Session V:

ENVIRONMENT: LAND AND WATER

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COAL ASH CHEMICAL PROPERTIES AND POTENTIAL INFLUENCE ON WATER QUALITY

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Abstract

Disposal and/or any use of coal ash is becoming a major issue because of its potential to contaminate surface and groundwater with arsenic, boron, heavy metals, etc. Knowledge on the chemistry of fly ash is essential in developing a methodology that can predict release rate(s) and concentration(s) of chemical constituents of environmental concern (pollutants). Safe disposal of fly ash with respect to surface and groundwater protection depends on having the know-how to evaluate the potential of a given fly ash to release toxic pollutants. Coal ash is made of three types of solids: 1) chemically water stable solids (SiO, FeO, AlO), 2) relatively water soluble solids (e.g., metal-SO_4, metal-BO_3,), and 3) water reactive metal-oxides (e.g., CaO, MgO, K20, Na20, etc). Ash varies from acidic to alkaline because of the chemical make-up of the source coal. Physical appearance varies depending on coal type and furnace. All fly ash samples are mainly composed of glass-like porous beads that vary in chemical composition with respect to Al/Si/Fe ratio and pH from extremely low (pH near 3) to near pH 12. Alkaline fly ash is often associated with high boron levels and exhibits extremely low pH buffering capacity. Potentiometric titrations show a fly ash PZC_{pH} somewhere around 4.6 with protonation and dissociation constants of $10^{6.2}$ and $10^{-7.8}$, respectively. Low pH buffering capacity appears to make fly ash extremely sensitive to pCO_2 with respect to pH and boron release. In some coal ashes, increasing pCO_2 increases boron release but heavy metal release remains unaffected. This suggests that some heavy metals are most-likely strongly chemisorbed. Acid fly ash showed greater metal adsorption potential after pH adjustment than alkaline fly ash.

Introduction

Ash is the byproduct of burning coal in steam-electric power plants. Statistics show that in the U.S. alone more than 80 million tons of ash are produced annually (Andriano et al., 1980 and references therein). Generally, amounts of ash produced vary with the source and grade of coal, but usually range from 12% to 16% of the coal burned (Terman, 1978 and references therein). Chemical composition of coal ash produced by various types of coal are shown in Table 1. Coal ash disposal is considered by some a major environmental issue because of its potential to contaminate groundwater with heavy metals, arsenic, boron, etc. Generally, composition of coal ash varies depending on the chemical make-up (source) of coal. However, knowledge on the chemical composition of ash is not all that is needed to predict potential release of toxic constituents to soil and groundwater; its chemical make up as well as its surface chemistry are needed to predict potential pollution. Below, a description of the major components of coal ash is presented and how these components could be put to safe use is described. The three major coal wastes by power plants are (a) limestone and other scrubber slurries (b) wastes from fluidized bed combustion boilers, and (c) fly ash. The first two wastes represent products of processes used to remove SO2 and many other stack gas pollutants.

Limestone Scrubber Sludge

Limestone scrubber sludge is generated by scrubbing SO2 from stack gases through suspensions of ground limestone. The slurry is usually pumped to ponded disposal sites and stored (Terman, 1978 and references therein). These sludges consist mostly of calcium sulfite hemihydrate ($CaSO_3 \cdot 0.5H_2O$), limestone ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$) and fly ash. Commonly, 1.3 moles of CO3 is needed per mole of sulfur (S) for scrubbing gases produced by the burning coal, or approximately 60 kg of CaC03 per 15 kg of S. For coal containing 3% S approximately 114 kg of CaC03 are needed per ton of coal

burned (Terman, 1978 and references therein). Limestone scrubber sludge could support vegetative growth if mixed with soil and fertilized with nitrogen, phosphorous and potassium. Fresh sludge could be toxic to plants because of boron.

Chemical and Phvsical Properties

Chemical composition of limestone scrubber sludge is controlled by the types of coal and limestone, furnace operating conditions, type and location of scrubber, quantity of scrubbing suspension used, suspension to stack gas ratio, and other factors. Fly ash content in the sludge depends primarily on the type of coal burned, and location of fly ash collectors (Terman, 1978). Chemical composition of dried up sludges is shown in Table 2.

The limestone scrubber system effluent with approximately 15% solids is usually pumped to a ponded area where excess water drains away leaving behind a sludge with approximately 50% solids. Further dewatering occurs slowly due to the hydrophilicity of the sludge. Increasing fly ash (fmer coal ash particles) content tends to increase sludge viscosity. Oxidation of the sludge, immediately after SO_2 absorption, forms SO_4. Thus, calcium sulfite hemihydrite ($CaSO_3 \cdot 0.5H_2O$), formed during SO2 absorption, converts to gypsum ($CaSO_4 \cdot 2H_2O$).

Gypsum ($CaSO_4 \cdot 2H_2O$) has little direct soil liming value. However, when gypsum is added to acid/aluminum rich soils aluminum is removed from the soil solution as relatively insoluble aluminum-hydroxy-sulfates. In addition, Ca limits bioavailability of aluminum. Therefore, the sludge in an indirect way acts as an ameliorant of soil acidity. The direct liming value of the sludge is expected to vary with its content of unreacted lime and the amount and chemical nature of its fly ash.

Fluidized Bed Waste

Fluidized bed combustion waste is formed when fine coal is burned in a bed of inert ash and crushed limestone. The bed is fluidized (held in suspension) by injection of air through the perforated bed at controlled rates (Terman, 1978). The lime reacts with SO2 released during combustion of the coal to form sulfates. The bed waste product is a granular solid material composed of $CaSO_4$, CaO, other metal oxides, and fly ash. Upon exposure to moisture and atmospheric air the bed waste forms first hydroxides and then carbonates (Andriano et al., 1980). Because of these reactions, pH is reduced from an initial value of around 12 to around 8, depending on partial pressure of C02. Chemical composition and ranges of fluidized bed waste material is given in Table 3. Fluidized bed boilers can also utilize residual oil, municipal wastes, sewage sludge, wood wastes, and other materials as heat sources and eliminate the need for costly scrubbers to remove SO2 from stack gases (Terman, 1978).

Fly Ash

Generally. fly ash is the finer material (65% to 80%) of the coal ash and its properties vary greatly with coal source, type of coal burned and type of ash collector, Fly ash is a low grade source of phosphorus. potassium, sulfur, boron, and other metals or metalloids, e.g., mercury, cadmium, lead, arsenic. selenium, etc, and its neutralizing value varies from near zero to high (Andriano et al., 1980 and references therein). Uses of fly ash include: a) improving soil moisture-holding capacity, b) serving as a concrete substitute. c) serving as tilling material, and d) forming various zeolites for heavy metal removal from water.

Chemical and Phvsical Properties

In general. fly ash is composed of three groups of solid components. The first group exhibits low water reactivity but posseses surface electric charge (may adsorb metal cations, e.g. Cd, Ni, Pb, etc., or oxyanions. e.g. arsenate. borate, sulfate, etc). These solids are made of SiO_2, Al_2O_3, Fe_2O_3, and TiO_2 (Terman, 1978; Adriano et al.. 1980). About 35% and 75%. respectively, of the fly ash from

mechanical collectors and precipitators typically has a diameter of less than 10 microns (Terman, 1978 and references therein). The ranges of chemical analyses of U.S. fly ashes from different types of coal are shown in Tables 4 and 5.

The second group of components present in coal fly ash represents metals or metalloids adsorbed onto the oxide surfaces. According to Adriano et al. (1980) heavy metals or oxyanions are mostly found adsorbed on to surfaces of oxides (discussed above) which are represented by the smallest of fly ash particles (largest surface area). The chemical behavior and release of heavy metals and oxyanions to water is highly interrelated to the surface electric properties of oxides described above.

The third group includes highly water reactive components. Generally, this group include oxides of Ca (215,000 ppm), Mg ($\sim$16,000 ppm), K ($\sim$23,000 ppm), Na ($\sim$2,000 ppm), Ba($\sim$1000 ppm) as well as gypsum ($CaSO_4 \cdot 2H_2O$), a nearly a neutral salt, and sulfite (S03). Some fly ashes from bituminous coal are acidic and have no liming value (Figure 1). Most fly ashes from lignites, however, have a considerable liming value because of their content of alkali oxides and significant quantities of anhydrous Ca- or Mg-sulfates (Roy and Griffm, 1982). Fly ashes from bituminous coal are low in Ca and Mg; hence the fly ashes retain little sulfate.

A great deal of research has been carried out on the chemical make-up of fly ash, and water soluble salts, heavy metals, and oxyanions (Adriano et al., 1980 and references therein; Terman, 1978; Phung et al., 1979; Roy and Griffin, 1982; Elseewi et al., 1978). Additionally, a great deal of research has been carried out on using fly ash as a soil amendment to improve soil physical properties and/or soil pH Furthermore, research has been carried out on the availability of heavy metals and oxyanions of fly ash to agricultural plants (Elseewi et al., 1978; Adriano et al., 1982). Although information is available on using fly ash as soil amendment, not all available fly ash can be used for this purpose. In other words, fly ash demand for agricultural uses is far lower than the available supply. For this reason, a big portion of the fly ash produced is disposed in landfills or is put into various beneficial uses. The physical-chemical properties of fly ash with respect to pollutant reactions must be known before disposal or any other uses. Roy and Griffin (1982) proposed a fly ash classification scheme based on the physical and chemical properties. The classification scheme and the basis of this classification is given in Tables 6 and 7. The idea of classifying fly ash has great merit but further research work is needed to link classification with potential uses.

Surface Properties

Fly ash consists usually of spheres composed of crystalline matter and some residual carbon. Figure 2 shows an overview of a Kentucky fly ash at a 100X magnification. The basic spherical shape indicate that particles were formed under uncrowded freefall conditions and a relatively sudden cooling maintained the spherical shape. In Figure 3 a larger ash-sphere appears broken and filled with numerous smaller spheres. Detailed analysis of a broken sphere in Figure 4 revealed gypsum crystals growing on its inner surface.

Acid-base Properties

Titrations in a nitrogen gas atmosphere (Figure 5) show ashes to be unbuffered around pH 7. Because of this. pH is expected to be controlled by the partial pressure of CO_2. Indeed, when CO2 was bubbled into the water-fly ash suspension pH fell almost immediately below 6 (Figure 6). Because CO2 is the predominant reactive gas in natural soil-water systems, this pH drop has some implications on metal release from ash. The potentiometric titrations shown in Figure 5 reveal an approximate pK_a in the vicinity of 10, which is indicative of CO_3^{2-} protonation. Note however, no equal-length titration plateau was obtained in the pH range of 6.2. The latter is indicative of HCO_3^- protonation. This suggested that the plateau at pH 10 was not due to CO_3^{2-} but most likely due to silicates. On the other hand, when CO2 was introduced (Figure 6), the fly-ash titrated at around pH 5. Again, this was not indicative of HCO_3^- protonation. Bicarbonate (HCO_3^-) titration behavior was demonstrated by the titration of NaOH plus

CO2 shown to titrate, as expected, around pH 6. The data in Figure 7 suggested that the surface was most likely composed of -Al-OH functional species.

Figure 8 demonstrates the "zero salt effect" on fly ash potentiometric titrations. It is represented by the cross-over point of the titrations revealing a PZC_{pH} of approximately 4.6 which is approximately halfway between the PZC_{pH} of FeOOH and the PZC_{pH} of SiO_2. In this pH region, the surface adsorbs both metal cations and oxyanions. Below the ZPC_{pH} oxides exhibit a net positive charge and prefer to adsorb oxyanions; above the ZPC_{pH} oxides exhibit a net negative charge and prefer to adsorb metal cations (Anderson and Malotky, 1979). In our own laboratory (Harsin and Evangelou, 1989) we have shown that a synthetic iron-oxide exhibits a ZPC_{pH} in the range of 6.5 to 7 while the ZPC_{pH} of Al_2O_3 is known to be around 9 and the ZPC_{pH} of SiO2 is known to be around pH 2 (Stumm and Morgan, 1970). Moreover, when minerals are made of chemical mixtures ZPC_{pH} changes. For example, if instead of Fe203 we have a chemical mixture of Fe203 and Si02 the ZPC_{pH} of this oxide will need to be determined experimentally (Stumm and Morgan, 1970). This means that the pH at which these mixed-surfaces act as metal cation adsorbers or oxyanion absorbers is not known. Figure 9 demonstrates protonation and dissociation intrinsic constants for one of the fly ash samples. They are in the range of intrinsic constants of As/Fe/Si-oxides reported in the literature.

Long-term Water Equilibration

Long-term water equilibrations were conducted in our laboratory using 50:950 fly ash:water suspensions by weight in 1000 ml plastic Erlenmeyer flasks under various pCO_2 levels. Accompanied by vigorous stirring, half of the fly ash suspensions were bubbled for one hour per day with pure nitrogen gas (simulating zero pCO_2), and the other half of the fly ash suspensions were bubbled with pure carbon dioxide @CO2 = 1). Conductivity and pH of the suspensions were measured after each bubbling, and six samples were collected at intervals throughout the duration of the experiment. After a 45-day equilibration, all fly-ash suspensions were equilibrated with atmospheric air @CO2 = 0.0003) and sampled. Chemical composition of two fly ash samples are given in Table 8. With regard to boron, of the two ashes in question, the ash which was originally high in pH released more boron (Figure 10) as the pH went down in response to pCO_2. The low pH ash did not respond to P_{CO_2} with respect to change in pH and boron release (Figure 11). With regard to nickel, neither the originally high nor low pH fly ash released nickel differently with respect to partial pressure of CO2 (Figures 12 and 13). Although the long-term equilibration experiment lasted for 62 days, the first sampling was only one hour after the start of the experiment, most of the release was complete by then. The breakthrough data in Figure 14 show the relatively rapid release of boron when fly ash is leached.

When fresh fly ash is exposed to the open environment (H20 and CO2 gas) two chemical pathways can be hypothesized with respect to the fate of heavy metals or oxyanions. If CO2 gas is introduced to a fly ash slurry most metals will precipitate as metal carbonates and the oxyanions are expected to be adsorbed by the oxide surfaces, depending on ZPC_{pH}. Therefore, release of heavy metals to water is expected to be dependent greatly on the partial pressure of CO2 (pCO_2). In the absence of excess pCO_2, a smaller fraction of the metals is expected to precipitate as carbonates and a larger fraction of heavy metals and oxyanions is expected to interact with each other and the surfaces of the oxides. If the oxide surfaces are physically blocked by the various precipitates, or the total quantity of the oxides available for metal cation and/or oxyanion surface adsorption is low, then both metal cations and oxyanions will be released to the water and may remain soluble or coprecipitate depending on types of minerals that can be formed, e.g. $Ba(AsO_4)_2$ a very insoluble mineral (Ksp = 8.0 x 10^{-51}). Some bituminous coal fly ashes do not contain metal oxides such as CaO and are quite acidic. In such fly ashes, oxide-surface ZPC_{pH} and surface charge behavior with respect to pH would be a major controlling factor in metal and/or oxyanion release.

Metal Adsoption Isotherms

The data in Figures 15 and 16 show the potential of the 'alkaline fly ash' and 'acid fly ash', respectively, to adsorb nickel. These two figures clearly show that the adsorption of nickel by fly ash is strongly pH depended as one would expect due to variable charge surfaces of the fly ash metal oxides. It is also quite clear from these data that the acid fly ash exhibits a greater potential for nickel adsorption at the two highest pH values tested. The data show that in the case of the 'alkaline fly ash' adsorption maxima at around pH 7 is only obtained for the 2 ppm nickel level (Figure 15). On the other hand, in the case of 'acid fly ash' nickel adsorption maxima was attained nearly by all solution nickel concentrations tested (Figure 16). These data clearly demonstrate that the acid fly ash exhibits greater potential than the alkaline ash to adsorb heavy metals at the higher pH values.

