The Contamination of Groundwater by Heavy
Metals From the Land Disposal of Fly Ash

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Introduction

It has been well documented that the residues of coal combustion (fly ash and bottom ash) contain enriched quantities of heavy metals and metalloids (1,2,3,4). Metals associated with fly ash have generated the most concern because of its small size diameter (.01-100 μ m in diameter) and adverse health effects when breathed. Of concern also are the water quality effects which result from common disposal practices. This report will speak to this latter problem by presenting information on the aqueous chemistry of fly ash followed by a specific case study of subsurface leaching from a fly ash disposal site. The chemistry of heavy metals in soil surrounding a fly ash disposal area is also discussed.

Chemical and Physical Properties of Fly Ash

Figure 1 gives some ranges and average values of heavy metals found in eleven different fly ashes used in this study, all of which were collected by electrostatic precipitators. It can be seen that fly ash is composed chiefly of aluminum, iron, and silica with variable amounts of calcium present also. The calcium exists primarily as the oxide, lime, as a surface concentrated mineral deposit. Figures 2 and 3 are photomicrographs of two different fly ashes, Figure 2 the residue of a "western" coal, Figure 3 for a coal mined in southern Illinois. The differences in appearance are striking. The "fuzziness" in Figure 3 is due predominantly to the surface coatings of amorphous iron ox-

FIGURE 1

FIGURE 2

FIGURE 3

ides which made up a large fraction of this fly ash. Many fly ashes have been shown to be amorphous to X-ray diffraction techniques (5).

Factors that are responsible for the location and degree of enrichment of metals on fly ash are total concentration in the coal, furnace temperature in relation to the volatility of the various metal oxides, and the geochemical matrix of the coal prior to combustion (4,6). Other important factors relative to contamination of aquatic resources are size of the particles and the method and efficiency of ash collection.

Although a certain amount of superficial similarity exists among fly ashes, it should be stressed that each one is chemically and morphologically unique. Not only is each power plant likely to produce its own type of fly ash, but the properties of the ash from a given plant will vary with time, depending upon the source of the coal being burned. Some indication of the differences among fly ashes can be illustrated by the pH effects in water. Figure 4 gives equilibrium pH values as a function of concentration for several different fly ashes used in this study. Theis and Wirth (4) found that a good indication of the ultimate acidic or basic character of a fly ash is its lime (measured by leachable Ca at low pH) and ammonium oxalate extractable iron. The lime will produce a basic reaction in water as follows,

Amorphous oxides of iron could be expected to behave as weak acids according to the reaction

FIGURE 4

Best

Figure 5 shows equilibrium pH as a function of the oxalate extractable iron - acid leachable calcium ratio (acid/base content) for several fly ashes. The assembled data represent a composite acid-base titration curve, hence the sigmoidal shape. From this figure, it appears that a ratio of approximately 3 to 1 ($\text{Fe}_{\text{ox}}/\text{Ca}$) is a delineation of the acidic or basic nature of a given fly ash.

The location of heavy metals on the ash particles is important in defining the percentage of the total amount available for release in aquatic systems. Those metals which are surface concentrated can be viewed as more immediately available while metals bound within the alumino-silicate ash matrix will be released only through long term weathering reactions. Table 1 gives some ranges and average values of surface percentages for heavy metals for several fly ashes studied. The values in Table 1 were determined by a comparison of surface washed metals by ammonium oxalate or hydroxylamine hydrochloride with amounts obtained from complete dissolution of the ash material in aqua-regia and hydrofluoric acid (7,8,9). Arsenic, which has the most volatile oxide among the metals listed, is the most surface concentrated. Evidently, arsenic undergoes virtual complete volatilization followed by condensation on the cooling ash spheres.

