CHAPTER 10. SOIL ADDITIVES AND SOIL AMENDMENTS

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10.1 INTRODUCTION

The use of coal ash and clean coal combustion by-products as soil additives or soil amendments to enhance establishment and growth of vegetation on coal mined lands as well as agricultural soils has been extensively studied (Adams et al., 1972; Capp, 1978; Plass and Capp, 1974; Jastrow et al., 1981; Stehouwer et al., 1995b). Collectively, conventional coal combustion ash (fly ash and bottom ash) and clean coal combustion by-products (flue gas desulfurization sludges and fluidized bed combustion ash) are referred to as coal combustion by-products (CCB) (Pflughoeft-Hassett et al., 1996).

Certain physical and chemical characteristics of CCBs make them potentially useful in mine land reclamation for ameliorating the adverse chemical and physical conditions often associated with coal mine soils. Coal combustion by-products also have characteristics that could adversely affect plant growth or environmental quality if improperly used. Soil amendment materials, including those commonly used in agricultural production, can have both positive and negative effects on soil and environmental quality. Thus, as with other soil amendments, the use of coal combustion by-products for mine reclamation must be managed to maximize their beneficial effects while minimizing any potential for negative effects on soil and environmental quality. Such effective management requires an understanding of the physical, chemical, and biological constraints for plant growth presented by the mine soil or spoil, an assessment of the physical and chemical properties of the coal combustion by-product, and a determination if the ash (either alone or combined with other amendments) can ameliorate conditions sufficiently to allow establishment and growth of sustained vegetative cover.

10.2 NATURE AND PROPERTIES OF MINE SPOILS AND SOILS

Mining activities result in severe disturbance of surface soils, even with modern mining practices where soil materials are segregated and replaced on the surface during post-mining reclamation. Often native topsoils and subsoils in mined areas are very thin layers that become commingled during excavation and replacement. Because the original soil material was so limited there is insufficient soil to allow successful revegetation. At abandoned or "pre-act" mine sites, or at remining areas, there is often no soil material available and vegetation must be established in mine spoil material. Many mine spoils and other mining wastes contain pyrite (FeS_2) which oxidizes to generate acidity. These spoil materials can be extremely acidic ($pH<3.5$). In extreme cases, the generation of acidity results in accumulation of aluminum and iron sulfates and other salts resulting in material with high soluble salts. Textural properties of mine spoils and soils can range from very coarse with a large amount of rock fragments to very fine textured high clay material. Coarse material has very low water holding capacity and is extremely droughty, while fine textured materials may have high bulk density and low permeability. Excavation and replacement activities frequently result in highly compacted soil or spoil layers. All of these physical properties limit water and root penetration and plant available water reserves. Finally, because mine spoils and soils often originate from subsurface layers they are typically very low in organic matter and microbially available carbon (energy). This together with chemical and physical constraints limits the diversity and activity of the microbial community they can support.

10.3 NATURE AND PROPERTIES OF COAL ASH

Combustion ash from coal-fired boilers is separated into bottom ash, which remains in the combustion chamber and fly ash which rises with flue gases. Bag filters or electrostatic precipitators remove slightly more than 99% of the fly ash particulates from the flue gases (Adriano et al., 1980). The physical, mineralogical, and chemical properties of coal ash depend on the composition of the coal burned, conditions during coal combustion, efficiency of emission control devices and the storage and handling of the by-products (Adriano et al., 1980). The American Society of Testing Materials (ASTM C 618, 2000) recognizes two classifications of pulverized coal fly ash based upon the relative concentrations of silica, aluminum, and iron oxide that correspond to a high-lime and low-lime content fly ash, Class C and F, respectively.

Fly ash generally has a silt loam texture with 65-90% of the particles having diameters of less than 0.010 mm (Chang et al., 1977; Roy and Griffin., 1982). In a study of fly ashes from various U.S. power plants, Theis and Wirth (1977) found that the major components were aluminum, iron and silicon, with smaller concentrations of calcium, potassium, titanium and sulfur. Silicon content of fly ashes ranged from 2-68% while aluminum content was 3-39% and iron content was from 3-29% (Haering and Daniels, 1991). Most naturally existing elements can be found in fly ash and a number of investigators agree that many of the trace elements in fly ash show a definite concentration trend with decreasing particle size. Concentrations of arsenic, cadmium, copper, gallium, molybdenum, lead, sulfur, antimony, selenium, thallium and zinc have been reported to increase with decreasing particle size (Davison et al., 1974; Kaakinen et al., 1975; Klein et al., 1975). Chemical compositions of 9 Class C and 49 Class F fly ashes are given in Table 10.1.

The alkalinity of coal fly ash attains 60% calcium carbonate equivalence (CCE) (Korcak, 1996). Class C coal fly ashes are high in calcium and magnesium oxides and typically have neutralizing capacities of around 50% (CCE) (Ritchey et al., 1998). (The neutralizing capacity of pure limestone is 100% CCE.) In contrast, the neutralizing capacity of Class F coal fly ash is normally less than 10% CCE, and these ashes have relatively low amounts of calcium and magnesium.

