. While these two minerals are rarely yield limiting to the grower, there is a growing benefit to these two materials in low organic matter soils and when the crop requirements are high. Scrubbing SO_2 emissions in recent years has reduced the atmospheric deposition of sulfur in normal rainfall.

Gypsum has long been known as a good soil conditioner, especially in regions

of the country with saline and sodic soils. Today, the effects of current farming practices have caused those same benefits to be noticed in more common soils. From the time the Corn Belt was settled in the early 1800s, farming has meant tilling the soil. While this practice was good for crop production, it was detrimental to soil structure and organic matter. As soil organic matter has diminished, so has soil structure. Many of the soil aggregates that were once stable are now vulnerable to the ravages of everyday rainfall. The chemistry of rainwater is such that it takes the electrolytes from the surface clays, which cause the clays to disperse. These dispersed clays form a crust on the surface which seals out both water and air when the clay dries. Healthy productive soils need both air and water in very large volumes. Gypsum applications to the soil surface provide the rainfall with an alternative source of electrolyte which prevents soil crusting, thus keeping the soil open and permeable to rainwater and air.

Finally, gypsum is more effective than liming materials at re-mediation of sub-soil acidity by detoxifying the excess exchangeable aluminum, which causes low pH. Excess aluminum prevents root development in that region of the soil. This most often occurs in the subsoils, since most liming materials are applied to the surface or shallowly incorporated. Since lime is only slightly soluble, it does not get to the subsoil in sufficient quantities to solve the problem economically. While gypsum is not a liming material

(liming materials are classified by their ability to neutralize acids) it does detoxify the aluminum by forming a non-toxic species of aluminum. This occurrence allows the crop roots to penetrate deeper into the soil to intercept greater volumes of water and nutrients. Farmers know that better roots equal better crops.

Greenhouse gasses are an ongoing concern of environmentalists everywhere. Two primary greenhouse gasses are carbon dioxide and nitrous oxide. Science and industry are looking for ways to sequester carbon to reduce the amount in the atmosphere. One proven way to sequester carbon is to fix it as organic matter in soil. Also, rooting is related to carbon sequestration because 90 percent of the carbon in roots is converted to soil organic matter, whereas 90 percent of surface residue is oxidized and the carbon returned to the atmosphere. Therefore, more carbon is sequestered by increasing root growth.

Another tie between FGD-gypsum and soil organic matter is the surface properties of soils. If soil surfaces crust, crop yields are reduced. Today's farmers must keep the soil surface from crusting to maintain profitable yields. The good news for the utility industry is that the farmer now has two options. The first is some type of tillage which has the detrimental effect of releasing more carbon dioxide into the atmosphere and reducing soil organic matter. Improved soil water management characteristics also reduce nitrous oxide emissions from agricultural soils. The better option is to apply FGD-gypsum to the soil surface which has the added benefits of those listed above. The utility's world is improved since the highest quality and lowest cost material is generated by an emission control scrubber as FGD-gypsum. The best part of all this is the volume. There are more than 175 million crop acres in the U.S. alone. Each acre would require ½ ton per year to prevent surface sealing. This means that the potential for FGD-gypsum use is more than 80 million tons per year. Now that is real volume!

The story keeps getting better but the next step depends on the regulations and the value of carbon and/or nitrogen credits. As is mentioned above, reducing or eliminating tillage in crop production tends to sequester carbon. In fact, as much as ½ ton of carbon is sequestered each year that tillage is avoided. That means that agriculture may become a very important source for low costs carbon credits. Of course, these credits will need to be aggregated and processed to offset the amount of carbon produced by energy production. While not high value today, the income will help to mitigate the costs involved in compliance if credits become an issue. Carbon credits on a small scale will not generate enough value to offset the transaction cost of making application for credits, so farmers are not likely to acquire them as individuals until the value per

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ton of credit is very high. However, a utility could aggregate credits on a very large scale and significantly impact the cost to produce energy. It goes without saying that any positive relationship between power generators and farmers has the potential for great public relations.

If the authors could be so bold to suggest a solution for the disposition of FGD-gypsum and sulfites, we believe that a trade is mutually beneficial to both industries. FGD-gypsum generators need to dispose of their materials and some day may benefit from carbon credits, while farmers could benefit from these materials. If CCP producers were to trade the transportation of FGD materials to agricultural areas and provide the verification and aggregation of carbon credits from farmers' lands, the growers would likely accept these materials in trade for the carbon and possible NOx credits they would generate. Since many generators are already in the transportation business, arranging back hauls with trucks, rail or barges would be a relatively simple, low-cost, in-house activity. There are a few good sources for making the aggregation and verification processes as simple as a phone call.

As is often the case, change is not comfortable. A bright future is in store for those who seek creative ways to improve a difficult situation. The authors believe that the utility industry can provide new and rewarding leadership by implementing change in beneficial ways. ❑

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