CODISPOSAL OF FBC BY-PRODUCTS AND COAL SLURRY SOLIDS: CHARACTERIZATION OF MATERIALS¹

by

D.E. Tungate, R.G. Darmody, G.B. Dreher, W.R. Roy, and J.D. Steele²

Abstract. The preparation and combustion of high sulfur coal generates many waste products including cleaning and combustion wastes. Pyrite is associated with coal cleaning wastes and it makes them potentially acidic. Coal slurry solids (CSS), the finest textured cleaning wastes, are stored in large impoundments. After the impoundments are retired, they must be reclaimed with a 1.2 m soil cap. Reclamation of abandoned CSS impoundments by direct revegetation would avoid costs associated with the required soil cap. However, CSS have physical and chemical limitations for plant growth including undesirable pH, surface temperatures, and moisture holding capacity. Fluidized bed combustion is a coal combustion technique designed to reduce smoke stack emissions of SO₂. It results in a highly alkaline by-product (FBC). The combination of CSS and FBC may allow direct revegetation of CSS materials. This would possibly be a more cost effective method of reclaiming CSS materials than using a soil cap while creating an economic value for FBC by-products. This will also preclude the necessity of disturbing a borrow area for the soil cap. An experiment was designed to evaluate the potential for CSS/FBC mixtures to support direct revegetation. Three test blocks with 18 plots each were established on a temporarily inactive portion of an active coal slurry impoundment. The addition of FBC increased the pH of the potentially acidic CSS. Soil fertility analyses indicated Al, B, Ca, Mg, Zn, and soluble salts increased with additions of FBC, while Cu, Fe, K, P, and S remained relatively unchanged, and Mn and Na concentration decreased. Particle size distribution of the CSS/FBC mixtures ranged from loam to coarse sandy loam. Crust strength was variable, but tended to increase with FBC addition. Direct revegetation of CSS materials may be facilitated by the addition of FBC by-products. However, other treatments in addition to FBC amendments may be necessary to optimize conditions for plant growth.

Additional Key Words: reclamation, Illinois, FBC, alkaline amendment, slurry ponds, tailings.

Introduction

Coal mining is an important component of the Illinois economy. Most coal mined in the state is used in the production of electricity (Torrens, 1990). The preparation and combustion of Illinois coal, however, generates waste products including cleaning wastes and combustion wastes (Lewis, 1984).

Coal is cleaned to separate it from noncombustible impurities and to produce a cleaner burning fuel (Couch, 1991). After coal is mined, it is cleaned in a preparation plant, usually located at the

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² David E. Tungate is Graduate Research Assistant and Robert G. Darmody is Associate Professor of Pedology at the University of Illinois, Urbana, IL 61801; Gary B. Dreher, William R. Roy, and John D. Steele are geochemists with the Illinois State Geological Survey, Champaign, IL 61820. same site as the mine. Coal cleaning wastes include coal slurry solids (CSS) and coarse refuse (Lewis, 1983). The coarse textured waste is generally disposed of on the mine property. The finer-textured CSS material is moved as a slurry and stored in ponds on the property. A particular component of coal preparation waste found in both CSS and gob, which causes many environmental problems, is pyrite. As a result of pyrite oxidation, extremely acidic drainage with a pH as low as 2.0 may result (Evangelou and Zhang, 1995).

Coal slurry impoundments must be reclaimed when they are full, according to Illinois law (Public Act 81-1015). The typical reclamation practice is to cover an impoundment with 1.2 m of soil, stored for that purpose or borrowed from another location, to prevent spontaneous combustion, slow oxidation of pyrite, and to allow the establishment of a vegetative cover. The costs, both environmental and economic, of capping a CSS impoundment with borrowed soil are enormous.

Direct revegetation of a CSS impoundment is a potential method to avoid using a soil cap. There are physical and chemical limitations on plant growth associated with CSS. Physical limitations include the dark color, coarse texture, decreased organic matter,

Proceedings America Society of Mining and Reclamation, 1997 pp 503-514 DOI: 10.21000/JASMR97010503 and low available water holding capacity of CSS (Buck and Houston, 1986). Dark color leads to elevated soil temperatures that could limit plant growth. Coarse texture and low water holding capacity make for droughty conditions. Chemical limitations include decreased N and P levels, low pH values, and soluble concentrations of Al, Fe, Mn or other toxic elements (Buck and Houston, 1986; Hossner and Hons, 1992).