Environmental Effects

Because fly ash contains toxic elements, disposal sites should be monitored for excessive buildup of heavy metals, salts and alkalinity. Potential heavy metal problems with power plant wastes are greatly reduced by the pronounced liming effects of the wastes.

A problem that some consider an environmental issue is the movement of heavy metals from fly ash in ponds or landfills to drainage waters. Levels of heavy metals or metalloids, e.g., selenium, chromium, boron, and in some instances, mercury and barium, exceeded EPA's public water supply guidelines. Passage of the leachates through soil columns removed most of the dissolved elements. Thus, passage of pond effluents through soil was found to provide significant protection against ground water contamination (Terman, 1978 and references therein). An important consideration is that soils that receive fly ash or ash disposal sites should always have the pH maintained at above 6 in order to keep most heavy metals immobile.

Agricultural Uses

Fly ash contains numerous elements found in coal and when fresh it is toxic as a plant substrate due to boron (B) and high alkalinity. About 20% of the fly ash produced in the U.S. is used in the construction industry as fill material or in concrete products; to minimize costs, most must be disposed of at nearby sites, largely in impoundments or in old mines.

Numerous studies have been carried out which demonstrate that fly ash could be used as source of K, P, Ca, Mg, S and many of the micronutrients (Adriano et al., 1980). Other agricultural uses of fly ash include liming, improving soil moisture holding capacity and the reclamation of surface mined lands. However, it has been demonstrated that some crops growing under fly ash-amended soil conditions may bioaccumulate heavy metals at concentrations greater than normal ranges. This is highly dependent on the type of fly ash used.

Some fly ashes may also introduce toxicity to plants due to the high boron content and high alkalinity. For this reason, when fly ash is to be used for any agricultural purposes is should be first allowed to age to some degree. Aging has two potential effects. One effect is carbonation which converts aikaline oxides to carbonates and the second effect is leaching, thus removing portion of the alkalinity as well as boron, selenate and some of the heavy metals (Adriano et al., 1980).

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Table 1. Variations in coal ash composition (Terman, 1980)

Rank	Composition, %									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	Ash
Crandall (1972)										
Anthracite	48–68	25–44	2–10	1.0–2	0.2–4	0.2–1	—	—	0.1–1	4–19
Bituminous	7–68	4–39	2–44	0.5–4	1.0–36	0.1–4	0.2–3	0.2–4	0.1–32	3–32
Subbituminous	17–58	4–35	3–19	0.6–2	2.0–52	0.5–8	—	—	3.0–16	3–16
Lignite	6–40	4–26	1–34	0.0–0.8	12.0–52	2.8–14	0–28	0.1–1.3	8.3–32	4–19
Meikle (1975)							$Na_2O + K_2O$			
Bituminous	30–55	10–35	10–40	1.0–3	0.0–15	0.0–5	1.0–5		0.0–3	—
Lignite	20–41	10–18	7–16	1.0–3	20.0–40	2.0–11	0.5–0		0.5–0	—
Endell (1958)										
Lignite (Fortuna)	4–40	2–4	14–16	—	49.0–55	9.0–15	—	—	8.0–12	—

Table 2. Partial chemical and physical composition of limestone scrubber sludge (Terman, 1978 ans references therein)

Element	Elemental composition, % of dry solids		
	A	B	C
SiO_2	31.6	4.9	0.58
Al_2O_3	18.3	3.4	1.21
Fe_2O_3	4.3	0.6	0.39
CaO	18.1	43.2	43.4
MgO	2.4	0.2	0.01
Total S	7.2	18.9	20.0
Component	**D**	**E**	**F**
$CaSO_4 \cdot 2H_2O$	22.0	15.0	6.0
$CaSO_3 \cdot 0.5H_2O$	18.0	21.0	49.0
$CaCO_3$	39.0	20.0	3.0
$MgSO_4 \cdot 6H_2O$	5.0	4.0	2.0
Fly ash	20.0	41.0	40.0

A – Eastern Power Plant–19% ash; 1.9% sulfur; sample taken upstream of fly ash collection device.
B – Same as "A" except sludge from scrubber located downstsream of fly ash collector.
C – Western Power Plant–Scrubber located downstream of ash collector.
D – TVA Shawnee Stream Plant, 2/1/73
E – Same, 7/12/73
F – Same, 3/19/94

Source: Ray and Parker, 1977

Table 3. Composition of 12 fluidized bed waste samples[a] (Terman, 1978 and references therein)

Macro elements			Micro Elements		
Element	Avg. %	Range, %	Element	Avg. ppm	Range ppm
Ca	27.2	21.0–34.0	B	136	110–240
S	9.1	7.0–13.0	Cu	62	57–75
Mg	0.96	0.8–1.2	Mn	190	178–196
Al	1.8	1.5–2.5	Zn	147	123–222
Fe	2.8	2.0–5.0	Ni	53	43–67
Na	0.17	0.14–0.19	Sr	164	132–193
K	0.38	0.24–0.52	Cd	–7	6–9
P	0.03	0.02–0.04	Cr	75	35–115
			Pb	74	63–85

[a] Analyses made by USDA, Morgantown, West Virginia

Table 4. Partial elemental composition of various fly ash sources[a] (Terman, 1978 and references therein)

Power plant	Location	Elemental composition							Neutralizing value,
		K	Ca	Mg	P	B	Zn	Mo	meq. H_3O^+/g
		%			ppm				
Big Sandy	Louisa, KY	3.10	0.72	0.53	0.04	319	51	7.4	0.12
Clinch River	Cleveland, VA	2.69	2.52	0.74	0.08	342	55	9.2	1.23
Glen Lynn	Glen Lynn, VA	2.41	0.58	0.23	0.05	307	36	6.8	0.09
Kanawha River	Glasgow, WV	3.19	0.67	0.27	0.03	391	46	5.6	0.09
Muskingum River (1)	Beverly, OH	2.33	0.45	0.84	0.06	301	115	11.8	Acidic
Muskingum River (2)	Beverly, OH	1.97	0.82	0.49	—	340	—	9.3	—
Phillip Sporn	New Haven, WV	2.51	0.65	0.09	0.05	340	88	11.1	0.05
Mount Storm	Mount Storm, WV	2.29	0.90	0.11	0.07	278	378	16.9	Acidic
Albright	Albright, WV	2.50	0.31	0.22	0.04	264	30	6.2	0.04
Rivesville	Fairmont, WV	2.45	0.65	0.26	0.07	236	13	7.8	Acidic
Fort Martin	Maidsville, WV	2.25	2.44	0.82	0.17	415	88	15.5	0.58
Crawford Edison	Chicago, IL	2.42	3.27	0.80	0.10	613	363	39.3	1.33
John Sevier	Rogersville, TN	3.14	0.61	0.46	0.05	323	74	9.4	0.01
E.C. Gaston (1)	Wilsonville, AL	2.70	0.71	0.82	0.15	428	186	24.4	0.25
E.C. Gaston (2)	Wilsonville, AL	2.65	0.97	0.30	—	367	—	24.8	—
Hoot Lake	Fergus Falls, MN	0.65	12.30	5.99	0.21	618	86	5.7	3.05
Lewis and Clark	Sidney, MT	1.07	12.56	6.02	0.28	414	132	7.5	3.73
Kansas Power and Light	Lawrence, Ks	—	—	—	0.06	48	353	—	1.87

[a] Martens *et al.* (1970), Martens (1971), Mulford and Martens (1971), and Doran and Martens (1972).

Table 5. Ranges and average chemical composition of fly ash[†] (Roy and Griffin, 1982)

Constituent	Range	No. of data	Avg.
	%		%
SiO_2	2.19–68.1	58	44
TiO_2	0.5–2.55	39	1.3
Al_2O_3	3.39–39.4	60	23
Fe_2O_3	3.60–29.2	58	11
CaO	0.2–31.0	58	8.2
MgO	0.4–12.8	58	2.7
Na_2O	0.2–8.0	50	1.8
K_2O	0.2–8.1	49	2.0
C	0.1–25.7	21	5.0
SO_2	0.1–7.28	48	1.6

† Data from the literature and unpublished data from Illinois State logical survey files.

Table 6. Fly ash groups (Roy and Griffin, 1982)

Group	Sialic component ($\Sigma SiO_2 + Al_2O_3 + TiO_2$)	Calcic component ($\Sigma CaO + MgO + Na_2O + K_2O$)	Ferric component ($\Sigma Fe_2O_3 + SO_2$)
	%		
1. Sialic (essentially Si + Al	>88	0–12	0–12
2. Fersic (Fe + sic from sialic)	48–77	0–29	23–52
3. Calsialic (Ca + sialic	48–<71	>29–52	0–23
4. Modic (from modal concept)	>48–88	0–29	0–<23
5. Ferric (Fe)	<48	0–29	>23
6. Calcic (Ca)	<48	>29	0–23
7. Fercalsic (Fe + Ca)	<48	>29–77	23–71

Table 7. Summary of nomenclature and examples (Roy and Griffin, 1982)

Group	pH character (prefix to group name)	Special compositional properties and texture (examples)
Sialic	acid	Acid C–Sialic silt
	neutral	Neutral Ba, C–Sialic
	alkaline	Alkaline B, Ba, C–Sialic
Modic	acid	Acid Ba, ZnModic loam
	neutral	Neutral B, Zn–Modic
	alkaline	Alkaline C–Modic
Fersic	acid	Acid B–Fersic silt loam
	neutral	
	alkaline	
Calsialic	acid	
	neutral	
	alkaline	Alkaline Zn–Calsialic
Ferric	acid	Acid Cd–Ferric silt loam
	neutral	
	alkaline	
Calcic	acid	Acid Ba, Cu, Zn–Calcic silt
	neutral	
	alkaline	
Fercalsic	acid	
	neutral	Neutral C, Ba, Cu–Fercalsic
	alkaline	

Table 8. Chemical analysis of aqueous samples taken during the long-term equilibration, and some elemental analyses of decomposed solid

	Aqeous analysis for long-term equilibration samples								Elemental Analysis of solid	
	Ash 3				Ash 6				Ash 3	Ash 6
	N_2	CO_2	Atm	Av	N_2	CO_2	Atm	Av		
pH	3.6	3.8	3.9	3.8	11.4	6.0	7.1	8.2		
Conductivity (mmhos cm^{-1})	1.6	1.6	1.6	1.6	3.4	1.9	7.8	2.0		
	ppm				ppm					
Aluminum	*	*	-	*	*	*	-	*	12 %	6 %
Arsenic	-	-	-	-	-	-	-	-	39 ppm	67 ppm
Boron	2.0	2.2	2.0	2.1	2.3	12.8	8.0	7.7	34 ppm	227 ppm
Cadmium	*	*	-	*	*	*	-	*	7 ppm	10 ppm
Calcium	68	75	-	72	16	133	-	75		
Chloride	2.3	1.8	-	2.0	2.0	1.5	-	1.8		
Iron	-	-	-	-	-	-	-	-	15.8 %	16.3 %
Lead	*	*	-	*	*	*	-	*		
Nickel	0.8	0.8	0.8	0.8	0	0	0	0	242 ppm	123 ppm
Potassium	176	178	-	177	24	24	-	24		
Silicon	12.7	13.6	22.2	16.2	1.2	13.	7.9	7.4		
Sodium	18	16	-	17	6	6	6	6		
Sulfate	129	130	157	139	19	14	93	85		

- Not analyzed
* Values below detection limits

Figure 1. Initial pH values of various Kentucky fly ashes.

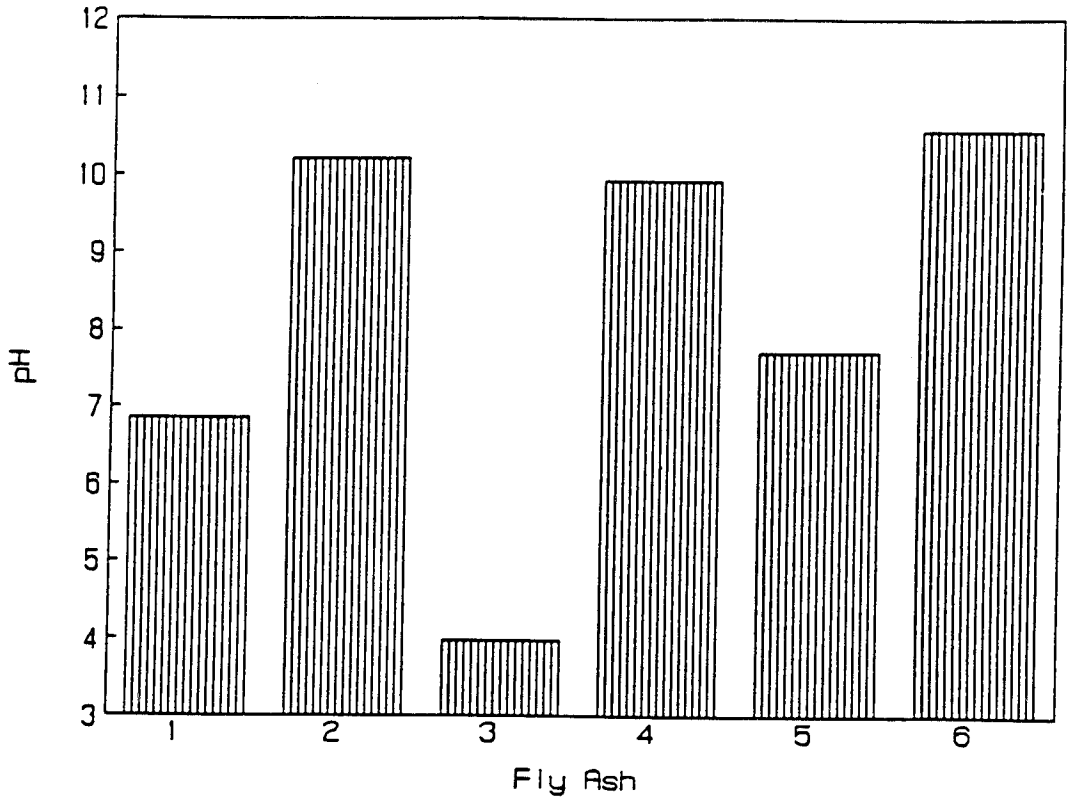


Figure 2. Scanning Electron Microsope photo of Kentucky fly ash.

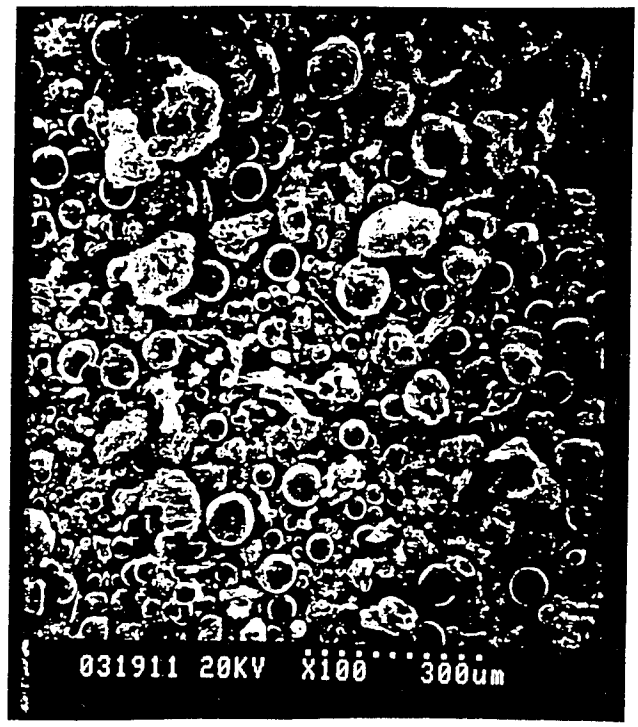


Figure 3. Scanning electron microscope photo of a Kentucky fly ash sphere containing numerous smaller ash spheres

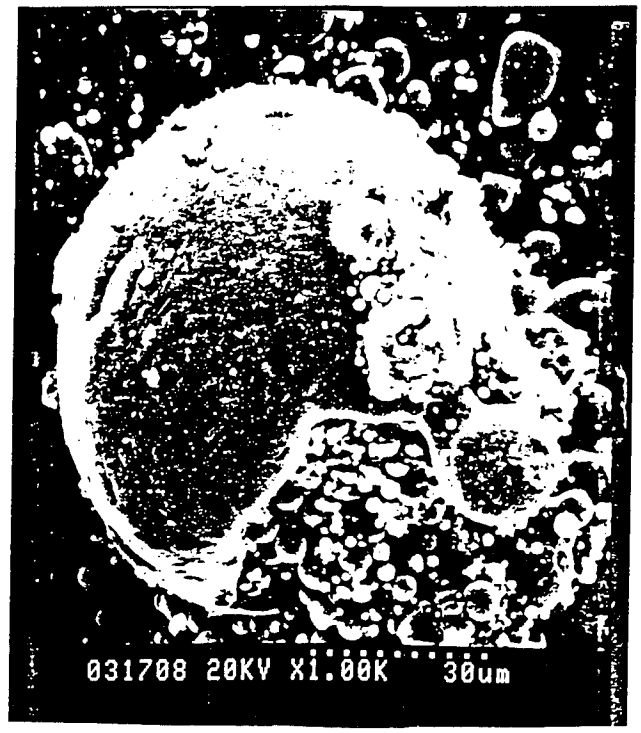


Figure 4. Scanning electron microscope photo of a broken Kentucky fly ash sphere.