Clean coal combustion technology refers to any of several coal combustion and scrubber systems designed to reduce sulfur and nitrous oxide emissions. These technologies generate by-products with chemical and physical characteristics that differ considerably from conventional fly ash. Flue gas desulfurization (FGD) scrubbers produce relatively pure $CaSO_3$ sludges, that in some cases may be further oxidized to $CaSO_4$. In most configurations, FGD scrubbers are downstream from particulate removal so the FGD sludge contains no fly ash. Another common clean coal combustion technology is the fluidized-bed combustion (FBC) process in which coal is burned together with crushed limestone. The limestone reacts with sulfur dioxide gas in the combustion chamber to form $CaSO_4$. Bottom ash and fly ash from FBC systems are mixtures of conventional coal ash, $CaSO_4$, and unreacted limestone, some of which has been calcined to oxide forms. Mineral composition of some fluidized bed ashes are given in Table 10.2. Chemical characteristics of FGD and FBC by-products are given in Table 10.3. The alkalinity of residues from clean coal combustion technologies varies widely. Pure FGD scrubber sludges have almost no CCE because they consist almost entirely of $CaSO_3$ or $CaSO_4$. Because alkaline reactants used in fluidized bed combustion or other clean coal combustion processes are not completely consumed, the by-products contain significant alkalinity with CCEs ranging from 20 to 80% (Terman et al., 1978; Korcak, 1980; Fowler et al., 1992).

Table 10.1. Chemical analysis (total digestion) of 9 Class C and 49 Class F fly ashes (from Miller et al., 2000).

	Class C ashes (9)			Class F ashes (49)		
Major elements (%)	Mean	Min	Max	Mean	Min	Max
Aluminum	6.8	5.1	10.4	11.0	6.3	14.4
Iron	5.1	2.9	9.5	8.0	1.7	17.4
Silicon	13.7	9.3	17.7	23.1	19.8	28.2
Phosphorus	0.36	0.10	0.63	0.14	0.08	0.26
Potassium	0.63	0.27	1.16	1.54	0.31	2.53
Calcium	17.2	10.1	22.5	3.2	0.2	11.5
Magnesium	2.19	0.44	4.18	0.89	0.30	2.70
Trace elements (mg kg^{-1})						
Arsenic	39.9	8.0	96.0	93	8	391
Boron	nd†	nd	nd	425	55.0	1108
Cadmium	nd	nd	nd	1.0	0.1	3.2
Cobalt	nd	nd	nd	47	14	120
Chromium	66.9	40.0	123.0	171	25	651
Copper	116.4	45.0	223.0	133	48	242
Lead	45.6	19.0	92.0	63	13.0	273
Molybdenum	14.6	5.3	32.0	29.8	3.7	139
Nickel	54.0	34.0	78.0	121	14.0	309
Selenium	11.4	6.0	14.2	11.4	1.0	47
Vanadium	nd	nd	nd	259	58	470
Zinc	266.0	25.0	658.0	270	27	2050

Table 10.2. Mineral composition of fluidized bed boiler ashes (Stehouwer et al., 1995a)

Mineral	Amount (weight %)
Fly ash	10-40
Calcite ($CaCO_3$)	1-29
Lime (CaO)	4-21
Portlandite ($Ca(OH)_2$)	1-3
Anhydrite ($CaSO_4$)	20-51
Dolomite ($CaMg(CO_3)_2$)†	17-31
Periclase (MgO) †	4-27

†High magnesium content samples were from a facility that used dolomite rather than limestone as the sorbent.

Table 10.3. Chemical composition of gypsum-containing clean coal combustion by-products (Miller et al., 2000)

	Fluidized bed combustion by-products	Flue gas desulfurization scrubber sludge
Major Elements	% dry weight	
Phosphorus	0.01-0.05	<0.1-0.2
Potassium	0.05-0.8	0.10
Calcium	24.0-46.0	21.0-23.5
Magnesium	0.1-1.6	0.02-0.2
Sulfur	7.2-14.0	16.6-18.6
Silicon	2.5-30.0†	0.07
Aluminum	0.3-2.0	0.03-0.2
Minor Elements	mg kg^{-1} dry weight	
Boron	95-170	75
Molybdenum	0.1-0.3	1.3
Copper	12-20	8.0
Zinc	12-20	36
Nickel	13-20	9.7
Lead	1.5-7.5	<0.1
Cadmium	0.5	0.01
Chromium	9-23	10
Selenium	0.2-0.6	0.3
Mercury	nd	0.01-0.4
Arsenic	nd	3.1

†from Stehouwer et al., 1995a

10.4 EFFECTS OF COAL ASH APPLICATIONS ON MINE SPOILS AND SOILS

According to literature reviews by Carlson and Adriano (1993), the main benefits of using fly ash on mined lands are increased alkalinity and improved water holding capacity (Stewart and Daniels, 1995). Dhaliwal et al., 1995 revisited a study site of Capp and Gillmore (1974) that used fly ash as a topsoil material on pyritic mine spoil. Even after 22 years, the fly ash treated site had higher soil pH than an adjacent area of reclaimed pyritic mine spoil not treated with fly ash. In addition, the fly ash treated area had more development of an A soil horizon and more prolific and deeper root development than the adjacent area. Spoil containing pyritic materials can have extremely high potential acidity and consequently very high ash application rates (up to 797 tons/acre) may be needed for complete acid neutralization (Capp, 1978). However, much lower applications (30 tons/acre) have been shown to increase pH on a 2.7 pH spoil (Taylor et al., 1988).