Pyrite oxidation is complex and involves chemical, biological, and electrochemical reactions, which vary with environmental conditions (Evangelou and Zhang, 1995). The four steps of pyrite oxidation as described by Evangelou and Zhang (1995):

 $FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$ [1]

 $Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O$ [2]

 $Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3(s) + 3H+$ [3]

$$FeS_2 + 7Fe_2(SO_4)_3 + 8H_2O = 15 FeSO_4 + 8H_2SO_4$$
 [4]

Each of these four reactions are mass and charge balanced, but they do not have any rate reaction meaning or molecular mechanistic meaning. As cited in Evangelou and Zhang (1995) Reaction 1 and 4 show that Fe^{3+} and O_2 are the major oxidants of pyrite. Oxygen reacts with pyrite to produce Fe^{2+} in reaction 1. Reaction 2 shows Fe^{2+} being oxidized to form Fe^{3+} by oxygen and reaction 3 shows $Fe(OH)_3$ precipitate formation. When the pH is below 4.5, Fe^{3+} oxidizes pyrite more rapidly than O_2 and more rapidly than oxygen oxidizes dissolved Fe^{2+} to Fe^{3+} . This is the reason reaction 2 is the rate limiting step in abiotic pyrite oxidation.

The rate of Fe^{2+} oxidation can be accelerated by a factor of 10^6 by the iron oxidizing bacteria *Thiobacillius ferroxidans*. *T. ferroxidans* is an acidophilic chemolithotropic organism that is found in geologic environments containing pyrite. It is responsible for the oxidation of pyrite at a pH below 4 (Arkesteyn et al., 1980). When *T. ferroxidans* is present, pyrite oxidation can be described by reactions 2 and 4 (Evangelou and Zhang, 1995).

At neutral to alkaline pH the system changes. The abiotic rate of Fe^{2+} oxidation rises rapidly (reaction 2) and Fe^{3+} concentration decreases due to $Fe(OH)_3$ precipitation (reaction 3). This is probably because there is little bacterial participation in the oxidation of pyrite in the pH range. Therefore Fe^{3+} will become a more important pyrite oxidant than O_2 . The major role

played by oxygen in the system is to oxidize Fe^{2+} . By oxidizing Fe^{2+} to Fe^{3+} the oxygen sustains the pyrite oxidation cycle. At pH values as low as 3, reaction 3 is a readily reversible dissolution/precipitation reaction that serves as a source as well as a sink of solution Fe^{3+} . This is a major step in the release of acid to the environment.

A strategy known as selective slurry disposal was developed by Nawrot et al. (1984) to aid in direct revegetation. The objective of their research was to use the settled fines, which contain relatively insignificant amounts of pyrite, to cover the coarse, pyrite-rich material. Pyrite is a heavy mineral with a density of 5.01 g cm⁻³, and the heavier, coarse fragments settle out of the slurry before the fines (Lindsay, 1979). Selective distribution of the slurry constituents is accomplished by strategically moving the discharge point to improve the physical and chemical characteristics of CSS impoundments (Nawrot et al., 1984).

Recent legislation to preserve air quality demands stricter emission controls on coal burning utilities and industries, forcing them to adopt technologies to reduce smoke stack emissions of sulfur dioxide and other pollutants. In doing so, however, the industry generates much solid coal combustion waste. One effective method of reducing SO₂ emissions from coal combustion furnaces is fluidized bed combustion (Torrens, 1990). However, fluidized bed combustion produces 2.5 times more solid residue than an ordinary boiler (Paul et al., 1995). Furthermore, use of the fluidized bed combustion process necessitates development of economically and environmentally sound by-product disposal systems (Bennett et al., 1977). In some cases, coal combustion facilities require the coal supplier to accept return shipments of fluidized bed combustion by-products (FBC) as part of the coal sales contract (Dreher et al., 1996). In such cases, the mine must dispose of both CSS and FBC.

Fluidized bed combustion by-product is a material that has potential uses as a source of lime. A combination of potentially acidic CSS and basic FBC has been shown in a greenhouse experiment to make a slightly alkaline rooting medium (Green, 1995). This research was designed as a follow up to the previous greenhouse study. The overall objective of our research is to develop a method for the direct revegetation of coal slurry solid impoundments. The specific objective of this research field project was to characterize a coal slurry impoundment treated with FBC as a lime amendment to make a suitable plant growth medium.