As would be expected, the release of heavy metals from fly ash into aqueous solution is highly variable, depending upon the factors already noted. One important determinative parameter is pH. For example, Figures 6 and 7 show ranges and averages among all fly ashes

FIGURE 5

TABLE 1

Surface Concentration of Trace Metals
on Fly Ash (Expressed as Percent of Total)
(after Theis and Wirth (4))

Metal	Range	Average
As	65-100	93
Cd	<2-58	25
Cr	15-84	44
Cu	25-75	48
Pb	5-40	8
Ni	5-42	11
Zn	10-70	30

studied for release into water for copper and cadmium. The amount released has been normalized as the fraction of the surface metal desorbed. The trend of decreasing release tendency as pH is increased was noted for all metals as shown in Figure 8 with the exception of arsenic. Release characteristics for this metal are somewhat distinct since it possesses an anionic chemistry in these experiments. As such, it forms precipitates with many trace metals, especially iron. The sudden rise in arsenic solubility at pH 12 is probably due to the unavailability of free metal ions (due to complexation with hydroxide) to cause its precipitation. Other metals precipitate in the neutral pH range, most likely as hydroxides or carbonates.

The results thus far suggest the case of greatest environmental concern to be those fly ashes which produce a low pH in the aquatic environment. Even at neutral pH values, however, significant fractions of cadmium, nickel, lead, and arsenic may be available from surface deposits. In the case of cadmium this may be of diminished importance because of its general geochemical sparcity. The high arsenic desorption at high pH may have consequences for the disposal of ashes generated from western coals which generally have large amounts of soluble lime associated with them.

Chemical Release in the Disposal Environment: A Case Study

Of the nearly 50 million tons of fly ash produced in the United States annually, only a small percentage is presently recycled or reused. Although there may yet be creative ways of disposing of this material which should be explored and encouraged, the anticipated in-

FIGURE 6

FIGURE 7

FIGURE 8

100

creased reliance upon coal in times ahead, plus evidence that many types of fly ashes (e.g., acidic forms) are simply unsuitable for most uses suggest that there will be a disposal problem of considerable magnitude into the foreseeable future.

Common disposal practice of fly ash generally involves on-site ponding followed by removal and deposition as fill. The ash is sometimes deposited as fill directly. In either case, the ash material comes into contact with water. Environmentally, subsurface leaching of water from the practice of ponding presents the greatest potential for degradation since there is more or less continuous loading of ash under essentially saturated flow conditions. The possibility of contamination by various dissolved constituents from the fly ash transported to the groundwater or a surface water exists.

A study has been undertaken on a specific ponded disposal site to determine the degree of subsurface leaching of various ionic forms, especially heavy metals. The location is the site of the Michigan City generating station of the Northern Indiana Public Service Company, Michigan City, Indiana. The plant has a generating capacity of 735 MW. The present ash ponding system was constructed and put into operation in 1974. It consists of two primary ash ponds (volume of each 16.5 million gallons) which are loaded alternately, i.e., when one is in service, the other is allowed to dry for the removal operation. The ash is sluiced to the ponds in a concentrated slurry. After primary and secondary settling the water is brought back for further ash sluicing. A constant elevation is maintained in the ponds at approximately

31.5 feet above the surface of Lake Michigan. The system cannot, however, be considered closed because of losses due to evaporation and subsurface leaching. A site layout is shown in Figure 9. The site is located within a dunal region and is underlain by a clean porous sand (effective size 0.16 to 0.18 mm, coefficient of uniformity 1.5).

The station produces 340-400 tons of fly ash per day, when operating at full capacity. A typical pond cycle required six to nine months between removal periods. The dominant coal used was from southern Illinois, although low sulfur coal from Wyoming was used occasionally to meet prevailing SO_2 emission standards. The chemical composition of the fly ash was variable, however a representative analysis is given in Table 2.

Observation wells were installed at various locations as shown in Figure 9. Samples were taken at monthly intervals, weather permitting. Details of the sampling and analysis procedures can be found elsewhere (10). Data presented in this study are primarily from primary pond one, which was being actively loaded with fly ash. Hydrologic analysis indicated that wells 2, 3, 10, 18, 13 and 15 were situated linearly along the flow path from the pond. The pond leachate was found to intercept the prevailing groundwater at approximately 150 meters from the pond, the location of well 13.