The use of such high application rates can significantly alter the textural properties of the mine spoil since fly ash will constitute over 50% of the resulting spoil-ash mixture. Capp (1978) reported that these high rates resulted in improvement in spoil texture and increased water holding capacity. Such effects are the result of adding predominantly silt-sized ash to coarse textured spoil and would be expected with either Class C or Class F ashes. Some studies have shown improved plant growth with much lower alkaline fly ash application rates (31 tons/acre) (Fail, 1987). Spoil pH was increased by only 0.1 pH unit but the ash improved spoil texture which increased soil moisture. Determining application rates of alkaline fly ash on acidic spoils needed to increase pH requires matching total spoil acidity with ash CCE.

While fly ash amendments can clearly improve spoil quality, the extent to which pH and textural improvements will occur varies depending upon the initial quality of the spoil and the type of fly ash used. The neutralizing capacity of conventional pulverized coal fly ash is normally less than 10% CCE in contrast with some residues of clean coal technology that contain large amounts of alkaline material. In a laboratory incubation study, Seoane and Leiros (2001) reported that additions of non-alkaline fly ash (4.8% CCE) to an acidic spoil at rates of 20-40% was able to gradually increase pH to 3.0 due to weathering of silicate minerals. However, addition of both limestone and fly ash was required to achieve rapid increases in pH. Textural and water holding capacity benefits will be most likely to occur on very coarse textured spoils with a high content of rock fragments.

In several studies, addition of sufficient fly ash to neutralize spoil acidity has resulted in other constraints on plant growth. High rates of fly ash addition can increase soluble salts in mine spoils; thus an initial planting of salt tolerant species has been recommended (Capp et al., 1975; Capp, 1978). Jastrow et al. (1981) found that lime application produced better growth on an acid spoil than did alkaline fly ash amendment. The difference was attributed to boron toxicity or high soluble salts with the fly ash. Problems with high boron in fly ashes can often be minimized by using weathered fly ash rather than fresh fly ash. Because boron is relatively soluble, it is readily leached from fly ash during the weathering process. Seoane and Leiros (2001) reported that addition of sufficient fly ash to sustain a pH increase in acidic spoil resulted in production of large amounts of soluble salts that would likely have inhibited plant growth.

Another problem with large applications of fly ash is increases in erodibility. Silt-sized soil particles are highly erosive and erosivity with fly ash is even greater due to the largely spherical shape of the ash particles. Silt sized materials are also susceptible to surface crust formation which reduces infiltration rates, leading to increased runoff and consequently increased erosion. Gorman et al. (2000) found that fly ash amended spoil had much greater erosivity than unamended spoil. The high erosivity was attributed to silt grain size, spherical particles, and lack of initial aggregation. This work also demonstrated that covering with a wood chip mulch reduced erosion by about one half. In addition to surface protection, the mulch stimulated growth of fungi and mosses which stabilized aggregates and appeared to be more effective than cover crops at reducing erosion. These authors caution that while large fly ash applications may improve pH and water holding capacity, special precautions to reduce erosion potential are required (reduced slope gradient and length) and also recommend combining ash with organic amendments.

Pure FGD sludges have limited value as an amendment for acidic mine spoils. These are wet, paste-like materials that are difficult to handle and provide no alkalinity or textural benefits. Because these materials are almost pure $CaSO_3 \bullet 2H_2O$ or $CaSO_4 \bullet 2H_2O$ (gypsum), they can be used as a source of soluble calcium. Pietz et al. (1989) found no beneficial effects from addition of gypsum for revegetation of acidic coal refuse. At some power plants, FGD sludges are mixed with fly ash and small amounts of lime to improve physical properties for landfilling. In a greenhouse study, Stehouwer (1997) found that such a FGD/fly ash/lime mixture was able to reduce acidity and permit plant growth. However, growth was much better with combined application of the FGD mix with yard waste compost.

Due to their generally high alkalinity, FBC ashes have been shown to be effective lime substitutes for neutralization of acidity in soils and mine spoils (Terman et al., 1978; Holmes et al., 1979; Korcak, 1980; Stehouwer et al., 1995a; Stehouwer et al., 1995b). The neutralizing capacity of FBC ash has been reported to range from 36 to 81% CCE (Carlson and Adriano, 1993). These materials are also effective sources of soluble calcium due to their gypsum content (Korcak, 1980). However, they can have extremely high pH (10 – 12) and high soluble salts, thus application in excess of what is needed to neutralize acidity can result in excessively high spoil pH and salt problems.

Large applications of fly ash or FBC by-products to acidic spoils can lead to mobilization of metals in the ash. This is most likely to occur if spoil acidity is not neutralized by the amendments since solubility of most metals increases rapidly as pH decreases below about 5.0. Stewart et al. (2001) found large quantities of manganese, iron, and copper were readily leached in a strongly acidic coal refuse amended with 5 – 20% of moderately alkaline fly ash. Leaching of these metals was controlled if alkalinity and potential acidity were balanced with fly ash and lime amendment.