Figure 5. Titrations of two Kentucky fly ashes

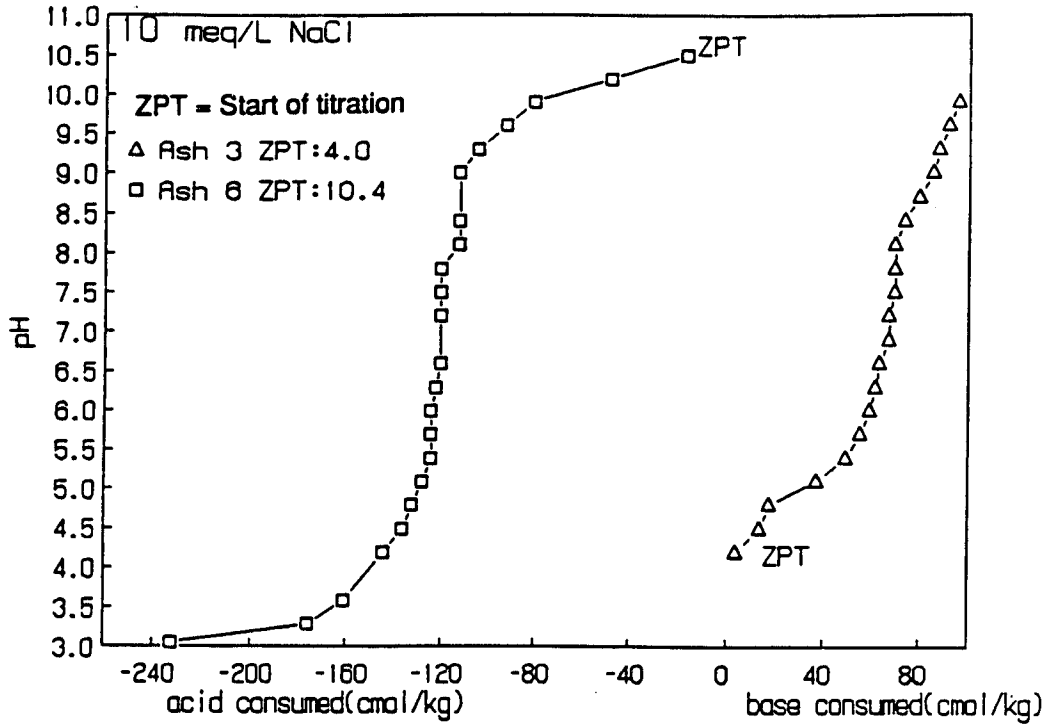


Figure 6. Potentiometric titrations of fly ash and NaOH with and without CO_2

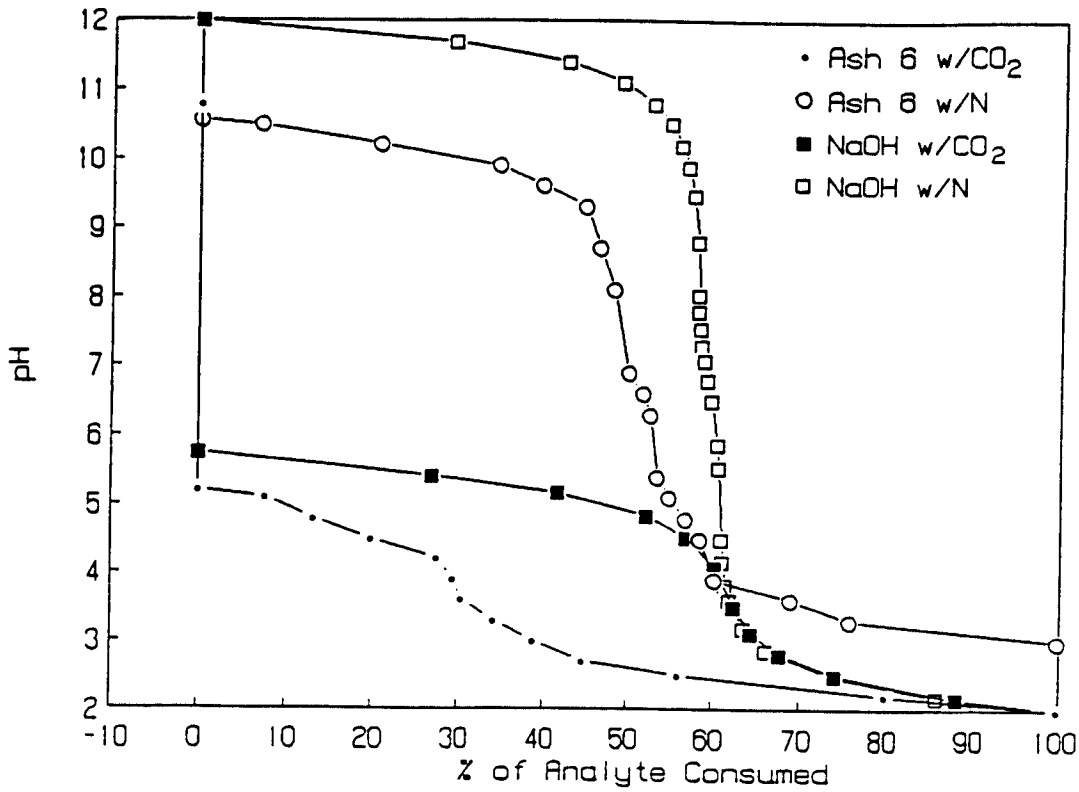


Figure 7. Potentiometric titrations of fly ash and $AL(OH)_3$

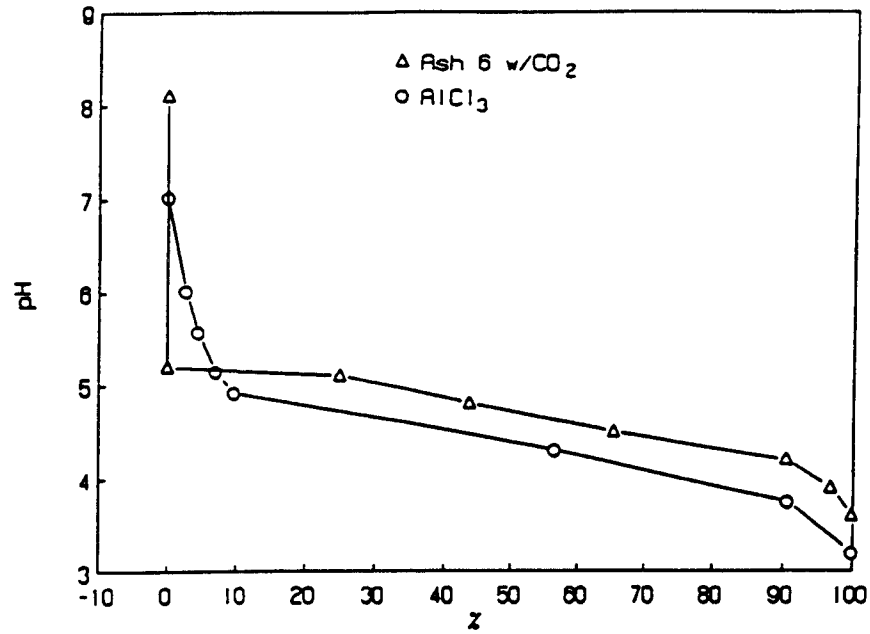


Figure 8. Potentiometric titration of fly ash demonstrating the "salt effect"

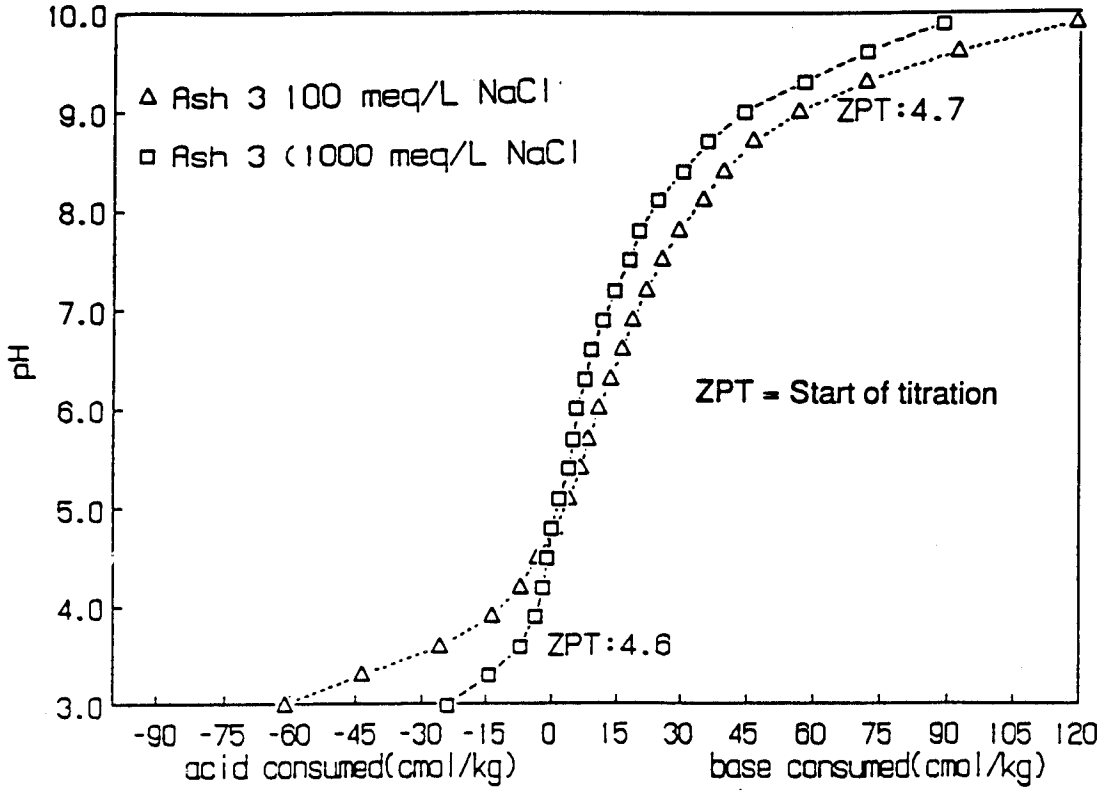


Figure 9. Protonation/deprotonation constants (K_{st}) of fly ash as determined by potentiometric titrations

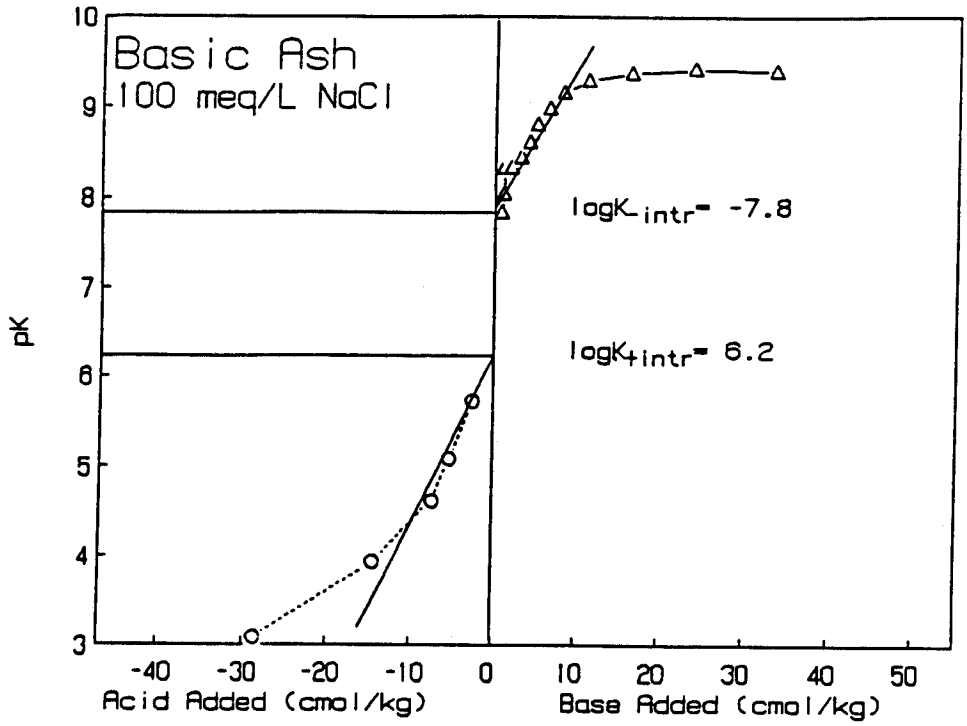


Figure 10. Boron release as a function of pH and partial pressure of CO_2 for an initially high pH fly ash (Data for CO_2=0%, and CO_2=100% are averages of six data points each. Value for CO_2=0.03% is from a single sampling.)

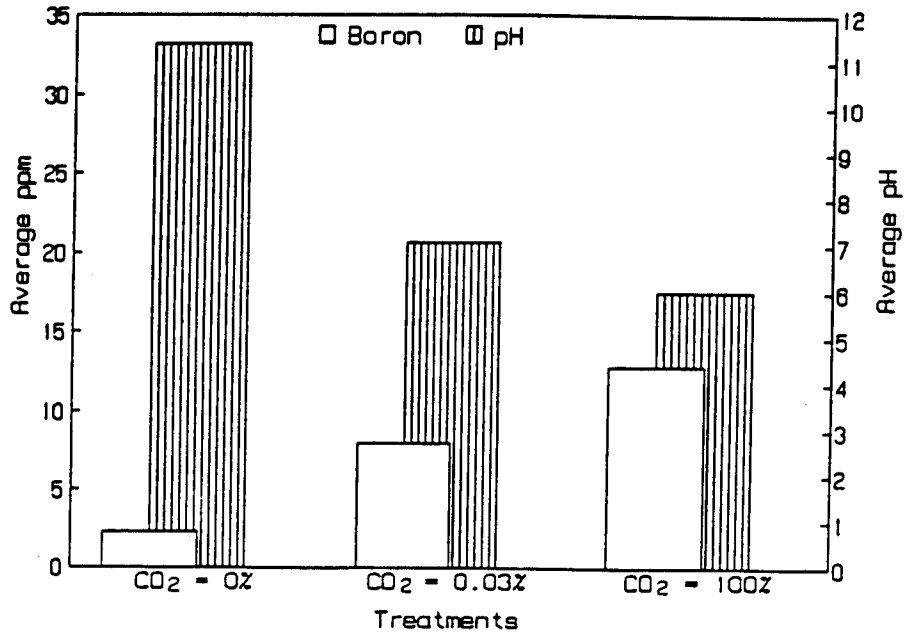


Figure 11. Boron release as a function of pH and partial pressure of CO_2 for an initially low pH fly ash (Data for CO_2=0%, and CO_2=100% are averages of six data points each. Value for CO_2=0.03% is from a single sampling.)