Materials and Methods

Plot Establishment

A replicated randomized complete block experimental design was used. Three test blocks with 18 plots each were established in May 1996 on a temporarily inactive area of an active coal slurry impoundment. The plots were designed to allow for future evaluation of plant growth. The blocks were laid out at increasing distances from the former discharge point for that portion of the slurry pond. The discharge point was moved temporarily to allow for this research project. Pyritic sulfur and inorganic carbon content were determined for each plot (ASTM, 1995; Cahill and Autrey, 1988). It was determined that between 0.31 g to 24.1 g of calcium carbonate would have to be added per 100 g of CSS to neutralize potential acidity, depending on the plots' pyrite content. Potential acidity refers to the possibility that all of the pyrite present is oxidized.

A grab sample of fresh FBC was analyzed before the plots were established in May 1996. It had a calcium carbonate equivalent (CCE) of 65% (Dreher et al., 1996). Therefore, 0.48 g to 37.1 g of FBC was required per 100 g of CSS to neutralize potential acidity. Fresh FBC was mixed into the top 15 cm of the experimental plots with a roto-tiller. The application of FBC took place on July 1 and 2, 1996. Treatment rates were nominally 0, 1, and 2 times the calculated amounts of CCE required. The calcium carbonate equivalent of the FBC added to the plots turned out to be greater than the initial FBC material upon which the calculations were based. Consequently, the actual treatment rates were 0, 1.2, and 2.4 times the predicted amounts needed to neutralize the potential acidity. For convenience, the treatments will be referred to as 0x, 1x, and 2x in this report.

Piezometers were placed in six randomly selected plots from each test block to allow replication with respect to the rate of addition of FBC. They were made from 5.2 cm inside diameter PVC pipes with a filter fabric fastened to the bottom to prevent sediment intrusion. The piezometers were installed at 180 cm and 60 cm depths. In addition, a piezometer was installed at a control site 75 m from the plots. The piezometers were designed to sample the water within the CSS material beneath the plots. The coal slurry impoundment is designed to keep the water associated with the delivery of the slurry solids isolated from local groundwater systems.

Field Sampling

Sixty days before the FBC was added, coal slurry solids were sampled at depths of 0 to 15 and 15 to 30 cm with a standard soil probe. Ten subsamples were extracted from each sample area, within the individual plots, and composited to form a sample for the area. The CSS/FBC mixtures were sampled using the same procedure, at two depths (0-15 and 15-30 cm) 74 days after FBC additions. A hand penetrometer was used in the field to measure crust strength at various times after FBC addition. Six penetrometer readings for each plot were used to calculate the average crust strength. Saturated hydraulic conductivity was obtained from the piezometers installed in the plots by the auger hole method (Amoozegar and Warrick, 1986). Water samples collected from the piezometers with a vacuum extractor were immediately cooled to 4°C. Bulk density was determined using the method described by Blake and Hartge (1986).

Laboratory techniques

Coal slurry solid pH determinations were done using a glass electrode with a standard 1:1 soil:water ratio (McLean, 1982). The hydrometer method for particle size analysis was used to determine silt and clay, and sieves were used for sand determinations (Gee and Bauder, 1986). The pH of the water samples was determined using a solid state pH meter, electrical conductance (EC) was determined with a conductivity meter (Rhoades, 1982). A pressure plate extractor was used to determine soil moisture release data for the CSS/FBC mixtures (Klute, 1986). Concentrations of B and SO_4^{2-} in the groundwater were determined using a Hach DR 2000 spectrophotometer and standard methods (American Public Health Association, 1985). Boron was analyzed using the Carmine Method (method 494 B) and SO₄² was determined using the turbidimetric method (method 426 C).

A commercial laboratory (Brookside Farms Laboratories, Inc., New Knoxville, Ohio) determined extractable elements on the materials sampled 74 days after mixing. Each of the samples was air-dried and ground to pass a 2-mm sieve. Soil sample measurement was by a standard soil scoop. The Mehlich III (Mehlich, 1984) extractant and a 1:10 soil:extractant ratio with five minutes of mixing were used for extraction of Al, B, Ca, Cu, Fe, K, Mn, Mg, P, S, and Zn. All nutrients except B, Ca, and P were determined with Inductively Coupled Plasma (ICP) emission spectrometry analysis of the Mehlich III extractant. The Ca data derived from the Mehlich III-ICP approach were correlated by the slope/intercept method to equivalent ammonium acetate levels; P was correlated to Bray II extractant levels, and B was correlated to hot water extractable levels.