10.5 COAL ASH RELATIONSHIP TO PLANT GROWTH

Plant growth is dependant upon a favorable combination of environmental factors to including nutrients, water, heat and air, and the absence of detrimental factors such as extreme acidity or alkalinity, salinity, or high availability of potentially toxic metals. The factor that is least optimum will determine the extent of plant growth (i.e. plant growth can be no greater than that allowed by the most limiting factor) (Brady and Weil, 2002). Seventeen elements have been demonstrated to be essential for plant growth. In addition to the elements carbon, hydrogen and oxygen that plants obtain primarily from air and water, there are six elements needed in relatively large amounts and referred to as macronutrients and eight elements needed in smaller amounts and referred to as micronutrients. The macronutrients are nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur. The micronutrients include iron, manganese, boron, molybdenum, copper, zinc, chlorine, and cobalt. Except for iron and manganese, these micronutrients are found sparingly in most soils and their availability to plants is often very low (Brady and Weil, 2002). Many of the micronutrients, however, can become phytotoxic if their availability in soil is increased.

Another potential benefit of fly ash as a soil or spoil amendment is as a source of nutrient elements for plant growth (Bennett et al., 1976; Chang et al., 1977; Taylor and Schuman, 1988). Of the macronutrients, fly ash can supply sulfur (Elseewi et al., 1978; Hill and Lamp, 1980) and alkaline fly ash can serve as a source of plant available calcium and magnesium (Martens and Beahm, 1976; Wallace et al., 1980; Hill and Lamp, 1980). However, fly ash is not a source of nitrogen or plant available phosphorus, and can only occasionally supply plant available potassium. Fly ash may be a source of plant micronutrients. Selected fly ashes at controlled rates of application increased boron uptake in alfalfa (Medicago sativa) increased alfalfa yields by the addition of soluble molybdenum and corrected zinc deficiencies in corn (Martens, 1971). Increases in alfalfa yields have been attributed to an alleviation of boron deficiency by application of fly ash (Plank and Martens, 1974). FGD sludges and FBC by-products can serve as major sources of base cations, calcium and magnesium (Stehouwer et al., 1998).

Rather than a direct source of plant nutrients, the major benefit of fly ash and FBC amendment for plant nutrition is the indirect effect of pH adjustment on nutrient availability. Figure 10.1 shows how the availability of plant nutrients (and aluminum) is affected by changes in soil pH (Pennsylvania State University, College of Agricultural Sciences). Knowing the neutralizing potential and element content of these coal ash materials and the characteristics of the land application site is extremely important for effective revegetation of coal mine lands. Application rates of alkaline coal ash need to be established based on the amount needed to adjust the mine soil pH to the optimum level for the vegetation to be established. Some coal surface mine operations involve the remining of coal waste piles or coal refuse banks and coal siltation basins. Coal refuse with low pH and associated toxic levels of aluminum, iron and manganese are found to be factors most limiting plant growth (Stewart and Daniels, 1992). The detrimental effects of low pH on plant growth have been identified and addressed in detail by many authors (Thomas and Hargrove, 1974; Bohn et. al., 1985; Brady and Weil, 2002). Aluminum toxicity is a growth limiting factor for plants in many acid soils below pH 5.0 and manganese is a problem in some strongly acid soils and mine soils below pH 5.5 whose parent materials are sufficiently high in total manganese (Foy et al., 1978). As soil pH decreases below 5.5, the availability of aluminum and manganese to plants increases and may reach a point of toxicity to the plant. Figure 10.1 shows how the availability of aluminum and manganese is affected by changes in soil pH.

Iron, aluminum and manganese have been identified as the main phytotoxic elements on acid mine spoils (Berg and Vogel, 1973; Bennett, 1971). As the pH of acid soils increases, aluminum, iron, and manganese become less available to plants and at a pH somewhat above 7.0, certain plants may suffer from a lack of available iron and manganese. Extremely acid soils suddenly brought to neutral or alkaline conditions by excessive applications of lime may result in lack of plant available iron and manganese. If soil pH is increased too much above 7.0, phosphate nutrition of higher plants is affected whereby complex insoluble calcium phosphates are formed causing indigenous and applied phosphorus fertilizers to become insoluble and unavailable to plants (Brady and Weil, 2002). Applications of fly ash to soil may cause phosphorus deficiency even when the ash contains adequate amounts of phosphorus because soil phosphorus forms insoluble complexes with iron and aluminum in ash (Martens, 1971; Adriano et al., 1978; Adriano et al., 1980).

The amount of alkaline material needed to ameliorate highly acid mine spoil can be 5 to 10 times greater than is needed when applied to agricultural soils that are typically only slightly acidic. Applying coal ash as the alkaline material to acid mine soils at rates necessary for adjusting pHs in ranges favorable for plant establishment and growth may result in high levels of soluble salts and loadings of certain trace elements detrimental to plants (Stehouwer et al., 1995b).