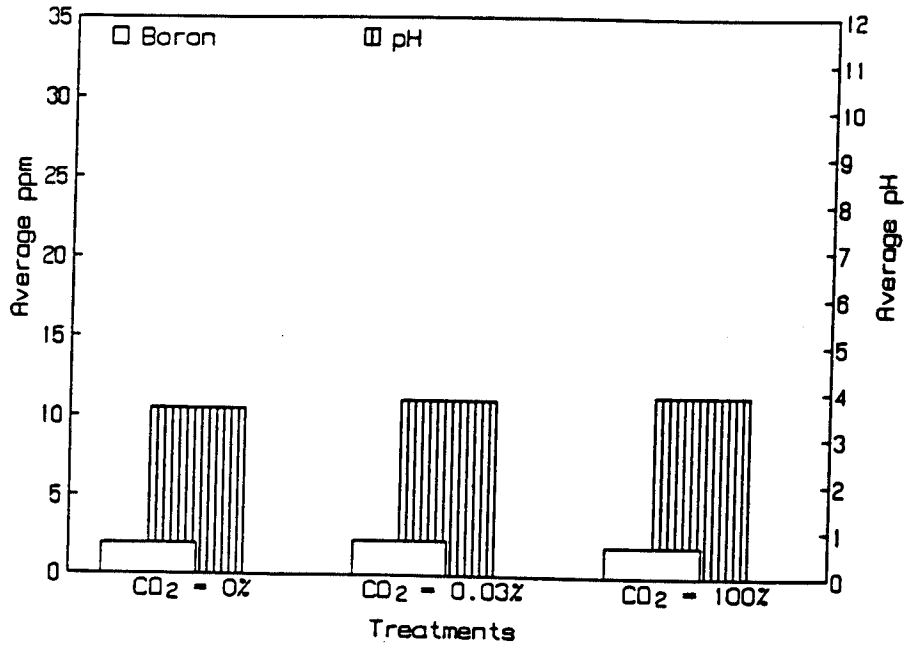


Figure 12. Nickle release as a funciton of pH and partial pressure of CO_2 for an initially low pH fly ash (Data for CO_2=0%, and CO_2=100% are averages of six data points each. Value for CO_2=0.03% is from a single sampling.)

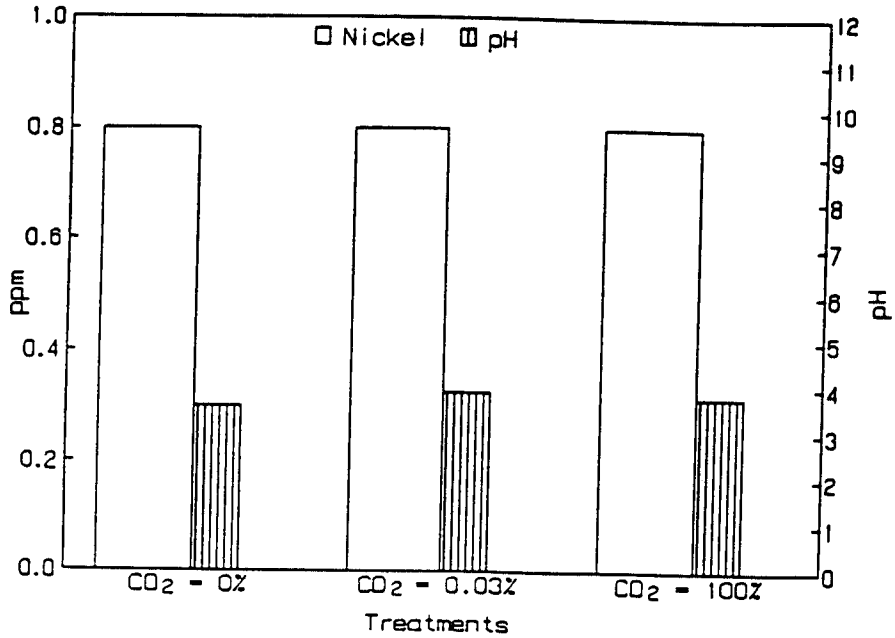


Figure 13. Nickle release as a funciton of pH and partial pressure of CO_2 for an initially high pH fly ash (Data for CO_2=0%, and CO_2=100% are averages of six data points each. Value for CO_2=0.03% is from a single sampling.)

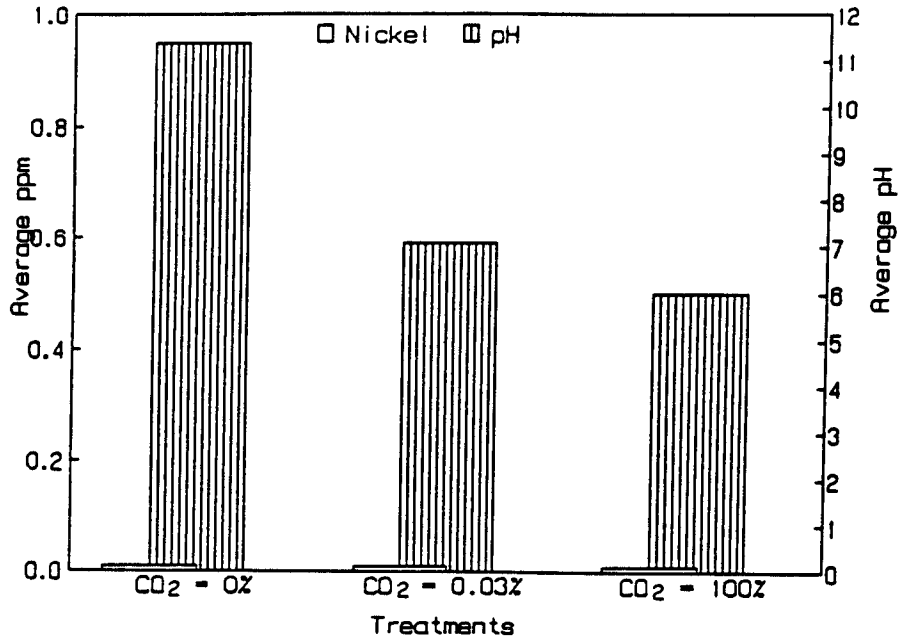


Figure 14. Breakthrough column data for boron in the presence of air with atmospheric composition

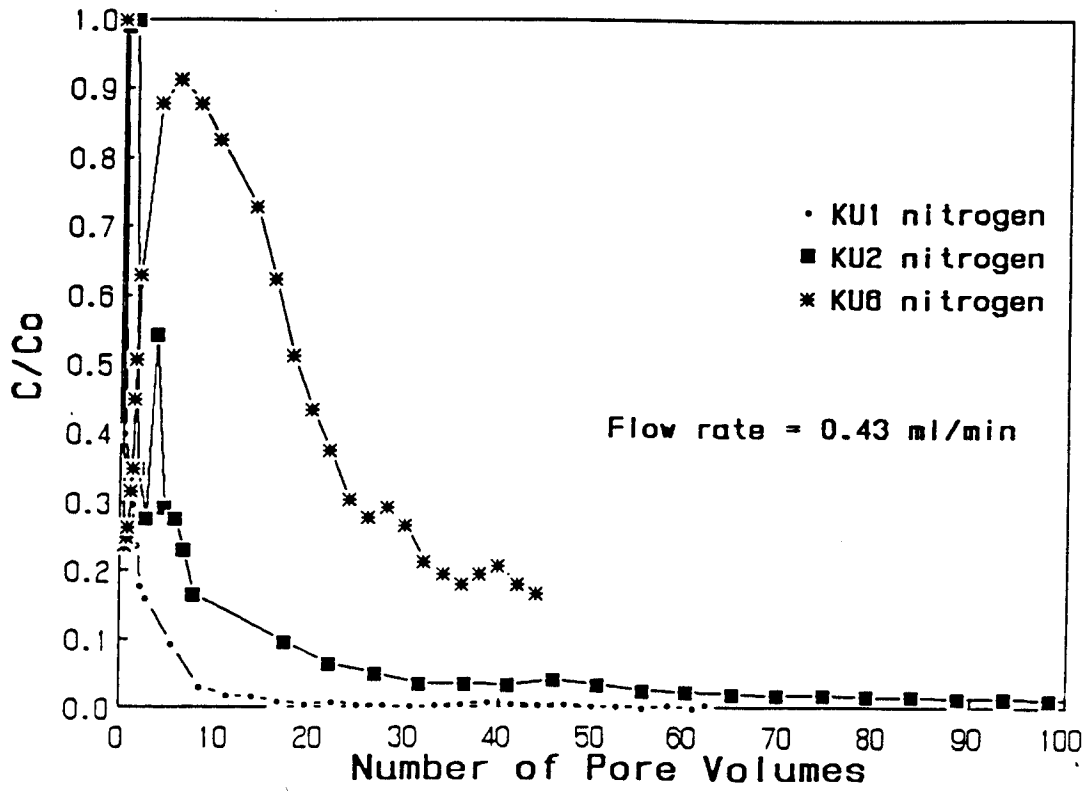


Figure 15. Relationship between precent adsorbed nickle relative to maximum adsorbed by the "alkaline fly ash" and suspension pH (Maximum adsorbed nickle was that obtained at the highest pH tested and at the highest total nickle solution concentration) (Dark squares suggest that the nickle is weakly adsorbed)

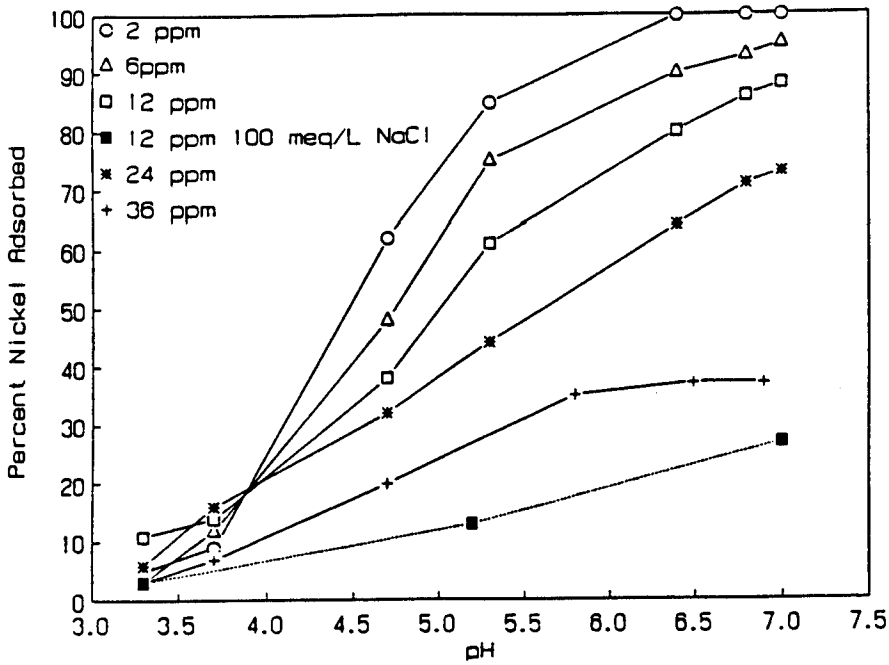
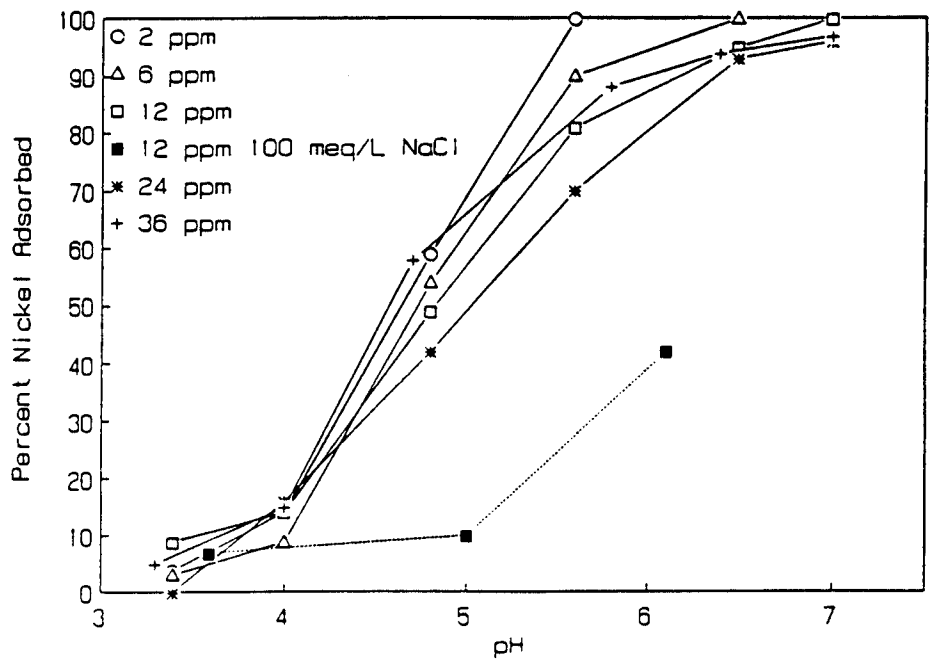


Figure 16. Relationship between precent adsorbed nickle relative to maximum adsorbed by the "acid fly ash" and suspension pH (Maximum adsorbed nickle was that obtained at the highest pH tested and at the highest total nickle solution concentration) (Dark squares suggest that the nickle is weakly adsorbed)



USE OF COAL COMBUSTION BY-PRODUCTS FOR RECLAMATION: ENVIRONMENTAL IMPLICATIONS

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Abstract

Coal combustion byproducts are made of incombustible materials contained in the coal or added to the boiler or stack gas streams. They are available in large quantities and in many cases are now hauled back to mine sites to be land-filled at their source. These materials have significant potential as bulk reagents, fills, and chemicals in mine reclamation. Many of the materials are alkaline and can be used for water neutralization, pH balance adjustments to Gob, and aIkaline recharges. Some materials are cementitious and can be used to strengthen soils and Gobs at mine sites or to produce impermeable caps. Still other materials are valuable fertilizers.

Combustion residues have been looked upon as dangerous waste products prone to degrade the ground and surface waters, cast dangerous dust clouds into the air, or create sterile organic free piles for anemic plant growth. Large field scale pilot projects that have followed laboratory tests suggest that most of these fears are unwarranted. A 50,000 ton scrubber sludge backfi11 in a final strip cut was instrumented with monitoring wells and cleans heavy metals from the groundwater. One hundred and fifty tons of FBC fly ash were used to neutralize an acid lake and heavy and toxic metals concentrations all dropped, even where the ash was expected to leach toxic metals that would not precipitate with changing pH. A 1,000 ton test bed of FBC fly ash and Gob was instrumented with a 15 by 20 foot lysimeter catchment basin beneath to determine if the leachate carried heavy metals or other toxics The bed is so impermeable that in 2 years it is not possible to get a 10 ml water sample for analysis. A 7 acre cap made of FBC ash and spoil has yielded no leachate to sample. Run-off from the cap area has slight elevation in potassium and sodium concentrations but no indication of heavy or toxic metals. There are no adverse impacts detectable in the adjacent stream. Engineered mixes of coal combustion residues and mine wastes seem to bind even mobile elements like boron. Open frame-less dump trailers filled with dry FBC fly ash have been unloaded in the field with practically no dust emissions. Much of the dust in handling can be avoided with attention to minor details in construction sequences. Experiments are under way to design mobile field systems that will render FBC fly ash non-dusty while retaining its dry fine granular characteristics. A power plant in Illinois produces a force oxidized synthetic gypsum from scrubbing operations that is more pure than the natural product and enhances plant growth. The low cost, high volumes. and excellent properties of combustion residues make suitable for beneficial use in the mines they are hauled back to.