Results and Discussion

Chemical Properties

The pH of the fresh CSS averaged 6.8 before the FBC was added (Table 1). This indicated a lack of

Table 1. Surface pH of CSS/FBC mixtures at the research site.

			pH						
	FBC		Days post treatment						
_	Rate		31 74 90 106						
	0 x	6.8 †	7.1	6.8	N/A	7.2			
	1 x		11.6	8.9	8.4	8.0			
	2 x		12.4	11.0	N/A	10.3			

† Before FBC addition on 07/02/96.

acid production from pyrite weathering despite the fact that pyrite content of the experimental plots averaged $3.1\% \pm 1.3$ on a weight basis (Dreher et al., 1996). The pyrite oxidation process, however, is complex because it involves chemical, biological, and electrochemical reactions, and varies with environmental conditions (Evangelou and Zhang, 1995). In addition, the CSS material was fairly rich in CaCO₃, the average inorganic C was $1.2\% \pm 0.5$ on a weight basis before FBC addition and would initially buffer any acid produced by pyrite oxidation (Dreher et al., 1996).

Addition of the FBC effectively increased the pH of the CSS material. The pH of the control plots (0x)

increased, possibly the result of cross contamination of the FBC material. Upon weathering the pH of the materials dropped (Table 1). On the basis of previous laboratory experiments, the CaO initially present in the FBC was converted on exposure to moisture and atmospheric CO₂ initially to Ca(OH)₂, then to CaCO₃. The pH of the pore water decreased with these reactions.

Standard soil fertility analyses were performed on samples collected 74 days after FBC addition. Aluminum, B, Ca, Mg, Zn, and soluble salts tended to increase with increasing amounts of added FBC, while Cu, Fe, K, extractable P, and soluble S remained relatively unchanged (Table 2). Sodium and Mn tended to decrease in concentration, possibly because of dilution effects.

Soluble S in the mixtures ranged from about 3,700 to 4,100 mg kg⁻¹ (Table 2). A typical soil contains between 100 to 500 mg kg⁻¹ total S, and 11 mg kg⁻¹ extractable S is considered sufficient for most crops (Troeh and Thompson, 1993; University of Illinois at Urbana-Champaign, 1994). The increased levels of S were the result of the S found both in the CSS and FBC and should not limit plant growth. The extractable S content will decrease as the mixtures age because of the leaching of soluble S and formation of gypsum as a product of the neutralization of oxidized pyrite.

Extractable P content of the mixtures ranged from 11 to 17 mg kg⁻¹, and may be insufficient for optimal plant growth (Table 2). Under alkaline soil conditions such as in the plots, phosphorous tends to precipitate as hydroxyapatite, a calcium phosphate of low solubility (Troeh and Thompson, 1993). Because of the increased

Table 2. Extractable soil fertility analysis on FBC/CSS samples collected 74 days after mixing.

Depth	FBC						Cons	stituen	t†					
(cm)	Rate	S	Р	Ca	Mg	K	Na	В	Fe	Mn	Cu	Zn	Al	Sol. Salt
all	0 x	3845	16	9641	200	99	444	4	218	75	2	7	21	0.27
0-15		37 8 1	17	8010	176	85	429	4	193	66	2	5	22	0.27
15-30		3908	14	11273	224	113	460	4	244	84	2	8	19	0.26
all	1 x	4027	12	11579	571	105	271	17	267	40	2	35	97	0.26
0-15		4019	13	14375	726	105	210	25	251	34	2	46	1 68	0.27
15-30		4036	11	8784	415	104	333	10	283	46	2	25	27	0.26
all	2 x	3899	13	17886	794	113	249	33	271	41	2	48	172	0.48
0-15		3696	13	20847	812	110	1 86	41	235	36	2	49	190	0.59
15-30		4102	13	14925	777	115	311	26	307	45	2	46	155	0.36

[†]Units are in mg kg⁻¹ except soluble salts are in S cm⁻¹, values represent 18 samples per depth.

Ca content of CSS/FBC mixtures, phosphorous deficiencies are likely to become a problem with direct revegetation unless sufficient P fertilizer is added.