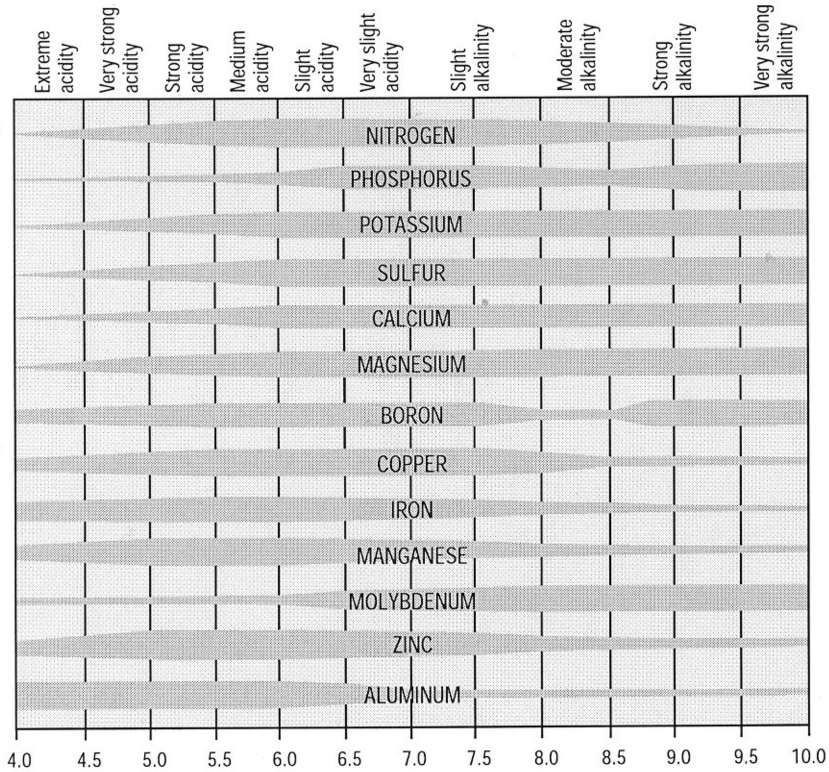

Figure 10.1. How soil pH affects availability of plant nutrients and aluminum.

When soluble salt levels measured by electrical conductivity exceed 2.0 mmhos/cm, yields of very salt sensitive plants are reduced (Rhoades, 1982). Electrical conductivity may affect seed germination at 1.0 mmhos/cm, reduce growth of some salt sensitive plants at 2 mmhos/cm, and result in severe injury to many plant species at 4.0 mmhos/cm (Jackson, 1958). Dry FGD by-products may contain high concentrations of soluble salts and some trace elements of environmental concern (Fowler et al., 1992). Plants differ markedly in their tolerance to salt levels.

Boron is a constituent of coal ash and is an essential plant nutrient. Coal ash may be applied to mine soils deficient in boron. However, boron applied in excessive amounts may be toxic to vegetation (Darmody, 1996). Boron concentrations greater than 1.0 mg/L in soil solutions may be toxic to sensitve plants (Bohn et al., 1979). Boron becomes toxic to most agricultural crops when hot water extractable boron exceeds 20 mg/kg (Hodgson and Townsend, 1969). Some agricultural crops such as alfalfa (Medicago sativa) require yearly applications of about 2.0 lb/acre of boron for maximum yields. Some sensitive agricultural crops have exhibited boron toxicities and decreased yields when boron was applied from 0.50 to 4.50 lb/acre (Stout et al., 1988). Normally, most soils contain sufficient molybdenum to supply needs for plant growth but molybdenum becomes less available to plants as spoil acidity increases or pH mixtures on coal mine spoils when legumes such as clovers (Trifolium species) and crownvetch (Coronilla varia) are grown (Bennett, et al., 1976). Molybdenum along with manganese are essential for certain nitrogen transformation in plants. Molybdenum is thought to be essential for nitrogen fixation (Brady and Weil, 2002). Increases in soil pH increase the availability of soil molybdenum. Increases in soil pH from application of alkaline fly ash would therefore likely increase the availability of molybdenum indigenous to the soil (Doran and Martens, 1972). Excess molybdenum has induced molybdenosis (a copper deficiency) in grazing cattle when present in forages at levels of 5 ppm or higher (Suttle, 1991). If fly ash is applied in moderation (from 25 to 50 tons/acre), forages can benefit from the nutrients. However, at extremely high application rates (100 to 600 tons/acre), phytotoxicities develop with most all forage species (Bennett et al., 1976). Studies of trace metal behavior in soils found trace metal solubility and mobility decrease as soil pH increases from the acid range (Chaney et al., 1987; Woodbury, 1992). It appears that if FGD by-products are applied in amounts that will not cause excessively high pH or phytotoxic salt concentrations, there is little potential for adverse effects on soil quality from trace elements (Stehouwer et al., 1995c).

10.6 CO-APPLICATION OF CCB AND ORGANIC RESIDUALS

While coal combustion by-products can alleviate plant growth limiting factors in mine spoils such as low pH and coarse texture, plant growth may still be limited by other factors. CCBs are poor sources of nitrogen and phosphorus (Carlson and Adriano, 1993; Bradshaw and Chadwick, 1980). Mine spoils are also typically low energy environments and CCBs provide no microbially available carbon sources. As has previously been noted, spoils amended with CCBs may have poor structure, have slow water infiltration rates, and be highly erosive. Several studies have indicated that these limitations can often be overcome with combined application of CCB and organic residuals such as composts, manures, or biosolids. Conceptually, blending large amounts of CCBs and organic residuals with mine spoils is a reclamation approach that approaches in-situ manufacture of a topsoil-like material. The objectives of this approach are not only to alter the adverse spoil properties, but also to build a soil-like matrix that is capable of supporting sustained vegetative growth.