Introduction

Reclamation of coal mines involves large amounts of material and requires significant input of bulk reagents or fills. The U.S. produces around 1 billion tons of coal annually, most of it by surface methods with stripping ratios in the range of two yards to over twenty cubic yards of overburden per ton of coal produced. In some locations the broken overburden rock can become susceptible to accelerated weathering which releases acidity or salt over a shorter space of time than would have occurred naturally. Since incombustible soils and rocks settled in ancient swamps along with plant material, the resulting coal today contains impurities. These impurities range between about 6 and 35 percent of the total coal

tonnage removed from a mine in the U.S. The impurities can be removed by coal preparation plants, but with waste product tonnages averaging around 20% of the raw tonnage. Frequently these coal washing products are at least partially acid producing.

The alternative to coal washing is to transport worthless impurities with the coal to power plants to become an unwanted byproduct at that location. Ultimately, rock not removed from the coal will be fired in the boiler and either carried up the stack as tiny fly ash particles to electrostatic precipitators for collection, or fused into slags or larger particles that must be mechanically removed from the bottom of the boiler as boiler slag or bottom ash. Acid forming pyrite in coal, if not removed by coal preparation, will report to the boiler and form sulfur dioxide gas (S02) for which strict emission limits now exist. Wet scrubbers use lime or limestone slurries as sorbants to remove the SO2 from the stack gasses. Fluidized Bed Combustors (FBC) inject limestone into the boiler with the coal to capture the SO2 as it forms. Of coarse injecting incombustible rock into the boiler usually doubles the volume of fly ash and bottom ash (called spent bed for FBC units) that must be dealt with, just as wet scrubbers form a similar amount of excess byproduct called "scrubber sludge".

By-products of coal mining, preparation, and combustion find a variety of potential uses, but unsuitable specifications and vast tonnages still leave hundreds of millions of tons of altered natural materials each year to become waste products. High carbon F type fly ashes and byproducts of SO2 control are especially likely to be wasted, since they have not found a place in regular concrete and shingles like other coal combustion ashes. To consume finite and expensive landfill space as a depository for rocks is becoming increasingly difficult to justify. Some states now allow combustion byproducts to be returned to the mine site, rationalizing that this new source of landfll space is in fact where the rock came from in the first place. But should combustion byproduct be land-filled at all?

Mine Site Uses of Combustion By-Products

Each independent handling operation is an additional cost to the use of coal. Returning combustion byproducts to mine sites for disposal still leaves the cost of landfill handling as a hidden cost to the consumer. If onsite handling of combustion byproducts returned to the mine site could be combined with other operations, cost savings may be achieved. Concurrent reclamation is a requirement of modem coal mining and a special tax on all coal mined now funds reclamation of long abandoned mined lands. Coal combustion byproducts have properties that make them suitable bulk materials and chemicals for land reclamation.

The most useful properties of coal combustion byproducts are alkalinity, cementitiousness and pozzolanic activity. Of course there are mine reclamation applications where a simple fill is required. In the case of the old Forsythe Energy #5 mine, near Marion Illinois, an unstable final cut strip-pit was located within 50 feet of a major road and airport. The unstable highwall was slumping and threatened to engulf the road and several accidents had involved motorists loosing control and plunging as much as 40 feet into the lake at the bottom of the pit. There were concerns too about accidents that could occur with planes making emergency landings at the nearby airfield. Available soil to fill the pit was scarce and would have to be trucked significant distances around the mine site. A local power plant had large quantities of wet sulfite rich limestone scrubber sludge and an agreement was reached for the utility to truck the material to the site and place it by the edge of the pit for use as a fill. The utility saved money on land-filling costs while the States reclamation division saved money on the handling of the fill materials.

Cementitious properties of FBC ash were used in another project to steepen the embankments used around slurry impoundments at mines. Coarse gob was amended with about 25% FBC fly ash to yield a mixture with several hundred psi of strength that could stand steeper and higher than ordinary berms. The ash was disked into the Gob in the field. Limited disk penetration indicated that lifts should be built only 1 foot at a time, which many mine operators would find unacceptable. Mixing the ash with the GOB before haulage or use of more penetrating "gator" tillers are alternatives.

GOB materials amended with FBC ash are as impermeable as a clay liner with hydraulic conductivities in the 10^-7 to 10^-9 cm/sec range. One test bed built at the Burning Star #l mine in 1994 was equipped with a 15 by 20 plastic lined sand-tilled catchment basin beneath it. A monitoring well was drilled through the bed and set in the sand. In two years the giant lysimeter-like structure has yet to capture enough water to allow a sample to be taken from a 2 inch diameter well.

A larger application of FBC ash amended regular mine soil, spoil material, and GOB at the Thunderbird mine site with about 35% FBC to create a cap over a 7 acre area. Acid producing Gobs were buried in a final cut strip pit and then covered with a one foot cap and two feet of soil cover. The cap was placed in two lifts with 10,000 tons of FBC ash disked into three types of loose mine material with the mix compacted by conventional roller. Lysimeters placed under the cap have failed to detect water percolating through the cap and monuments anchored into the cap have not detected heaving or swell that could threaten the liner integrity. The cost of the cap was about l/2 the cost of a cap using clay imported to the site. Ash handling operations for placement, spreading, disking, and rolling came to $5/ton of ash.

The cementitious properties of FBC ash involve entringite formation as opposed to alkali reaction complexes with alumino-silicate glass pozzolans like conventional concrete. If more conventional cement reactions are desired, conventional F type fly ashes from PCC boilers can be used with the lime in FBC fly ashes used as an activator. In a cooperative demonstration with the U.S. Department of Energy, PCC fly ash provides the pozzolon for a low grade cement made of scrubber gypsum (a setting retardent) and lime from a venturi scrubber on an industrial boiler. The material is pumped as a paste, bleed-water free backfill to stabilize underground mine openings against subsidence. Where soft floor conditions drive subsidence in places like Illinois it is not necessary to fill the opening to control the subsidence. The ability to custom design a cement has many uses in mine reclamation or even operation. In another project, high carbon (6% plus LOI) F type fly ash is activated with FBC fly ash to make fiber reinforced crib members with lower cost, similar weight, and greater strength than wood. Like wood, the members can be sawed and nailed. Blocks for sealing mine workings have been similarly prepared. Obviously preparation plant wastes can be amended with a wide range of combustion residue cements and used to construct semi-permanent enhanced earth structures around the mine. Caution should be exercised in use of FBC ash for preparation of surface road pavements as some highway tests have suffered from material degradation and delayed swelling. A test by SIU-C researchers suggests that appropriately formulated rolled concrete does not have this limitation. Any application of combustion residues as a structural cement should be approached with careful attention to formulation as most mixes in a random array of tests produced useless materials and potentially unpleasant behavioral surprises.

The alkalinity in combustion residues from SO2 control is useful as a bulk chemical. A two million gallon pond of highly acidic water was neutralized before discharge using FBC fly ash with a calcium carbonate equivalent (CCE) value of 71%. FBC spent bed has a texture of agricultural lime and 76% CCE. It releases a much more powerful burst of alkalinity (around pH 12.5) on initial hydration than does agricultural lime, while stabilizing to the same long term pH values around 8. For spreading in alkaline recharges where an acid mine drainage problem already exists, the powerful burst of alkalinity would be far more effective in precipitating the ferric oxidant than limestone. While code H lime also has this property, it is much more expensive and has problems with caustic dust. The user should be cautioned that FBC spent bed will self cement, unlike agricultural limestone.

Sulfite rich limestone and dual alkali scrubber sludges (CCE 30% and 54% respectively) can also be used for alkaline recharges where a damp more soil-like material is desired for handling reasons. At the Harco mine site a 35 acre area of acid producing Gobs and coal slurries was capped with sulfite rich limestone scrubber sludge. The material was handled like soil. It was picked up and put down with scrapers, leveled with a dozer and roller compacted to limit permeability. Field hydraulic conductivities for unrolled sulfite rich limestone scrubber sludge were in the lower 10^-5 cm/sec range so near clay like hydraulic conductivities are expected at Harco. If scrubber sludges compete against borrow clay for

capping applications they would have the advantage of a significant alkali reserve that would make seepage more like an alkaline recharge. A problem with clays from some Illinois basin and Eastern mine sites is that native clays near the coal seam are highly acid producing and may become the source of the problem they were intended to solve. Dual alkali scrubber sludges have a strong initial alkali burst, while wet limestone scrubber sludges have pH values around 8. Initial pH and permeability can be chosen by the reclamation engineer.

Combustion residues can also assist and enhance revegetation. Synthetic gypsum from force oxidized limestone scrubbers is a natural sulfate fertilizer. It helps to restore structure to mine soils that have been over-compacted by the equipment used for reclamation. It easily leaches to carry calcium into soil zones that are normally accessible only with expensive deep tillage equipment. There the calcium reduces problems with aluminum toxicity and enhances root penetration. In experiments carried out by SIU-C investigators the gypsum was delivered by frame-less dump truck, loaded into a lime spreader with a tractor, and spread on the ground with an agricultural limestone spreader. **FBC** spent bed has been applied to agricultural lands in Illinois using lime spreaders. FBC fly ash is too fine and dusty for a lime spreader, but if it is left outdoors for a season it will clump into a weak cement mass that can be broken with a loader and ground to make a coarse granular product which can be spread with a lime spreader. FBC byproducts have both strong alkali potential and sulfate fertilization. When they are loose in the upper soil the byproducts can degrade and alter into gypsum which will then aide in reducing aluminum toxicity. Of coarse it takes several seasons to create gypsum from FBC ash and then it will not help the soil texture.

Environmental Issues for Coal Combustion By-Products in Reclamation

Coal combustion byproducts can be chemicals, alkaline recharges, caps, and custom structural materials in mine reclamation. Unfortunately there are environmental issues with their use. coal combustion residues are most commonly classed as a special waste, though some states regulate under RCRA subtitle D, and some expect FBC ashes to receive mandatory subtitle D or even subtitle C requirements when the Bellville amendment exemption runs out. The mentality that combustion residues are a sinister waste product from an industrial plant has caused a presumption of environmental liability and a general neglect of environmental enhancement potential. Much regulation and concern centers around the notion that industrial waste products release dangerous leachate into the water supply. Fugitive dust concerns are receiving more attention as companies move to dry disposal alternatives. Finally a last concern with coal combustion byproducts, noticed most frequently by mine reclamationists, is the general lack of organic material to spur plant growth.

Many of the field scale pilot projects in which SIU-C has participated have been heavily monitored to determine if leachates were detrimental to ground or surface waters. For a year before the final strip pit at Forsythe Energy #5 was filled, laboratory column leaching experiments were run on the scrubber byproduct proposed for the fill. Monitoring wells were located within 15 meters of the area to be filled and groundwater quality was followed for about a year before filling. Water from the upgradient monitor well was used as the leaching medium for the column experiments. Before any fill was placed in the field, a channel was dug at the bottom of the pit and perforated well pipe was laid in silica sand. The “drain” was piped to the surface as the pit was filled. This allowed leachate from the fill to be collected before significant attenuation in the environment. By knowing the source concentration and the down-gradient concentrations in the monitoring wells it is possible to calibrate the dispersivity in groundwater flow and contaminant transport models.

The water at the Forsythe site was of poor quality, though the pH of 6.7 could hardly be called acidic. TDS values were high. Iron ranged between about 100 and 350 ppm and manganese values were around 35 ppm. Other heavy metals were above class I water standards and many were above class II standards as well. One would suspect that the water quality had been degraded by the loose spoil material broken up by mining, though pre-mining groundwater quality is not known. and Southern Illinois groundwaters are often of poor quality with no human intervention. The column experiments

indicated calcium, potassium, sodium, boron, and molybdenum could potentially leach out of the material. Dissolved solids changed only slightly due to ion exchange since less mobile alkali metals like magnesium were removed from the water.

Contrary to popular fears of heavy metal contamination, the scrubber byproduct removed most of the iron and manganese from solution and a significant part of the trace metals such as lead, cadmium, and nickel, bringing most of these parameters into compliance with class I or class II groundwater limits. The slight increase in pH might be argued as a possible cause of iron removal by precipitation, but pH values around 8 could never have precipitated the manganese from solution. For manganese, and many of the other heavy metals, the removal is much more consistent with surface adsorption or incorporation into secondary mineral phases. Removal of manganese from degraded mine waters is difficult using conventional technologies. Manganese can only be precipitated out of solution by raising the pH to 10, but pH values above 9 constitute alkaline mine drainage. One cannot meet one standard without violating the other. The sulfite rich scrubber sludge at Forsythe appears capable both of cleaning manganese in both laboratory columns and in the field, where the results of the column experiments were mirrored almost exactly on all 24 elements analyzed.

The heavy metals cleaning potential of the scrubber sludge raises an interesting question in environmental values because the boron release from the material is significant and reached a high of 100 ppm in the field drain before falling off. Computer models indicate a leachate plume of around 100 acres that exceeded the 2 ppm class I groundwater standard for 20 years after the fill. Most boron concentrations are too low to cause salt damage to grasses commonly used in reclamation, but more sensitive cultivated plant species might suffer ill effects if the water from the plume was used for irrigation. Shake tests using pure water indicate that enough calcium can dissolve to cause hard water. One might certainly have reasons to avoid placing the scrubber byproduct in communication with high quality potable aquifers, but in mine settings with high TDS waters were toxic and heavy metals drainage is a problem a case could be made that the environmental enhancements far outweigh the risks.

In another experiment, 150 tons of FBC fly ash was introduced into a 2 million gallon pond of pH 2 mine water. Ordinarily, such an action would not be permitted since the conditions would be expected to release toxic and heavy metals from fly ash surfaces. The pond was carefully monitored during and following introduction of the ash. Obviously iron and aluminum precipitated as the pH rose, but the heavy and toxic metals concentrations fell around an order of magnitude. No heavy or toxic metals contamination was detected. The same result was observed for arsenic which can be mobilized by acidic conditions but solubility for arsenic reduces very little as water is neutralized. One might still hesitate to use FBC fly ash as an additive to ones daily cup of coffee but the experiment suggests that, for acidified mine waters that already contain heavy and toxic metals, the metals release by fly ash (if it exists at all) will be overpowered by effects related to neutralization of the water.

If combustion byproducts are used as a capping material there may not be enough leachate to create a groundwater plume. The well placed beneath the test embankment at Burning Star was intended to provide leachate source concentrations just like the drain at Forsythe. No such data has been obtained because there is too little water in the well to take a sample, even by lowering about a weighted 10 ml cup into the well. Lysimeters placed beneath the 7 acre cap at Thunderbird also have not been able to collect any leachate from the cap. It was possible to get a sample of infiltrating run-off water from an ash pile storage area during the winter. This sample had slightly elevated sodium and potassium levels, but no heavy or toxic metals could be detected. A network of sampling stations on a surface stream adjacent to the Thunderbird cap has been monitored for a year now with no detection of any contaminants, not even the sodium and potassium identified in infiltrating run-off. Some data collected in ongoing projects suggests that even boron, which leaches from many fly ashes, may be immobilized by cementitious reactions in designed mixes of combustion residue and mine material.

Fugitive dust may also be an issue in the use of some combustion residues, especially dry col!ected fly ash. For FBC fly ash, which is useful as an alkali chemical and as a soil cement, the fact

that the dust is caustic poses a special risk to individuals in close proximity. Similar risks are routinely accepted in mine reclamation or construction work involving code H lime and dry cement. For FBC fly ash, conventional dust control techniques like spraying with water tend to be ineffective. At the Thunderbird site, where the 7 acre cap was constructed, the highest dust levels resulted from water trucks spraying the ash to prevent dusting. Observations and dust measurements at Thunderbird indicate that significant reductions in fugitive dust can be achieved simply by arranging the order of construction operations to avoid tire contact with loose fly ash. A tarping method tested at Thunderbird resulted in essentially complete elimination of the dust cloud from frame-less dump unloading of fly ash. A practical field unloading system is being developed in an ICC1 research project this year. The project is also following through on methods of rendering fly ash non-dusty. Originally the system was intended for installation at the ash source, but large cost reductions may be possible by making this a mobile system for use in the field as well.