The CSS/FBC mixtures contained 8,000 to 17,900 mg kg⁻¹ of extractable Ca, with increasing amounts corresponding to FBC by-product application rates (Table 2). As a comparison, most agricultural soils contain between 100 to 5000 mg kg⁻¹ of extractable Ca in the plow layer (Troeh and Thompson, 1993). Decreased solubility and possible deficiencies of B, Fe, Mn, P, and Zn may occur since the CSS/FBC mixtures have an excess of Ca (Troeh and Thompson, 1993). These nutrients might need to be added to the system as fertilizer for optimal plant growth.

The mixtures contained 176 to 812 mg kg⁻¹ Mg, which increased with additions of FBC (Table 2). This Mg level is greater than the minimum 25 to 50 mg kg⁻¹ required for plant growth (Tisdale et al., 1985). The high Ca content of the mixtures may present a problem because the desired Ca:Mg ratio in agricultural soils is about 7:1, and these mixtures have a Ca:Mg ratio on the order of 40:1 (Tisdale et al., 1985).

Sodium in the mixtures ranged from 186 to 460 mg kg⁻¹ (Table 2). Sodium will not pose a problem for plant growth after it leaches from the system (Troeh and Thompson, 1993). The coarse texture of the CSS are conducive to leaching. Under humid conditions Na leaches from the soil, and the matrix Na content will gradually decrease with time (Troeh and Thompson, 1993). Sodium toxicities become a problem when there

Table 3.	Average	sand.	silt.	and clay	content of CS	S.†

			-%-	
Block	Depth (cm)	Sand	Silt	Clay
Α	0-15	62	28	10
	15-30	65	25	10
В	0-15	61	28	11
	15-30	63	27	10
С	0-15	57	31	12
	15-30	62	27	11

† Means of 32 determinations.

is a lack of leaching, which should not be a problem at the research site.

Extractable iron concentrations in the mixtures ranged from 193 to 307 mg kg⁻¹ (Table 2). The initially elevated pH values of the mixtures will make Fe less available to plants (Troeh and Thompson,

1993). However, this may not be a long-term problem due to leaching and fixation of Ca, coupled with pyrite oxidation. In addition, Fe can be added as a fertilizer if necessary. Aluminum concentrations in the mixtures ranged from 19 to 190 mg kg⁻¹ (Table 2). This range should not be a problem to plants unless the soil pH is less than 5, at this pH Al becomes active in the soil system (Troeh and Thompson, 1993).

The soluble salt concentration as measured by electrical conductivity, ranged from 0.27 to 0.59 S cm⁻¹. Soluble salt concentrations at these levels could pose a problem to plant growth until the salts leach (Table 2) (Troeh and Thompson, 1993). Salt concentrations indicated by conductivities greater than 0.4 S cm⁻¹ may be a problem for plant growth in the mix.

The concentrations of the extractable nutrients B, Cu, K, Mn, and Zn were similar to typical soil values (Whetstone et al., 1942; Kubota, 1983; Troeh and Thompson, 1993). Boron concentrations of the mixtures ranged from 4 to 41 mg kg⁻¹ (Table 2). Agricultural soils typically have from 4 to 88 mg kg⁻¹ B. (Whetstone et al., 1942). The K concentration in the mixtures ranged from 100 to 115 mg kg⁻¹ (Table 2). Potassium in soils ranges from 50 to 200 mg kg⁻¹ (Troeh and Thompson, 1993). The Mn concentrations in the mixtures ranged from 34 to 75 mg kg⁻¹ (Table 2). Average Mn concentrations are 10 to 100 mg kg⁻¹ in agricultural soils (Troeh and Thompson, 1993). The Cu concentrations average 2 mg kg⁻¹ in the CSS/FBC mixtures (Table 2). Typical agricultural soil concentrations of Cu are 1 to 191 mg kg⁻¹ (Kubota, 1983). Zinc concentrations in the mixtures ranged from 5 to 49 mg kg⁻¹ (Table 2). Background Zn concentrations in agricultural soils average between 10 and 300 mg kg⁻¹ (Troeh and Thompson, 1993). Zinc deficiencies at high pH values may be a problem, but the pH at the site is decreasing as the materials weather.

Physical Properties

The particle size distribution of the CSS was relatively constant across the plots and the USDA textural class averaged sandy loam (Table 3). There seemed to be no clear trends in particle size or pyritic sulfur content as indicated by Nawrot et al. (1984). Nawrot (1984) indicated a fining upwards sequence in relation to coal slurry solids. The observed lack of correlation in this work may be the result of the small size of the research area and to possible variable locations of the CSS discharge points. The relatively high infiltration rates associated with these textures will help alleviate any Na toxicity problems. However, the coarse texture will not allow for satisfactory soil moisture storage.