Schumann and Sumner (1999) evaluated nutrient availability in mixtures of fly ash and biosolids or poultry manure. Maximum maize (*Zea mays*, L.) growth with fly ash amendment alone was just 50% of a fertilized control soil, and maximum growth with organic amendments alone was 49 – 71% of control. Combined fly ash and organic amendments, however, achieved up to 94% of growth on the control. The ability of a fly ash and biosolids mixture to allow establishment and growth of vegetative cover under extreme conditions has been demonstrated at a Palmerton, PA zinc smelter site (Oyler, 1988). A 1:1 blend of ash and biosolids plus lime and potash was used to coat an acidic, eroded mountainside with extreme zinc and cadmium contamination. The blend was able to supply nitrogen, phosphorus, and potassium as well as water to allow vegetation to become well established and sustained for over 10 years. Stehouwer et al. (1998) reviewed four greenhouse and four field experiments in which highly acidic mine spoils or coal refuse were amended with alkaline FGD or FBC materials alone or combined with biosolids or yard waste compost. In all but one experiment, application of either the CCBs or organic amendments separately allowed plant growth to occur. One experiment with hyper acidic coal refuse amended with only compost remained phytotoxic. Co-application of FGD or FBC with biosolids or compost gave varied results. In three experiments, co-application increased plant growth over either amendment alone (Fig. 10.2). In one experiment, yield was suppressed with compost application due to nitrogen immobilization. Addition of nitrogen fertilizer overcame this problem. In the remaining experiments, there was not a clear plant yield advantage to co-application.

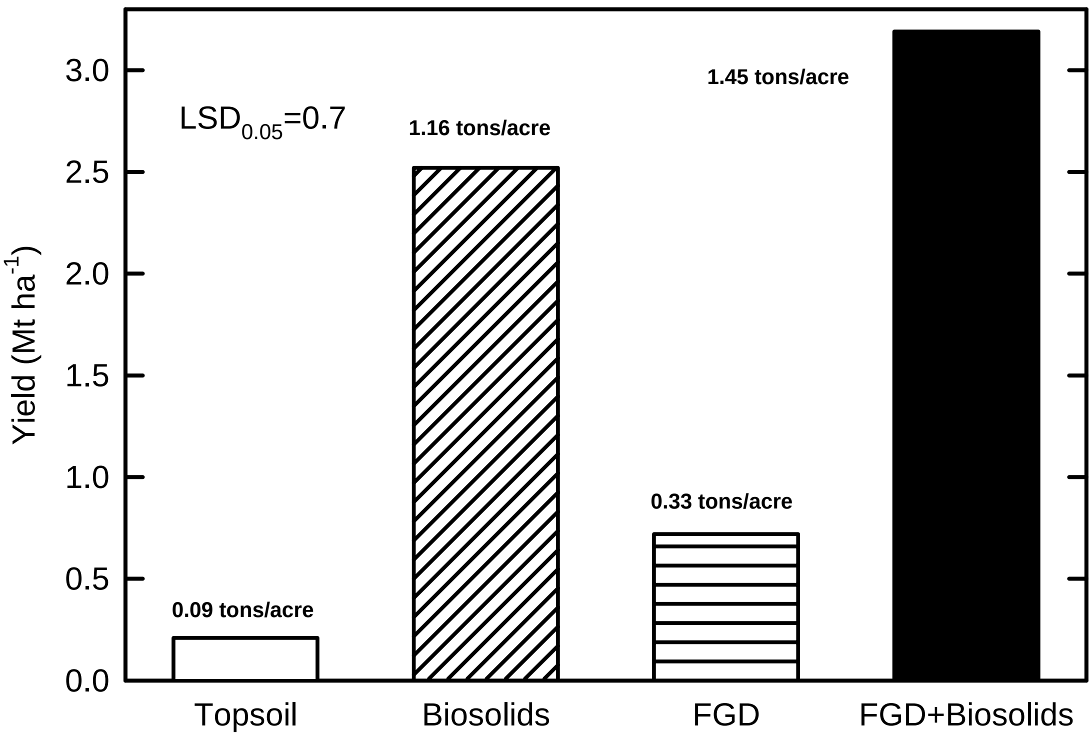

Figure 10.2. Plant yields on acidic mines spoil covered with 20 cm depth of borrow topsoil or amended with biosolids (100 Mt ha^{-1}) (45 tons/acre), FGD (670 Mt ha^{-1}) (299 tons/acre), or FGD+biosolids (Stehouwer et al., 1998). [note: 1Metric tonne/hectar = 0.445 English tons/acre].

Shumann and Sumner (1999) reported that fly ash did not supply nitrogen, phosphorus, and potassium. In fact alkaline fly ash alone exacerbated phosphorus and magnesium nutrition due to precipitation of phosphorus and cation imbalance from excess calcium. However, these macronutrients were provided by biosolids (nitrogen and phosphorus) or by poultry manure (phosphorus). These researchers also noted boron toxicity from fly ash reduced plant growth and that co-application did little to reduce boron availability. Stehouwer et al. (1998) reported that while organic amendments did little to increase spoil pH, they caused large reductions in soluble and exchangeable aluminum and iron, likely due to complexation of these metals by organic ligands. Stehouwer et al. (1998) found some evidence that co-application affected spoil chemistry below the depth of amendment mixing. One experiment showed clear evidence that co-application of alkaline FGD and biosolids increased transport of calcium into subjacent mine spoil and reduced exchangeable aluminum and iron (Fig. 10.3).