Typically, the chemical composition of the groundwater varied with both time in the pond cycle as well as distance from the pond. An example of the latter phenomenon can be seen for macro-ionic species concentrations given in Table 3. Well 18 is within the zone of pond

FIGURE 9

TABLE 2

Composition of Fly Ash at Michigan City
(after Theis, et al., (10))

Component	Concentration
Al_2O_3	30.2%
SiO_2	25.9%
Fe_2O_3	39.5%
CaO	2.9%
As	1200 $\mu\text{g/g}$
Cd	19 $\mu\text{g/g}$
Cr	320 $\mu\text{g/g}$
Cu	350 $\mu\text{g/g}$
Hg	24 $\mu\text{g/g}$
Mn	600 $\mu\text{g/g}$
Ni	600 $\mu\text{g/g}$
Pb	1120 $\mu\text{g/g}$
Se	88 $\mu\text{g/g}$
Zn	3300 $\mu\text{g/g}$

leaching, while well 15 (350 meters from the pond) is not. Well 13 shows the transition of water quality from a dominance by calcium, sulfate, and sodium, to carbonate (as measured by alkalinity). It is reasonable to assume that a similar transition occurs as the leachate intercepts the lake on the opposite side of the pond.

Heavy metal concentrations also displayed a variation with distance of less obvious causes. Figure 10 shows the concentrations of several metals as a function of distance from the pond for a specific sampling date. There is a rapid attenuation of metals from the rather high levels found in the pond followed by peak concentrations some 100 meters from the pond. This was found to occur at other sampling times also. It is easier to conceptualize the causes of these fluctuations if a concentration-time type of graphical approach is used as in Figure 11. Here the concentrations of several metals are shown as a function of time within the cycle of pond one. Of special note is the "events" axis at the bottom of the figure. Peak concentrations were found to occur twice during this particular pond cycle, once at the start of pond filling and once following a prolonged shut down of two generating units which were started up simultaneously. Pond filling produced a higher ash concentration per unit volume of pond water, while the start-up of a sizeable portion of the generating capacity brought about a large increase in the ash loading rate. Normal, or steady-state, pond operation generally resulted in lower concentrations of heavy metals. The dominant mechanisms of attenuation are adsorption of metals onto hydrous oxides of iron and manganese and precipitation of various solid phases (10).

TABLE 3

Macro-Ionic Composition of Water at
Wells 18, 13, and 15 for 1/4/77
(all values in mg/l)
(after Theis, et al., (10))

Specie	Well 18	Well 13	Well 15
Na ⁺	52	7.5	16
K ⁺	24	8.2	13.6
Ca ⁺²	424	96	166
Mg ⁺²	41	17	25
Alkalinity (as CaCO ₃)	8	80	478
SO ₄ ⁻²	1250	210	28
Cl ⁻	65	2.5	7.5
Fe	2.25	0.14	4.5
Mn	1.48	0.03	0.60
Si	4.60	2.85	9.0
pH	7.0	6.9	6.5

FIGURE 10

WELL No.18 METAL CONCENTRATIONS vs. TIME

FIGURE 11

The quantity of seepage from the pond is governed by the hydraulic gradient and the equivalent coefficient of permeability of the stratified fly ash-soil system. Since the water level in the settling pond is controlled by an overflow weir, seepage from the pond can be analyzed as a constant head problem. The equivalent coefficient of permeability of the fly ash-soil system is not constant, however, but changes as the fly ash is deposited in the settling pond.