Addition of FBC increased the amount of available water on a gravimetric basis (Table 4). The water

Table 4. Soil moisture release for CSS/FBC materials at various tensions.

	Depth	М			ent (%	-		is)	Avail.
FBC Rate	range (cm)	0.1	0.33	<u> </u>	tensio 1	5 5	10	15	Water %
0 x	Both	29.9	22.8	22.0	22.6	14.9	15.4	15.4	7.4
1 x	Both	31.0	22.8	22.2	22.4	16.5	15.2	15.1	7.7
2 x	Both	31.5	24.9	23.1	23.4	17.5	15.2	15.9	9.0
0 x	0-5	34.9	25.4	25.0	24.8	16.0	16.6	16.6	8.8
0 x	10-15	24.8	20.2	19.0	20.4	13.8	14.3	14.2	5.9
1 x	0-5	34.6	24.6	24.2	23.7	18.1	16.6	16.1	8.5
1 x	10-15	27.4	21.0	20.2	21.1	14.9	13.9	14.0	7.0
2 x	0-5	37.5	26.8	24.8	24.4	18.2	15.8	16.6	10.1
<u>2 x</u>	10-15	31.5	23.1	21.4	22.4	16.9	14.6	15.2	7.8

holding capacity of the CSS-FBC by-product mixture is important if it is to be directly revegetated. The available water-holding capacity was comparable to similarly-textured natural soils. The addition of FBC also decreased the bulk density of the CSS material (Table 5).

Table 5. Bulk density and field moisture contents at time of sampling.

FBC Rate	ρ _b g cm ⁻³		%H ₂ O wt (g)	% H₂O Vol.
 0 x	0.85	†	33.7	28.7
1 x	0.81		35.0	28.2
2 x	0.73		37.9	27.8

† Means of 6 samples.

Surface crusting can be a concern with seedling emergence on the plots. Crust strength, as measured with a hand penetrometer, was variable (Table 6). Moisture content probably partially controlled crust strength, but greater crust strengths were associated with the 2x plots. There appeared to be a general weakening of strength upon weathering. However, after nearly 90 days of weathering the plots still showed a treatment effect.

Table 6.	Crust	strength	at	research	site.

	Penetrometer Resistance kg cm ⁻²							
FBC	Days post treatment							
Rate	37	90						
0 x	1.10	0.86	0.38					
1 x	0.53	0.59	0.61					
2 x	1.07 1.81 1.4							

Groundwater Chemistry

Groundwater was sampled from the research site 9 days after the FBC and the CSS were mixed (Table 7). The values for pH and electrical conductivity obtained from the water samples may not be representative of the specific plots in which thepiezometers were located, because of the small plot size $(2.4 \times 1.8 \text{ m})$ and the significant saturated hydraulic conductivity (390 cm day⁻¹) of the CSS. The elevated pH values determined 9 days after mixing were possibly due to contamination during piezometer installation (Table 7a).

Table 7a. Groundwater pH at 180 cm below plots.

		рН							
FBC		Days post treatment							
Rate	9	9 90 133 161 218							
0 x	6.9	6.5	6.8	7.0	7.1				
1 x	7.5	6.8	6.7	7.1	7.1				
2 x	7.8	6.9	6.8	7.2	7.2				
control	6.8	6.8 6.3 6.9 7.1 7.2							

Electrical conductivity (E.C.) of the groundwater nine days after treatment was about 0.60 S cm⁻¹ in all of the water samples, it increased after 133 days, and decreased after 161 days (Table 7b). For comparison purposes, the E.C. of a water sample taken from the associated slurry pond water after 161 days was 0.36 S cm⁻¹.

 Table 7b.
 Groundwater electrical conductivity

 (E.C.) at 180 cm below plots.

	E.C. (S cm ⁻¹)							
FBC	Days post treatment							
Rate	9	161	218					
0 x	0.59	0.76	0.57	0.56				
1 x	0.58	0.74	0.57	0.56				
2 x	0.59	0.68	0.55	0.54				
control	0.61	0.74	0.67	0.65				

Additions of FBC apparently were responsible for increased B and SO₄² concentrations in water samples over those found in the control piezometers and lake water samples (Tables 8 and 9). Concentrations of B and SO_4^{2} at the control site were smaller than those at the plots, hence the additions of FBC apparently increased B and SO42 concentrations in groundwater local to the plots. As pyrite is oxidized it releases SO₄²⁻ ions and the SO₄² concentrations in the groundwater samples are indicative of the pyrite oxidation process. As pyrite is oxidized it releases SO_4^2 ions. The increased amount of SO42- in the groundwater samples indicates that pyrite oxidation is not hampered by the increased pH of the mixtures. As with the pH and E.C. results, the individual plots could not be resolved. The direction of groundwater flow can be

Table 8. Boron concentration (mg L⁻¹) of groundwater at 180 cm below plots.