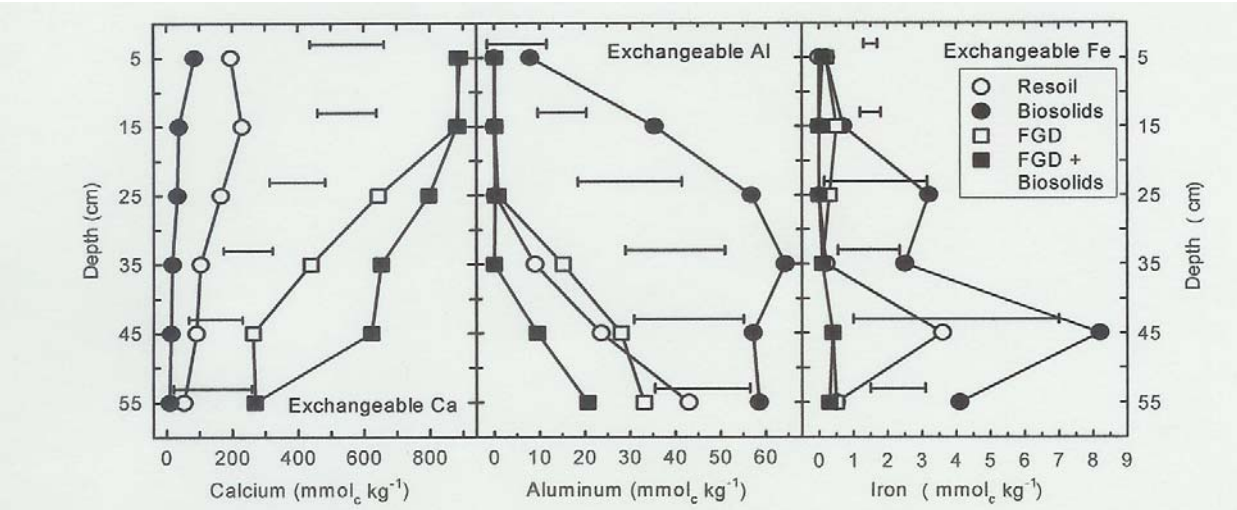

Figure 10.3. Distribution of exchangeable calcium, aluminum, and iron in the acidic mine spoil profile nine months after treatment application. (Error bars indicate the width of the $LSD_{0.1}$ value for comparison of treatment means at each depth.) (Stehouwer et al., 1998).

10.7 PLANT SPECIES RESPONSE TO DIFFERENT MINE SPOIL AND SOIL CONDITIONS

Plant species vary as to their optimum range of soil pH, needs for plant nutrients and tolerances to high levels of metals. Most plants grow best within a defined soil pH range. Table 10.4. shows ranges of soil pH for best growth of selected plants (Lyle, 1987; USDA Natural Resources Conservation Service, 2004).

Table 10.4. Soil pH ranges for selected plants

Plant Species	Soil pH Range
Birdsfoot trefoil (Lotus corniculatus)	5.0 – 7.5
Alsike clover (Trifolium hybridum)	5.2 – 7.0
Orchardgrass (Dactylis glomerata)	5.0 – 7.5
Redtop (Agrostis alba)	4.0 – 7.6
Perennial rye (Lolium perenne)	5.5 – 8.0
Switchgrass (Panicum virgatum)	4.5 – 7.5
Timothy (Phleum pretense)	4.5 – 8.0
Black locust (Robinia pseudoacacia)	4.8 – 7.5
Northern red oak (Quercus rubra)	4.3 – 6.5
Red pine (Pinus resinosa)	4.5 – 6.0
Eastern white pine (Pinus strobes)	4.0 – 6.5

Woody species vary greatly in tolerance to aluminum toxicity. In laboratory studies using hydroponic systems, hybrid poplar (Populus maximowiczii X trichocarpa) were very sensitive to concentrations of aluminum as low as 10 ppm while red oak (Quercus rubra) and pin oak (Quercus palustris) were most tolerant of aluminum at 120-160 ppm. Yellow birch (Betula alleghaniensis), gray birch (Betula populifolia), paper birch (Betula papyrifora), Virginia pine (pinus virginiana), pitch pine (Pinus rigida) and scotch pine (Pinus sylvestris) were intermediate in tolerance to aluminum at 80-120 ppm (McCormick and Steiner, 1978).

Manganese toxicity to legumes in acid soils is well documented (Hewitt, 1946; Morris, 1948; Jackson, 1967). Manganese toxicity was observed on sericea lespedeza (Lespedeza cuneata) growing in mine spoils with a pH of 5.0 or lower. Species more tolerant of manganese like birdsfoot trefoil (Lotus corniculatus) and black locust (Robina pseudoacacia) seldom developed manganese toxicity symptoms on mine spoils with a pH greater than 4.4 (Berg and Vogel 1973; National Academy of Science, 1973).

As has been previously discussed, alkaline fly ashes and FBC by-products are effective limestone substitutes and can be effectively used to adjust spoil pH and reduce aluminum, iron, and manganese toxicity. Thus, these materials can be used to aid establishment of a variety of species on acidic soils and spoils. Furthermore, species selection should be done to match the pH range achievable with whatever alkaline amendments are used.