Finally, there are the concerns about lack of organic material in combustion residues. This concern would be most valid if combustion residues were used as a growth medium for plants. Most of the applications cited in this paper do not require the bulk material or chemical used to be a plant growth medium. Work done by the National Mined Land Reclamation Centers used sewerage sludge and fly ash as a plant growth medium without heavy metals uptake problems. Certainly other mixes of mine preparation wastes and combustion residues might be tailored and augmented to be suitable plant growth mediums if this were needed. Gypsum from force oxidized scrubbers is already a valuable plant nutrient, even though it is not organic. A force oxidized scrubber in Illinois produces a gypsum that is far more pure and free or trace metals than any commercially available natural gypsum.

Conclusions

The existing practice of hauling coal combustion residues back to the mine site can be significantly enhanced to provide cost savings and environmental advantages both to boiler operators and to mines. Handling of combustion residues can be made a part of mine reclamation or even active mining operations reducing the need for separate land-filling operations and their associated costs. When combustion residues are hauled back to the mine they become a free delivered source of bulk chemicals that would be difficult for conventional manufactured reagents to challenge. Indeed, there are many times when Gob treatment or capping would be beneficial to the environment, but would be cost prohibitive if such quantities of manufactured reagents were purchased. In applications, such as FBC ash used in alkaline recharges, combustion residues are more effective than the conventional reagents commonly used. The environmental risks of water contamination or fugitive dust are either over-rated or manageable and are eclipsed by the environmental benefits that can be realized in most mine settings.

COAL COMBUSTION RESIDUES AS SOIL AMENDMENTS: SURFACE COAL MINING

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Abstract

Coal combustion by-products have received increased attention as possible soil amendments and/or as substitutes for normal agricultural amendments such as limestone and gypsum. However, there remain a number of concerns with their widespread use. These concerns include elevated trace element loadings to soils, especially for arsenic (As), selenium (Se), molybdenum (Mo), boron (B), and increases in soil soluble salts. Several issues such as determination of application rates, long term effects of induced calcium (Ca):magnesium (Mg) imbalances from application of high Ca by-products, and clarification of beneficial utilization versus disposal, need to be understood. This report will examine these current concerns and issues in regards to the use of conventional fly ashes, oxidized flue gas desulfiuization (FGD) residues, and fluidized bed combustion (FBC) residues. The concept of co-utilization of by-products will be introduced and discussed as well as the need to consider cropping systems and site management in reclamation of surface mined areas.

Introduction

This report addresses a number of topics important for the utilization of FGD, conventional fly ash, or FBC residues applied to soils with emphasis on surface mined areas. There are a number of review articles that detail the potential utilization and effects of coal combustion residue applications on the terrestrial ecosystem, [Adriano, et al. (1980) and El-Mogazi et al. (1988)], agriculture and horticulture, [Korcak (1995)], the environment in general, [Page et al. (1979), and Carlson and Adriano (1993)], and use in mine land reclamation [Haering and Daniels (199 I)].

Unlike most agricultural soils, the extremely acidic nature of mined lands, resulting from oxidation of sulfur and sulfide, requires additions of alkaline materials to bring pH into the range where plants can grow and where trace element availability is controlled. Consequently the use of coal-fired power plant by-products, many of which are basic (FBC residues and Class C fly ash), can assist in moderating pH to the desired levels to reduce trace element availability. However, the use of alkaline fly ash and other coal combustion by-products with the addition of an organic material may provide a better environment for long-term revegetation of mined lands.

Since more is known about the potential use of coal combustion by-products on agricultural soils than surface mined lands, information is drawn from the agricultural utilization literature to help highlight problem areas and potential solutions.

Residue Characteristics Important for Land Use

The soil/plant system requires a balanced nutritional media for revegetation. Coal combustion by-products can be a supplier of many of the nutrient needs of plants, either in whole or in part, with the exception of nitrogen and usually P. However. nutritional imbalances and excesses can occur. Regardless of whether by-products are being used for amendment of agricultural soils or for reclamation of mined lands. a number of by-products properties should be taken in account.

Ca:Mg Ratio

Application of FGD or FBC by-products, which usually originate from facilities using a

Ca-based sorbent, can create a Ca:Mg imbalance. This imbalance may induce a Mg deficiency in the plant species being established. Therefore, before an application is made, care must be taken to monitor both the Ca:Mg ratio of the material applied and of the unamended soil. Fortunately, Mg deficiency is usually easily corrected by a soil application of magnesium sulfate (Epsom salts) or by application of dolomitic limestone. Currently, research in Ohio and West Virginia is exploring the use of a Ca-rich FGD by-product plus a MgOH by-product (personal communication, R. Stehouwer and Dale Ritchey). This type of Ca and Mg mixture should help to alleviate the occurrence of Ca-induced imbalances.

Plant available potassium (K) may likewise be lowered due to the high soil Ca status after coal combustion by-product addition to soils.

The high levels of Ca, Fe (iron), and Al (aluminum) in some coal combustion by-products (including most ashes from western coals) may combine with soil phosphorous (P) to form insoluble complexes. These complexes reduce the availability of P to plants, which may result in an induced P deficiency. However, there may be situations where the formation of insoluble Ca-P (or Fe-P, or Al-P) complexes is desirable. For example, one of the limitations on land utilization of animal manures is the potential for P pollution of surface and sub-surface water supplies. The co-utilization of FBC ash (high in Ca) and animal manures is currently being examined (R. F. Korcak and W. L. Stout, unpublished data).

Solution I

A program of yearly tissue monitoring should be established to assist in identifying plant nutrient imbalances. In the short-term, Ca:Mg imbalances may be of less concern (and can usually be easily corrected) in the revegetation of surface mined soils since the overwhelming problem is soil pH control and maintenance.

pH Effects

Because of the alkaline nature of many coal combustion by-products, a number of studies have examined their effect on modifying soil chemistry, primarily pH The basic property used to quantify the effects of these by-products on soil pH is the $CaCO_3$ equivalence of the materials. The neutralizing effect of pure $CaCO_3$ is 100 percent and that of coal combustion by-products usually ranges from near 0 to 60 percent. Therefore, if a coal combustion by-product has a $CaC0_3$ equivalence of 50 percent, twice as much coal combustion by-product as $CaC0_3$ is needed to neutralize the same amount of soil acidity. FBC residues will most likely provide the highest amount of acid neutralizing power due to un-reacted sorbent while FGD materials, by their nature, will have very little, if any, neutralizing power. For fly ashes, Haering and Daniels (199 1) provide a rule of thumb for determining their alkalinity: if the ratio of amorphous Fe to water-soluble Ca in a given ash is less than three, the ash will be alkaline.

A computerized automatic rapid weathering apparatus which predicts actual potential acidity and lime application rates for reclamation of coal wastes has been developed and tested (Gitt and Dollhopf, 1991). The use of this type of predictive model for calculating basic coal combustion residue application rates has not been reported.

Since successful modification of soil pH has been demonstrated with a wide range of coal combustion by-products. future agricultural applications of alkaline by-products will probably be based on soil pH modification. The situation with acid surface-mined soils is more complex. A one-time application of an alkaline by-product, at typical agricultural application rates (1 to 10 tons per acre), may not be effective in environments where pyrite is continuously oxidized.

Repeated application of FBC residue (about 3 tons per acre per year for 3 years) to reclaimed surfaced mined pastures resulted in no deleterious effects to forages or grazing lambs (Cochran et al., 1959). In controlled greenhouse studies, Stehouwer and Sutton (1992) amended acid (pH about 3.0) spoil

and underclay materials with alkaline Lime Injection Multi-Stage Burner FGD or pressurized FBC materials (pH range from 10 to 12) at rates up to 24% (by weight) and found increased plant survival and growth and successfully modified media pH. Similar studies in the field on acid mine spoils are currently underway in Ohio (personal communication, R. Stehouwer).

Plass and Capp (1974) amended an acid spoil with 150 tons per acre of an alkaline fly ash which raised the media pH from about 3 to 6 and increased available P. At such rates significant soil physical effects were noted, including higher subsurface water retention resulting from increased infiltration, soil porosity and percolation to a depth of 4 feet.

High application rates of coal combustion by-products can increase media pH, as noted above, and have positive effects on soil physical parameters; however, there are examples where excessive applications rates have been detrimental.

Solution II

Formulas exist for predicting the amount of aglime to be applied to reclamation sites. However, with the exception of basing FBC application rates on calcium carbonate equivalency, these formulas have not been tried with basic coal combustion residues. Due to site variations, trial plots should be established to identifyappropriate rates. One of the adverse reactions to high application rates of coal combustion by-products is elevation of soluble salts which can limit or narrow the choices for appropriate vegetation to be established.

Soluble Salts

One of the major concerns with the agricultural or reclamation use of coal combustion by-products is the high soluble salt content of many materials. Most agricultural or reclamation application methods homogenize the applied ash into the surface which results in maximal seed contact. At high application rates, salt injury can occur to germinating seeds or established plants. The problem of high soluble salts may be alleviated in a number of ways. First, selection of by-products with low soluble salt contents. Because subituminous and lignite coals tend to produce ashes with higher salt contents, they should be avoided.

There are a number of methodologies which may lessen the impact of soluble salts on revegetation. Surface application of coal combustion by-products followed by plowing or mixing may allow seed germination due to a dilution of the salts within the plow layer. A novel technique was used by Jacobs et al. (1991) where ash was banded into the soil at a 45” angle to the surface. These application methods tend to isolate the applied material from initial root contact. Additionally, the timing of application can have a significant impact on avoiding initial problems with soluble salts. Applying residues in the fall prior to plant establishment in the spring allows time for leaching a portion of the salts out of the root zone.

The occurrence of soluble salt problems can also be lessened if by-products are stockpiled and weathered before application rather than applied fresh. During weathering a substantial portion of the soluble salts are removed by percolation, and some of the oxides and hydroxides are stabilized by carbonation. Martens and Beahm, (1976) found that weathered ash could be used on corn at rates of up to about 70 tons per acre whereas salt-related problems with fresh ash occurred at about 45 tons per acre. Also the incidence of B toxicity (often related to the soluble salt problem) was lower with weathered ash because a relatively high percentage of the B in ash is usually soluble. Therefore, smaller amounts of water-soluble B will be applied to soils with weathered ash. The use of weathered materials also decreases the dust hazard associated with applying fresh, dry, coal combustion by-products because bonding and recrystalization during moist weathering reduces the proportion of small-size particles.

Soluble salt problems can also be circumvented by using FBC residues as a soil ‘cap’ wherein a

thick (5-cm) layer of FBC residue is surface-applied around the plant or within tree rows and not plowed or mixed with the soil (Korcak, 1988). Since the entire soil surface is not amended when this method is used for horticultural or forestry crops, it provides either sufficient soil mass for the roots to avoid contact with the initial flush of soluble salt or reduces this initial flush to levels that can be tolerated by crops. The 'cap' remains porous and acts as a one-way valve, allowing water to infiltrate, but decreasing evaporation from the surface.

The potential value of FBC soil 'caps' as well as selection of salt tolerant plant species will be discussed later in this report.

Solution III

If required application rates will produce soluble salt problems, the easiest remedy is to used weathered materials or apply materials as far in advance of plant establishment as possible. As noted, one of the associated problems with soluble salts is B. Boron is one of several trace elements that have received attention as being either potentially phytotoxic or of concern due to bioaccumulation.

Trace Elements

Most reports on the use of coal combustion by-products in agriculture conclude that the most serious potential hazards stem from Se, As, Mo and B accumulation in soils and plants. However, coal combustion by-products, at times, can act as a supplementary source of Ca, S, B, Mo, Se, and other nutrient elements when soil concentrations are deficient for adequate plant growth. Determining the best rates for applying ash as a nutrient supplement is very site specific.

Selenium is not an essential element for higher plant growth, although it has been shown to be a required element for some lower plant species. However, Se is an essential element for animal growth. One problem with Se in animal nutrition is that it is needed only in very low concentrations; slightly higher concentrations cause Se toxicity. Recommended food and feed concentrations to provide adequate animal Se range from 0.1 to 1 mg Se kg^{-1} plant material. Food and feed Se concentrations above 5 mg kg^{-1} can cause animal Se toxicity (Mengel and Kirkby, 1987). It is estimated that one-third of the forage and grain crops in the United States contain below-optimal levels of Se for animal nutrition (Mengel and Kirkby, 1987). Mbagwu (1983) showed that fly ash could be used as a soil amendment to increase forage Se concentration on low-Se soils. Increased Se in corn from seleniferous fly ash in New York (Combs et al., 1980) was used to replace supplemental Se added to poultry feed diets.

Arsenic is not essential to either plants or animals. Arsenic in the oxidized form (arsenate) may be bound by the soil clay fraction or with iron oxides. There also exists a strong soil/plant As-P interaction. Added P interferes with As uptake at the plant root and P may aid in moving As downward in the soil profile. Generally, As has not been included in the analytical data presented by many researchers in the past. It appears that As will gain added attention as a environmental contaminant in the near future.

Molybdenum is an essential element for both plants and animals and its availability in soils increases with soil pH. As with Se, the concern with Mo is that the optimal concentration range in animals is narrow and any substantial increase in plants may result in imbalances or toxicities in animals. Plant tissue Mo concentartion ranges of 10 to 20 mg kg^{-1} (dry weight basis) have been associated with adverse effects on animals therefore monitoring of plant tissue Mo should be included in any management plan (Elseewi and Page, 1984)..

Boron, like Mo, is an essential element for plants and animals. Plant species vary in their ability to tolerate high levels of available soil B. In some regions, such as the dairy farm areas of New York, B is added to commercial fertilizer for use on high-B requiring crops like alfalfa.

As noted, coal combustion by-product can be used in agriculture to supplement crops and soils low in Se, Mo, Cu, Zn or B (Adriano et al., 1980 and El-Mogazi et al., 1988). The application of by-products should be based on crop needs and current soil levels of the particular nutrient. Additional studies are needed to define mineralogy, solubilities, chemical speciation, uptake rates, and plant responses in order to calculate optimum application rates for soil application of ashes.

Solution IV

There are many reports in the literature that do not provide soil, plant or environment assessments of these four (Se, As, Mo, B) potentially hazardous elements. It is strongly recommended that any revegetation plan include analytical determinations of these elements to assess bioaccumulation potential.

Ca-Sulfate vs. Ca-Sulfite

Gypsum has been an agricultural soil amendment for over 200 years and the list of benefits to soils and plants is lengthy (Shainberg et al., 1989: Wallace, 1994). In the past, flue gas desulfurization sludges have received little attention as agricultural or reclamation amendments. However, our knowledge of FGD-derived $CaS0_4$ and $CaSO_3$ is increasing due primarily to the research being performed in Ohio (e.g. Stehouwer and Sutton, 1992) and West Virginia (e.g. Ritchey et al. 1994 and Clark et al. 1995).

Among the agricultural benefits of FGD-$CaCO_4$ application to soils is the potential for decreasing problems associated with subsurface soil acidity and increasing plant rooting depth and drought tolerance. These are equally important effects for the reclamation of surface mined soils. Additionally, the application of gypsum to mined areas may aid in reducing phytotoxic effects of Al under acidic conditions as well as aid in reducing plant uptake of ash-derived Se (Arthur et al., 1993). The effect appears to be due to a competitive interaction between Se and S.

Unoxidized FGD scrubber sludges, predominantly $CaSO_3$, will require more careful monitoring When mixed with acid soils, $CaSO_3$ decomposes to form SO_2 (toxic to plants) and oxidizes to $CaSO_4$ (Ritchey et al. 1995). Sulfur dioxide formation is favored at low soil pH. Since conversion to $CaSO_4$ can be relatively rapid, FGD-derived $CaS0_3$ may be applied to lands in advance of plant establishment to avoid any phytotoxic responses (e.g. fall or winter application followed by plant establishment in the spring).