FBC		Days post treatment				
rate	Block	137	161	218		
0 x	overall	1.5	1.1	1.2		
1 x	overall	1.7	1.3	1.4		
2 x	overall	1.5	1.1	1.2		
overall	Α	1.4	1.1	1.3		
overall	В	1.4	1.0	0.9		
overall	С	1.8	1.4	1.5		
Control		0.8	0.6	1.0		
Pond Water		N/A	0.1	0.1		

interpolated from the piezometer data, assuming that B and $SO_4^{2^{\circ}}$ act as tracers. The groundwater appears to flow towards block C, because there were larger concentration of B and $SO_4^{2^{\circ}}$ beneath block C.

Table 9. Sulfate concentration (mg L⁻¹) in groundwater 180 cm below plots.

groundwater 100 em below plots.								
FBC		Days	post treat	ment				
rate	Block	137	161	218				
0 x	overall	2,008	1,900	1,945				
1 x	overall	1,950	2,100	1,945				
2 x	overall	1,808	1,925	2,095				
overall	Α	1,500	1,683	1,775				
overall	В	1,875	1,916	1,845				
overall	С	2,392	2,325	2,366				
Control		1,500	2,100	2,150				
Pond Water		N/A	700	50				

Conclusions

Untreated CSS would likely provide a harsh environment in which to establish plants. These materials have potentially decreased pH values resulting from pyrite oxidation and sulfuric acid generation, a droughty environment, saline soil conditions, and excessively elevated soil surface temperatures. The addition of FBC to CSS materials may create a more suitable environment for plant growth. The experiment described in this report was designed to test the hypothesis that the addition of FBC by-products to CSS would result in a more favorable plant substrate. However, fire prevention must be factored into the decision to directly revegetate a CSS impoundment.

Results after 106 days indicate that FBC additions had a major impact on some CSS properties. The pH of the CSS increased initially from 6.8 to 11.6 on the 1x plots and to 12.4 on the 2x FBC plots. The pH has subsequently decreased to a more favorable level of 8.0 in the 1x plots and 10.3 in the 2x plots and may continue to decrease as pyrite oxidizes and CaO weathers to Ca(OH)₂ and then to CaCO₃.

Exceptionally large Ca concentrations in the mixtures, may lead to deficiencies of B, Fe, Mn, P, and Zn for optimal plant growth. FBC additions also increased Fe, Mg, P, S, and soluble salts in the CSS/FBC mixtures. None of these solutes appeared to be inhibiting for plant growth.

Soil water-holding capacity was improved by the addition of FBC, but it was still low and comparable to that of a similarly textured soil. The limited water holding capacity may be a challenge for revegetation. Additions of FBC also made the surface lighter colored, and should reduce maximum surface soil temperature to create a more favorable plant environment. Although surface crusting occurred as a result of FBC additions, the crust strength appeared to be weakening as the mixtures weather and may not be an issue for plant growth after sufficient time.

Other treatments, in addition to FBC amendments, may be necessary to optimize the conditions for direct revegetation of CSS. Application of N-P-K fertilizers will help overcome nutrient deficiencies in the materials caused partially by the large Ca content. Mulch should help in the regulation of surface temperature and moisture in the critical phase of seed germination and plant establishment. Direct revegetation of CSS materials by the addition of FBC should be an acceptable method of disposal of both waste materials. In addition, it precludes the establishment of a soil borrow area as might be necessary for conventional CSS revegetation. This research reports some of the challenges associated with this method.

Future Work

The current research project is designed to create a suitable rooting medium for plant growth. Additional research is planned to document plant growth in the research plots. Kentucky-31 tall fescue, alfalfa, and sweet clover were selected as possible plant species, because of their tolerance for the CSS/FBC mixtures' conditions. Also, the effect of mulch on the surface temperature, soil moisture holding characteristics, and seedling emergence and survival will be incorporated into future research projects.

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