10.8 MANAGEMENT PRACTICES FOR LAND APPLICATION OF COAL COMBUSTION BY-PRODUCTS

Strongly acidic mine spoils often contain pyrite that continues to generate acidity as it oxidizes. For this reason application rates of alkaline materials to mine spoil must be much higher than for acid agricultural soils to neutralize both active and potential acidity (Dick et al., 1994). However, when alkaline CCBs are used for neutralizing mine soil acidity, the large application rates needed must be balanced against potential negative effects on soil quality such as potentially increased loadings of trace elements, the possibility of increased soluble salt levels causing phytotoxicity problems, excessively high pH, decreased infiltration rates and increased erosivity. Factors that may preclude the use of some CCBs are high heavy metals concentrations, high boron content, high soluble salts and low neutralization potential (Carlson and Adriano, 1993; Clark et al., 1995; Stehouwer et al., 1995a). Use of some FBC by-products could lead to conditions of high pH, high calcium and sulfate concentrations. With adequate moisture, these conditions could lead to the formation of ettringite. Ettringite is highly expansive and cementitious and would severely restrict water movement and root development (Stehouwer et al., 1995a,b).

Coal combustion by-products with high soluble salts may cause problems with seed germination and plant establishment. Surface applications of coal combustion by-products followed by incorporation of the ash into the mine spoil would decrease the potential negative impacts of high soluble salts on seed germination. Timing of the ash application plays a significant role in avoiding problems of high soluble salts on seed germination. Ash used as a soil additive or soil amendment should be applied as far in advance of plant establishment as possible to allow time for the salts to leach out of the root zone (Korcak, 1996). If applying coal combustion by-products as a soil additive or amendment after vegetation is established, application rates should be adjusted accordingly considering incorporation of the materials would not be feasible without destroying some of the existing vegetation. Under these circumstances, applying the coal combustion by-products when the vegetation is dormant would be beneficial in avoiding problems of adverse effects to plants due to soluble salts. Use of weathered ash can alleviate problems of soluble salts. Martens and Beahm (1976) reported use of weathered ash at rates of 58 tons/acre was successful while fresh ash caused salt related problems at 29 tons/acre.

Studies of the effects of using fly ash applied to coal refuse found that bulk blends of fly ash and coal refuse had higher plant yields than surface applied ash treatments. These higher yields were attributed to the lower levels of soluble salts. Some blends of the fly ash and coal refuse had higher water holding capacities than the native sandstone derived soils (Stewart and Daniels, 1995).

Selection of equipment for applying and mixing fly ash with mine spoil or coal refuse depends primarily upon the relative roughness of the surface and the grades of slopes. On gentle slopes, contour plowing or ripping deep furrows along contours was more effective for controlling erosion. Survival of seeded grasses was more successful in the furrows and particularly during dry weather (Adams et al., 1972). Germination and growth of seeded grasses on coal refuse amended with fly ash was reported to result in poor vegetative growth partly due to dry weather but mostly due to the variable pH conditions from uneven fly ash application.

The physical and handling characteristics of CCBs can also present challenges for hauling, stockpiling, spreading and incorporating. Material can range from fine, extremely dusty dry fly ash to coarse granular bed ash. Ash may be conditioned with water to reduce dust but then may stick or bridge in trucks and spreaders. FGD sludges can be very sticky and paste-like. Wetting and drying of alkaline materials can result in formation of extremely hard clumps due to pozzolanic reactions. Conventional agricultural limestone and fertilizer application equipment may not be able to spread material with these characteristics, or may not be able to spread them uniformly or at high enough rates. When desired application rates become extremely large (223 tons/acre) it becomes difficult to uniformly incorporate such a large volume of material into the soil or spoil. In such cases, spreading in multiple lifts, with tillage after each application may be necessary.

10.9 CONCLUSIONS

Coal combustion by-products have the potential to improve mine spoil and soil quality for establishment of sustained vegetative cover. The major benefits are improved physical properties and neutralization of acidity. Most fly ashes and FBC ashes will increase the water holding capacity of coarse textured, high rock fragment spoils. Alkaline fly ash and FBC ashes contain significant alkalinity and are effective liming materials for acid soils and spoils. While CCBs can supply some plant micronutrients, notably boron, they generally are not good sources of macronutrients with the exception of calcium. The major benefit of alkaline CCBs with respect to plant nutrition is the indirect effect of pH increases on increased nutrient availability and decreased availability of phytotoxic metals, especially aluminum, iron, and manganese. Some of the shortcomings of CCBs as amendments for mine spoil revegetation can be overcome by combined application with organic amendments. Materials such as biosolids, manures, and composts can be good sources of nitrogen, phosphorus, and potassium, increase plant available water, reduce erosivity, promote structural development and stability, and stimulate microbial activity. CCBs can also have negative effects on mine soil and spoil quality such as decreased water infiltration, increased erosivity, decreased phosphorus availability, high soluble salts, and potentially phytotoxic amounts of boron. Amending of mine spoils and soils with CCBs requires balancing both the positive and negative effects on soil quality. Application rates, timing, and methods, use of other amendments, and selection of plant species to maximize positive effects, minimize negative effects and insure that the overall result is an increase in the ability and capacity of the mine soil or spoil to support a sustained vegetative community.