Some scrubber sludges contain significant amounts of fly ash, which is often added at the end of the waste stream to aid in stabilization of the slurry (Terman 1978). Under these conditions, the amount and composition of the added ash should be determined prior to utilizing the scrubber sludge.

Gissel-Nielsen and Bertelsen (1988) evaluated a number of FGD products in trials with barley. One of these contained 10 percent sulfite, 24 percent sulfate, 8 percent fly ash, and 0.5 percent nitrate. Although not noted, the high amount of sulfate present apparently indicated some oxidation of the material. Plant Se concentrations were increased from 0.05 mg kg^{-1} (the level of the control) to 0.18 mg kg^{-1} at the highest application rate. Plant Se at the highest FGD rate (0.5 percent by weight) should provide an adequate level of Se for animal nutrition.

Ransome and Dowdy (1987) used scrubber sludge containing 4.1 g B kg^{-1} as a B source to correct a B deficiency on a loamy sand soil. Although soybean yields were decreased during the first application year from rates of about 5, 10, and 20 tons per acre because of elevated salt content, yields were enhanced by scrubber sludge at all rates by the third year. Adequate soil B for soybean growth was achieved with the 10 tons per acre application rate. The type of scrubber sludge, whether oxidized or not, was not indicated.

Gypsum has also been used for the correction of sodic (high sodium) soil problems. The many benefits of gypsum for both soil chemical and physical improvement indicate that significantly more gypsum can be used to assisst in revegetation of surface mined lands.

Solution V

The use of FGD-$CaSO_4$ in the reclamation of surface mined spoils will probably increase as research findings showing beneficial effects on revegetation establishment and longevity accumulate.

Auulication Criteria

Beneficial Use vs Disposal: To justify its use, any amendment to the soil- plant system must clearly benefit the environment (soil, water or air) and the plant. These benefits must exceed the costs and potential hazards whether one is applying fertilizer, organic mulch, irrigation, or an industrial by-product. Potential benefits and hazards from the agricultural or reclamation use of various coal combustion by-products have been noted above. If the application of a particular by-product enhances plant establishment or growth a beneficial use can be established. Lacking an identifiable beneficial use, application of materials to lands is disposal.

Application Rates: For the agricultural utilization of FBC residues, a manual for determining application rates is available (Stout et al., 1988). Although this manual does not include reclamation of surface mined lands, it should prove useful as a starting point. The manual is modeled after the USEPA guidelines for sewage sludge application to agricultural soils. A schematic flow diagram allows the user to determine how much FBC should be surface applied for a given soil.

However, there are no known manuals or tables that can be referenced as guides for determining land application rates for any other coal combustion residue, including gypsiferous FGD. Where needed, gypsum is usually applied to agricultural soils at rates not exceeding 10 tons per acre. However, a number of 'quick' tests and laboratory procedures for determining responses from the application of gypsiferous materials are under investigation (personal communication, K. Ritchey).

SolutionVI

When considering coal combustion residues, it is suggested that a flow diagram similar to that in the above cited FBC manual (Stout et al., 1988) be followed. Additionally, the chemical composition, inclusive of trace element assays, pH, total salts, and lime equivalency, of the residue to be applied and the recipient soils should be determined. These types of analytical results will work well when a single residue is applied. However, if more than one type of material is to be used for remediation purposes, other parameters have to be considered.

The Future

The Concept of Co- Utilization: Co-utilization is the composting, blending or mixing of two or more waste products in order to produce a new by-product that has enhanced economic value or fulfills a predetermined need (e.g. designed to correct a known nutrient deficiency or aid in remediating a potential phytotoxicity). An example of co-utilization is the work reported by Beeghly et al. (1992). They successfully mixed sewage sludge and LIMB ash to produce a soil-like product. The LIMB ash was used successfully as the alkaline reagent to pasteurize and dewater sewage sludge. Similarly, Logan (1992) reported that a soil product made from sewage sludge and cement kiln dust was as effective as lime and fertilizer when applied to acidic mine spoils.

Additionally, there have been reports on applying coal combustion by-products and sewage sludges, but not necessarily as a premixed product (Korcak, 1980; Stehouwer and Sutton, 1992). Others have found beneficial responses in crops grown on soils from amending manure or sewage sludge

compost with fly ash (Adriano et al., 1982; Garau et al., 1991; Menon et al., 1992; Ghuman et al., 1994) and amending bottom ash with compost made from grape marc and cattle manure (Chen et al., 1991).

Pietz et al. (1989) studied the use of lime and sewage sludge for amending acidic coal refuse materials. They suggest that for long-term revegatation (greater than 5 years) rates of about 300 tons per acre of sewage sludge and about 50 tons per acre lime should be initially applied. Lower initial application rates usually require additional applications over time. However, these types of high application rates need to be considered in relation to plant N requirement to avoid elevating nitrate leaching.

It should be noted that sewage sludges are usually lacking in sufficient plant K particularly for long-term plant establishment. Supplemental K should be provided either from a synthetic fertilizer source for from the incorporaton of an additional by-product (e.g. waste rice hulls contain a high level of K and have been used as a K-supplement).

One of the benefits of blending an organic material with an alkaline material such as fly ash or FBC is the maintainence of a higher pH with concomitant reduction in heavy metal availability. This effect was noted by Pietz et al. (1989) from adding sewage sludge and lime to acidic coal refuse material. Beaver (1995) recently reported on the co-composting of separated cow manure with up to 32% fly ash (calculated on a dry weight basis). The initial pH of the ash was 11.6. However, the final composted product had a pH of about 8.6, which is normal for most composted materials.

Another benefit of co-utilization of coal combustion by-products with an organic material is the addition of N and P to the revegetation area. More importantly, the N applied is in a more stable (slow-release) form.

Co-utilization, by definition, should result in products that can assisst in meeting the nutritional requirements of plants as well as alleviate the adverse growing conditions present at reclamation sites.

Cropping Systems and Site Management: Crop selection can have a significant effect on the success of revegetation activities. Sims et al. (1993) screened several crop species for revegetation of fly ash landfills. Hairy vetch, red clover, and tall fescue performed the best, however, when the ash was amended with a co-compost made from municipal refuse and sewage sludge, lespedeza and a fescue-lespedeza mixture showed better early growth. Similarly, Carlson and Adriano (1991) recommended planting a number of tree species on abandoned ash basins to be able to assess metal toxicities or deficiencies for a particular site.

It is difficult to predetermine the type of vegetation to recommend for a particular revegetation site. Two of the most important initial factors will probably be matching salt tolerance of the plant species to be planted with the by-product and meeting nutritional needs of the plant while avoiding weed competition. Carlson and Adriano (1993) note a number of plant species that are salt tolerant and local extension personnel will probably also be helpful in recommending specific cultivars to be established.

The other persistent problem particularly with tree establishment is competition from weeds. One option to eliminate herbicide use would be to utilize FBC residues as a post-planting ‘cap’ around the tree. This may help to eliminate or reduce weed competition for up to 2 to 3 years.

Summary and Recommendations

Potential benefits from coal combustion by-products include alleviation of soil trace elemental deficiencies, modification of soil pH, and improvement of calcium and sulfur, infiltration rates, depth of rooting, and drought tolerance. Flue gas desulfurization products and residues from fluidized bed combustion which contain appreciable amounts of gypsum appear to have particularly high potentials for improving water use efficiency, product quality and productivity of soil-crop systems.

The existing literature on utilization of coal combustion by-products needs to be expanded to include data from long-term exposure of these materials in the soil environment. Potential sites for examination exist. Additionally, researchers should evaluate the potential utilization of by-products resulting from new Clean Air technologies as they are developed. These studies should also address innovative strategies for application and clear documentation of potential benefits.

Documentation of hazards involved and benefits derived, especially from field studies, will be required to reduce present regulatory barriers to utilization of coal combustion by-products either used alone or co-utilized with other wastes. On-site disposal may result in environmentally hazardous concentrations of certain elements in water supplies and the food chain.

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PUBLIC CONCERNS
REGARDING THE MANAGEMENT OF COAL COMBUSTION WASTES

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Introduction

Your perspective is changed when you are the landowner next to an operation that is proposing to dispose of coal combustion waste, or you are a person who will be drinking ground water that may be affected by disposal practices. The disposal of coal combustion wastes at surface coal mines is a serious issue for **90** percent of Kentuckians who live in rural areas and rely on ground water as their sole source of drinking water. This is an issue that needs to be approached in a serious and judicious manner. It needs to address the concerns of neighbors in a compassionate, understanding, and responsible manner. This is not a responsibility that is framed by the 2 year post closure care period that typically attends special waste landfills, or one that is framed by the 5 year liability period of surface mining performance bonds. Rather, it should be a responsibility that understands that our knowledge of the fate, partitioning, and transport of metals in the environment over the long term is limited. We need to thoroughly understand what it is we intend to do with these wastes, before we dispose of them in the environment where they will remain a potential concern long after the persons responsible for the disposal will be gone.

I will be speaking as a representative of neighbors. There are significant concerns that have been voiced in Kentucky regarding the disposal of coal combustion wastes. We have not had a lot of disposal of coal combustion wastes at mine sites. The reason for this is that the utilities in Kentucky will not release their ash to be managed by any third party. They understand that there are liabilities associated with the management of these wastes. They do not want it mixed with other wastes or disposed of at mine sites where they do not have the ultimate control over the management of that disposal process resulting in an open ended disposal liability. This is not the case, however, for utilities from other States. Representatives of the coal industry have sought changes in the Kentucky law during the 1994 legislative session which would facilitate the disposal of wastes at mine sites. This was done to create a competitive advantage so that they could provide a full service of hauling coal to the utilities and returning with the waste.

Specific Concerns

Why are we concerned about coal combustion wastes? You look at the literature and it indicates that the wastes do not typically leach metals at hazardous concentrations. If you understand the definition of hazardous under the Resource Conservation and Recovery Act (RCRA), you see that there is a range of potential concern. The range is from the innocuous, completely inert, or insoluble wastes to wastes that leach metals at 100 times the public drinking water standard. The waste becomes hazardous if it exceeds 100 times the drinking water standard. I think that any of us would be concerned if we were drinking water that contained heavy metals at concentrations up to 100 times the drinking water standard. What we should be looking for, when we dispose of these wastes, is to insure that there is no leaching of any constituents of concern, be they organics or heavy metals into the ground water where they may contaminate someone's drinking water.

The question of how to manage coal combustion wastes (CCW) under the Surface Mining Reclamation and Control Act of 1977 (SMCRA) is as open question. It is open because, in large part, the Office of Surface Mining has not historically addressed such issues with the specificity that such an issue deserves. The fact that we are all here talking about the issue is a statement that there are concerns about proper management and beneficial use of coal combustion wastes. I would suggest that the Office of

Surface Mining has a responsibility to move forward in establishing some basic benchmarks in how we manage these wastes on surface coal mines.

Why are we concerned about these wastes? The US EPA assessment of coal combustion wastes in its report to Congress under RCRA stated that these wastes did not need to be managed as hazardous wastes provided that they were properly managed as solid or special wastes. This disposal should be mitigated as appropriate with the installation of liners, leachate collection systems, ground water monitoring, and corrective actions as necessary to clean up the ground water.

A study of CCW in Indiana (Boulding, 1991) indicated that CCW does contain high enough concentrations of leachable toxic elements to create environmental concern. Characterization of the wastes is extremely important. Significant findings of the report by Boulding were that: (1) neither TCLP nor extraction procedure provide a complete assessment of the leaching potential of the wastes. Long term leaching tests, conducted until equilibrium has been achieved for each element of concern, using a leaching solution that simulates natural groundwater, would give a more accurate depiction of potential groundwater contamination; (2) there are 17 potentially toxic elements have been found in CCW including: aluminum; antimony; arsenic; barium; beryllium; boron; cadmium; chromium; copper; lead; manganese; mercury; molybdenum; nickel; selenium; vanadium; and zinc; (3) fluidized bed combustion wastes retain volatile and semi-volatile elements in the bottom ash to a greater extent than conventional CCW, thus enhancing the leachability of these elements; (4) leachates from CCW typically exceed drinking water standards, but by less than hazardous levels. CCW leachate typically exceed the standard by 1.1 to 10 times and often by more than 10 times for one or more element; (5) disposal of CCW in coal mines may be of particular concern, due to the increase in surface area available for leaching elements resulting from the fracturing of layers of overburden. There is also the potential for the higher total dissolved solids in mine spoils to compete for sorption sites with toxic elements released by CCW.

The US EPA report and the Boulding study indicate that the management of special wastes must be attuned to the specific concentrations of potentially toxic elements in CCW, the specific characteristics of the disposal site, and the specific type of CCW. Other reports indicate a concern with enhanced levels of radio nuclides, including radium-226 and other daughters of uranium and thorium, that could pose significant long term management challenges. A summary of studies on ground water contamination potentially associated with CCW disposal is provided at the end of this report.

Principles For Responsible CCW Management

A principle that should apply to the management of disposal of these materials is that it is irresponsible to place these materials where ground or surface water can be contaminated by leachate from the wastes. There is a great variability in the geohydrology across the coal fields. In eastern Kentucky, we have a ground water regime that is characterized by secondary permeability or fracture flow such that any contaminants would be leached into the shallow ground water system where most people get their drinking water. In western Kentucky, there is an isolation from mining areas and ground water used as a source of drinking water. These have different management concerns related to disposal sites.

The standards governing management of CCW should differentiate at least three categories of CCW that will be managed under greater scrutiny, including individual permits for any disposal or reuse. These categories include: (1) FBC waste which, as noted in the Boulding report, presents a higher potential for leaching elements of concern; (2) CCW generated through the firing of hazardous waste fuels and waste oils; and (3) CCW co-fired with waste tires and refuse-derived fuels. Each of these categories adds constituents to the combustion which may significantly increase the hazards of improper disposal, including a range of products of incomplete combustion of chlorinated and other synthetic organic compounds that warrant extensive analysis and careful management beyond that necessary with CCW alone.

Clarification should be provided that CCW should not include utility wastes such as metal and boiler cleaning waste nor other wastes generated at power plants beyond those directly resulting from combustion and control of emissions from the combustion process.

CCW will potentially be of concern for far longer than the post closure liability period for the disposal area. Long term fate, transport, and partitioning of the wastes need to be understood in the planning and characterization process.

The potentially affected landowners need to be notified and involved in the decision making process. The rights of landowners and users of water in these areas are paramount.

Potential Radioactivity

There is an Oak Ridge National Laboratory report that addressed the issue of radio nuclides in terms of emissions from utilities and in the resulting ash. This needs to be assessed in the waste characterization and management process. We tend to manage radioactivity in a very uneven fashion depending upon its source. Radioactive materials need to be properly managed and disposed of, if it is a concern. It is especially important that we do not contaminate soil materials with radioactive wastes.