The equivalent coefficient of permeability of a two-layer system in which the flow is perpendicular to the layer boundary is given by (11):

$$k_{eq} = \frac{d_1 + d_2}{\frac{d_1}{k_1} + \frac{d_2}{k_2}}$$

where k_{eq} is equivalent coefficient of permeability,

d_1 and d_2 are layer thicknesses, and

k_1 and k_2 are the respective coefficients of permeability of the layers.

An analysis of this equation will show that if k_2 is one or two orders of magnitude less than k_1 , d_1 is constant and d_2 varies from zero to a maximum value, then k_{eq} decreases rapidly for initial increments of d_2 and approaches k_2 asymptotically at higher values of d_2 . These conditions are approximated in a fly ash settling pond.

The coefficient permeability of the dune sand is estimated to be 0.1 cm/sec based on effective size (12) and correlation with the type of soil deposit (13). The coefficient of permeability of the fly ash is estimated from the Hazen formula to be on the order of magnitude

of 10^{-3} cm/sec (13). The equivalent permeability of the fly ash-soil system varies from 0.1 cm/sec (no fly ash deposit) to 1.4×10^{-3} cm/sec when the fly ash in the pond is 12 ft. (3.66 m) deep. This calculation considers d_1 , the thickness of the soil, to remain constant at 5 ft. (1.52 m), the approximate depth from the bottom of the pond to the static groundwater level. The quantity of discharge per unit area of pond will decrease as the pond fills with fly ash as both the equivalent coefficient of permeability and the hydraulic gradient decrease.

The hydraulic gradient as measured in wells adjacent to the pond is 2.5×10^{-2} . The gradient beneath the pond is estimated to be one order of magnitude greater than this or 2.5×10^{-1} . The quantity of seepage at the conclusion of the pond filling is then

$$Q = 3.97 \frac{\text{ft}}{\text{day}} \times 2.5 \times 10^{-1} = 0.99 \text{ ft}^3/\text{day}/\text{ft}^2$$

or 122,000 ft^3/day (.9 mgd) from the pond.

At the beginning of the pond filling period, the rate of seepage is (with 0.5 ft. of fly ash)

$$Q = 28.3 \text{ ft}/\text{day} \times 2.5 \times 10^{-1} = 7.08 \text{ ft}^3/\text{day}/\text{ft}^2$$

or 870,400 ft^3/day (6.5 mgd).

This seepage rate is greater than the pumping rate of sluice water to the settling ponds which indicates that until the fly ash deposit on the bottom of the pond reaches 1 to 1.5 ft. (.32 to .49 m), all of the sluice water leaves the pond by seepage. This assists in explaining the high concentration pulse at the start of pond filling.

If the pond fills with fly ash in approximately 6 months, the seepage rate for the first two weeks is the same rate as sluice water is pumped to the ponds (measured as 2.85 mgd). Once the fly ash layer is approximately 1 ft. thick, the seepage rate averages approximately 1 mgd for the remainder of the filling period. This analysis is presented graphically in Figure 12 for seepage rate as a function of time within the pond cycle. The curve is only approximate but accurate at significant points. When this analysis is applied to the concentrations of metals measured in the ash leachate with time (Figure 11) it is possible to estimate the total amounts of metals leaving the system via subsurface leaching. A generalized representation is given in Figure 13 for any ion, Me, measured during the cycle of primary pond one of this study. Peak metal discharge occurs at pond start-up while the local rise at three months is related to the bringing on-line of generating units which had been undergoing maintenance.

The Chemistry of Heavy Metals at Fly Ash Disposal Sites

As a result of this investigation, it is possible to comment on some of the important factors regulating the transport of heavy metals at ash disposal sites. It is clear that the heavy metals sorbed on the surface of the fly ash particles are held loosely and are solubilized rather easily in aqueous solution. Although the specific surface area of fly ash can be quite high, the equilibrium sorptive capacity relative to the quantities of metals present must be considered low. The degree of desorption of heavy metals is dependent on solution pH, becoming less pH increases. Arsenic desorption is an exception, showing significant increases at high pH. Because of the high temperatures under which

FIGURE 12

FIGURE 13

fly ash is formed, the alkalinity of ash pond waters is very low. Thus, the solubility of the metals is regulated by their respective hydroxides. The importance of this lies in the fact that the heavy metal hydroxides are generally more soluble than the carbonates.