All CCW should be screened for radio nuclides and managed as low-level radioactive wastes in accordance with the applicable State and Federal laws, where such wastes exhibit activity that is above background. Protocols for the characterization of CCW for elevated radio nuclides and management of wastes with enhanced radioactivity must recognize the inadequacy of traditional solid waste management tools for disposal. Protocols that should be adopted by agencies for evaluation of applications for disposal of CCW that contain elevated radio nuclides (and are properly classified as technologically-enhanced low-level radioactive waste) include: (1) complete characterization of waste composition and chemistry based on actual samples measured for Ra 226 and daughters (i.e. Lead 210), specific radium analysis, and gamma spectroscopy. Leachate analysis should use actual leachate from the proposed facility where possible, and TCLP or other appropriate leaching tests; (2) a fate and transport analysis including a multi-path risk assessment; (3) a "cap" on the radioactivity of waste allowed for disposal at other than a commercial LLRW disposal facility, with an upper-bound limit on activity associated with the material established, as necessary, to satisfy the most restrictive pathway (which will likely be the drinking water at 4 mrem/yr) and which in no instance should exceed 15 mrem (consistent with NRC proposed standards); (4) the measurement of activity must be based on representative sampling, with higher activity wastes and hot spots managed separately. No dilution of clean waste or soil to lower the activity levels prior to disposal should be allowed; (5) management of wastes with lower volumes and higher activity, such as scale, or equipment, should be handled through licensed low-level radioactive waste storage/disposal facilities. Any equipment with micro R readings above twice the background level should be sent to a licensed commercial facility; (6) wastes to be disposed of at a solid waste landfill or mine-site should first be stabilized and containerized in order to minimize air emissions during handling and to provide a primary barrier allowing some decay of the material prior to loss of primary containment; (7) disposal in a solid waste landfill must be in a separate constructed cell with secondary containment, grouted in place, and controlled with separate leachate collection system; (8) long term cap maintenance and groundwater monitoring after the end of post-closure monitoring and care period (30 year plus corrective action period for landfills, 5 years after reclamation for minesites) through perpetual care, funded by owner/operator/disposer, and managed by the State and local government; (9) approval by the landowner and local government for disposal of the material. A public comment period should be provided with a requirement for approval for any new waste stream from a particular facility. All proposals should be subject to major modification review.

The Role of the Office of Surface Mining

OSM has a responsibility to do more than has been done in assuring that these wastes will be properly characterized and managed For potential environmental concerns. Currently, the disposal of non-coal mine waste is required to be placed in a controlled manner and isolated from water. Beyond that there has been an absence of Federal guidance. This has resulted in increased conflict in enforcement related to disposal activities. It produces one downs-man-ship that the States have engaged in concerning environmental quality and the regulation of coal mining. This was the pattern that characterized the early 1960s and 1970s before the Federal law was passed. In Kentucky, during the 1994 legislative session, we were faced with an argument that Kentucky should take a minimalist approach to CCW because other States had done so. Because of the significant concern by the Kentucky legislature, we were able to avoid that type of approach. I feel that we have a very responsible approach in Kentucky that characterizes the waste and collects extensive background data in order to determine if there are changes in the prevailing hydrologic balance. Additional requirements concern the design and placement of CCW in the disposal facility in order to isolate them from potential leachate contact with water.

Conclusion

In conclusion, I would like to take a quote from Dr. Hassett, in the context of testing CCW, and apply it to the entire management of CCWs. He said, "disposal is forever, and if scientifically valid conclusions are to be made concerning the potential for environmental impact of disposed materials, then valid tests must be performed." I would simply add that once valid tests are performed, responsible measured should be developed to address whatever concerns arise from that valid testing. Responsibility for the disposal should be commensurate with the potential risks posed by the material.

DOCUMENTED CASES OF GROUND-WATER CONTAMINATION FROM DISPOSAL OF COAL COMBUSTION WASTE

Arthur D. Little, Inc. 1985. Full-Scale Field Evaluation of Waste disposal From Coal-Fired Electric Generating Plants. EPA-600-7-85-028 (EPA Contract #68-02-3167). [Summary information obtained from Appendix E io U.S. EPA, 1968)

Evaluation of coal ash and floe gas desulfurization (FGD) waste disposal practices it 6 power plants:

1. The Allen Plant in North Carolina shows elevated levels of trace elements io ground water downgradient for unlined ash disposal ponds. Arsenic (up io 31 times) and cadmium (up lo 5 limes) exceeded primary drinking waler standards (PDWS) in the ash ponds. Water samples obtained from under the active pond exceeded secondary drinking water standards (SDWS) for too and manganese (up to 90 and 280 times respectively) whereas ponds liquor samples did not indicating that pod leachate was mobilizing imn nod manganese from the soil beneath. Downgradient monitoring wells exceeded PDWS for iron and manganese up to 82 rod 102 times. Downgradient contamination had not reached steady-state concentrations with respect to mixing of leachate generated by the ponds and ground-water and it was expected that further degradation would in downgradient wells.

2. The Elrama plant in western Pennsylvania disposes of a fixated FGD sludge-fly ash mixture on coal mine spoils rod river alluvium. Leachate collected beneath and within the wastes found that arsenic exceeded PDWS by 3 lo 5 times. Cadmium exceeded PDWS by up io 20 times in both water in and under the waste and in downgradient monitoring wells. It was difficult to separate effects of contamination from acid mine drainage rod ash disposal, but the cadmium contamination was considered lo probably be from the ash. Again, steady state concentrations from ash leachate did not appear to have been reached at the monitoring wells so the effects from the leachate were expected lo increase with lime.

3. The Dave Johnston plant in Wyoming disposes of ash in two unlined landfills. Cadmium exceeded PDWS, and maogaoesc and sulfate exceeded SDWS in ground water beneath the waste and in pond liquors. Concentrations of boron were also elevated Chemical attenuation by soils at the site was found lo be low for trace metals such as arsenic. Actual impacts on groundwater were difficult to determine because of the presence of other waste disposal sites and naturally high mineralization in the ground water.

4. The Sherbourne County Plant in central Minnesota disposed of fly ash and FGD waste in one day-lined pond sod bottom ash is an adjacent clay-lined pond. Pond liquors contained chromium up to 16 times the PDWS and downgradient ground-water exceeded the PDWS by 1.2, whereas upgradient samples did not. Sulfate aod boron had apparently migrated from the waste into ground-waler, but did not exceed SDWS. Steady state conditions had not been achieved between the leachate and the ground water so continued increase in trace element concentrations was expected The surrounding soils did not effectively attenuate selenium and exceedance of PDWS for this element was considered possible when steady state conditions were achieved

5. The Powerton Plant disposed fly ash, bottom and slag in a landfill, part of which was underlain by a liner consisting of ash and time. Downgradient wells exceeded PDWS for cadmium up lo 3 times, and SDWS for iron. manganese, and sulfate. Concentrations of these elements in downgradient wells was significantly higher than io upgradient wells. Dilution and chemical attenuation may have prevented significant downgradient concentrations of arsenic rod selenium.

6. The Lansing Smith plant in southern Florida disposed of a mixture of fly ash and bottom ash in an unlined disposal pond located in a coastal area. Cadmium (up to 5 times PDWS) and chromium (up to 4 limes PDWS) were measured in the downgradient groundwater. The impact on groundwater quality was considered lb be measurable. but since the leachate migrates into a shallow, unused tidal aquifer health risks were mosidcred lo be minimal.

Boulding, J.R. 1992. **Disposal of Coal** Combustion Waste **in Indiana: An Analysis** of **Technical and** Regulatory **Issues. Final** Report **March** 31. **1992, Prepared for** Hoosier **Environmental** Council. **Indianapolis, IN,** 104 pp. [Summarized from **Appendix C.3]**

Downgradient monitoring well data fmm the Peabody Universal Mine in Indiana where coal fly ash was being backfilled without a liner showed that average concentrations exceeded PDWS for selenium by almost a factor of 2, and that average concentrations of arsenic, cadmium, and lead were right al PDWS. Average concentration of total dissolved solids, molybdenum and nickel, rod possibly barium exceeded SDWS. This contamination was coming from ash that was relatively benign based on analysis of laboratory leaching test on 50 samples of coal combustion waste from coal mined in Indiana.

Cherkauer, D.S. 1980. **The Effect** of **Fly** Ash Disposal **on a Shallow Ground-Water** System. Ground Waler **18(6):544-550.**

The **Cedarsauk site, a fly ash** landfill **in southwestern Wisconsin** is **located** in as abandoned sand **and gravel pit.** After eight years of disposal **the contaminant** plume apparently stabilized **about 200 meters downgradient** of the disposal site. No **exceedance of** RDWS **were** observed. but SDWS were exceeded for **iron, manganese, total dissolved** solids rod sulfates. Neutralization of **the** acidic ash probably served **to** precipitate **many** of the **trace metals** in the **leachate.**

Dames **and Moore. 1982.** Review **of** Existing **Literature** and Published **Data** to Determine **if Proven Documented Cases of Danger to Human Health** and **the Environment Exist** as **a** Result of Disposal of Fossil **Fuel** Combustion Waste. **In: Report rod Technical Studies on the Disposal and Utilization** of Fossil Fuel By-Products, **Utility** Solid Wastes **Activities Group, Appendix** il. [Cited in U.S. EPA, **1988]**

Leaching from two By **ash disposal** ponds at the Michigan **City** site is **northern** Indiana near **Lake** Michigan, resulted in **downgradient** concentrations of arsenic exceeding PDWS with **one** observation by more than **100** limes the standard Lead **also** was observed to **exceed** PDWS **downgradient** by as much as 7 times, but **upgradient** wells **also** exceeded the **PDWS** for lead by as much as 3 times. A steel slurry wall installed between the site and **Lake** Michigan was intended **to** keep **contaminated groundwater** from reaching the lake.

Environsphere. 1979. **Environmental Effects of** Utility Solid Waste Disposal. **Prepared for Utility Solid Waste Activities Group and** Edison **Electric** Institute. **[Cited** in **US. EPA, 1988]**

Environsphere (1982) analyzed paired **upgradient-downgradient** ground-water **observations at** 25 **disposal sites in the U.S. Out of 4079 total observations,** 128 **downgradient** observations (3.1%) exceeded PDWS **when the upgradient well** did **not.** In addition **122 downgradient observations** (3.0%) exceeded PDWS **while at the same time upgradient observations also** exceeded **PDWS. Apparently no attempt was made to analyze** the **extent** lo which **downgradient concentrations were** higher **than upgradient but still** below PDWS. which is the typical **situation** judging from the **more detailed** site specific **studies** by A.D. Little. **Inc** (1985). **Furthermore, apparently** no **attempt** was **made to distioyish between observations where both upgradient and downgradient concentrations exceeded the PDWS but the downgradient was still higher than the upgradient concentration. Cadmium most frequently exceeded** PDWS **(10% of observations)** followed by lead **(5%)** and chromium (3%). II is **interesting that the combined percentage**

of downgradient wells exceeding PDWS (6.1%) is not far from the 7.4% in the Franklin Associates (1984) study. This indicates the perhaps half of the observations io the study could be considered to be definitely caused by ash leachate with the other half possibly caused, hut less certain.

A similar analysis of SDWS constituents found that downgradient wells exceeded the standards in 681 out of 4728 observations (14.4%) and an additional 875 observations indicated exceedance both upgradient and downgradient (185%). Downgradient, manganese most frequently exceeded the SDWS when the upgradient did not (32% of observations), followed by sulfate (28%). rod total dissolved solids (18%).

Given the observations in the ADL study (Arthur D. Little, 1985) that steady-state moditioos had not been achieved at any of the situ studied, it would appear that in the bog run the frequency of observed exceedance of drinking water standards will be higher than indicated by this study.

Also at an unspecified location id Indiana, leaching from two large, unlined ash disposal ponds resulted in downgradient concentrations of arsenic and lead about 2 times PDWS and about 4 times PDWS for selenium.

Franklin Associates, Ltd. 1984. Survey of Groundwater Contamination Cases at Coal Combustion Waste Disposal Sites. Prepared for U.S. Environmental Protection Agency. [Cited in U.S. EPA, 1988; no document number given]

This study analyzed water quality data from 4700 wells in the vicinity of ash disposal situ at 66 situ is 13 states. PDWS were exceeded in 1129 cases out of 15,000 observations (7.4% of total). Ninety two percent of the exceedances were less than 10 times the PDWS and 8 exceedances were more than 100 times the PDWS (cadmium, lead, mercury rod selenium). There were 5952 exceedances of SDWS (29.9%). Unfortunately this study made no attempt to distinguish between upgradient and downgradient wells. It only makes sense, however, that an undetermined number of the exceedances can be attributed io contamination from ash disposal

Given the observations in the ADL study (Arthur D. Little, 1985) that steady-state conditions had not been achieved at any of the sites studied, it would appear that in the long run the frequency of observed exceedance of drinking water standards will be higher than indicated by this study.

Groenewold, G.E. and B.W. Rehm. 1981. Applicability of Column Leaching Data to the Design of Fly Ash and FCD Waste Disposal Silts in Surface-Mined Areas. In: Proceedings of the Low-Rank Coal Technology Development Workshop. DOE/ET/17086-1932 CONF-81006235, pp. 3-79 to 3.95.

This study reports cm Geld monitoring of the ash disposed at the Center site in North Dakota. Natural background levels of sulfate. iron and manganese all may exceed SDWS at the site. No PDWS constituents were exceeded in natural background levels. Groundwater samples in the area influenced by the ash disposal showed concentrations or arsenic as much as 12 times PDWS and of selenium as much as 80 times the PDWS. While natural sulfate levels exceeded SDWS by a factor of 2 to 4, in the vicinity of the ash disposal the concentrations ranged from 22 to 211 times the SDWS. The maximum concentration of iron near the disposal site was 8.6 time the SDWS (compared to a natural maximum exceedance of 43 times. Maximum exceedance of SDWS by manganese increased from 55 limes SDWS (natural) lo 130 times near the ash disposal site. The chemistry of lignite ash, and spoils in North Dakota are very different from coal ash and spoils in Indiana, so the results are not directly relevant. However, it is not encouraging that the one study where good data are available on the ground-water impacts of ash disposal at a coal mine indicate dear evidence of significant deterioration of ground-water quality.

Gschwend, P.M., DA. Backhus, J.K. MacFarlane, and A.L. Page. 1990. Mobilization al Colloids in Groundwater Due to Infiltration of Water PI a Coal Ash Disposal Site. J. Contaminant Hydrology 63-7.320.

This study reports a significant discovery while studying a plant ash disposal site in the western U.S. They found that silicate colloid particles in ground-water samples taken from near the ash disposal situ had been released by the dissolution of secondary carbonate minerals by water percolating through the ash. These particles are small enough to move in suspension through pore spaces in the aquifer and may serve as a means io transport toxic elements that are sorbed io the particle surfaces. Normally suspended colloids are filtered out before ground-water samples are analyzed, because they are assumed to be local aquifer material. There is no way of knowing how commonly the phenomena observed by Gschwend et al. (1990) exists, but conventional ground-water sampling methods will fail to detect contaminants that move through aquifers by this mechanism.

Hardy, M.A. 1981. Effects of Coal Fly-Ash Disposal on Water Quality in and Around the Indiana Dunes National Lakeshore, Indiana. U.S. Geological Survey Water-Resources Investigations Report 81-16. [Cited in U.S. EPA. 1988]

At the Bailly site, near Indiana Dunes National Lakeshore, fly ash is slurried into interim settling ponds which are periodically drained and the drained ash disposed in an on-site pit. Maximum downgradient concentrations of arsenic was 4.6 times PDWS, whereas arsenic never exceeded PDWS in upgradient wells. Aluminum. boron, iron, manganese, molybdenum, nickel strontium and zinc all increased in concentration downgradient from the disposal area, but not in levels exceeding DWS.

Rai, D. and J.M. Zachara. 1989. Field Investigation of a Flue Gas Desulfurization (FGD) Sludge Disposal Site. EPRI U-5923. Electric Power Research Institute, Palo Alto. CA.

This study provides detailed data on the chemistry of pore water (pH range 6.7 to 8.2) in a FGD sludge basin at an unspecified disposal site in the Midwest. Concentrations of boron. manganese, and sulfate exceeded SDWS in pore waters. Only boron was stated in the study to have penetrated to a maximum depth of 1.5 meters into the soil below the basin. However. data in the report indicates that manganese and sulfate had also migrated into the soil pore walers. This study notes that reducing conditions in the sludge basin immobilized many toxic metals through sulfide precipitation reactions, but that these might be remobilized if drying should create oxidizing conditions in the future.

U.S. Environmental Protection Agency (EPA). 1988. Report to Congress: Waste from the Combustion of Coal by Electric Utility Power Plants. EPA/530-SW-88-002.

Where indicated, information on reports summarized above are derived from this report