If the metal-laden ash pond waters are allowed to leach into the surrounding soil a number of reactions can take place affecting metal transport. In this study, even though the prevailing soil consisted of silica which has a low sorptive capacity for most heavy metals, significant attenuation occurred as the leachate moved through the soil. A comparison of total bound metals in the soil (as determined by coring followed by appropriate analysis) with typical soluble metals found in observation wells shows that the soluble fraction generally accounted for less than one percent of the total. Some representative data are shown in Table 4.

The reactions which are most responsible for this attenuation phenomenon are precipitation and adsorption. Figure 14 shows the thermodynamic speciation of copper as a function of distance from the ash pond as determined by program REDEQL2(14). For this metal the formation of malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) is the major controlling reaction, adsorption being of lesser importance. For other metals, adsorption can be more significant. Results of similar analyses for other metals studied are given in Table 5. Those metals which were removed through adsorption show the dominant sorptive reservoir to be iron oxide. Although some of the iron at the site is present naturally, the possibility exists that significant quantities of the iron are supplied by the leachate itself.

TABLE 4
Particles and Soluble Metals in
Soil-Water System at Michigan City*

Metal	Particulate ($\mu\text{g/g}$)	Soluble ($\mu\text{g/L}$)	% Soluble ⁺
Arsenic	4.12	29	0.28
Cadmium	0.48	3.4	0.28
Chromium	13.0	12.0	0.04
Copper	12.6	275	0.87
Lead	8.8	50	0.23
Nickel	24.4	410	0.67
Zinc	26.2	480	0.73

*Data for 10/18/76 sampling date at Well #18. Data for other wells and dates do not differ substantially.

⁺Computed using an average void ratio of 0.5.

TABLE 5

Dominant Particulate Forms of Heavy
Metal in Leaching Field at Michigan City

Metal	Forms
Cadmium	Cd-Fe, Cd-Mn
Chromium	Cr(OH)_3 , Cr-Fe, Cr-Si
Copper	$\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s})$, $\text{Cu}_2(\text{AsO}_4)_2(\text{s})$, Cu-Fe, Cu-Mn, Cu-Si
Lead	$\text{Pb(OH)}_2(\text{s})$, Pb-Fe, Pb-Mn, Pb-Si
Nickel	Ni-Fe, Ni-Mn
Zinc	Zn-Fe, Zn-Mn

The iron associated with the fly ash is released in the low pH of the pond environment and deposits in the soil where conditions are more favorable for precipitation. Thus, although the case of acidic fly ashes are perceived to be the most potentially harmful, to the extent that iron oxides are present they may provide simultaneously a control mechanism for certain heavy metals.

Regardless of which mechanism controls the chemistry of specific heavy metals in the subsurface environment, the extent of both adsorption and precipitation are strongly dependent on pH and to a lesser extent on other solution parameters. Variations in solution chemistry induced by variable pond loading procedures are seen as responsible for the peaks of heavy metals found in the leaching field and shown in Figures 10 and 11 of this report. The particulate-soluble metal equilibrium is influenced by the high particulate to soluble ratio in the soil-water system. Relatively minor changes in solution conditions can create comparatively large perturbations in soluble metal concentrations. The extent of influence of a given change of solution conditions emanating from the fly ash pond is large at the site studied because of the unbuffered nature of the water and soil. Other soils could be expected to give different results.

Proposal for Future Study

The large number of influencing parameters associated with metal migration at fly ash disposal sites underscore the difficulty of making generalizations about the environmental problems associated with the disposal process. The complexity of the system can bring about very subtle changes which are difficult to access without a suitable model capable of

taking into account the reactions involved. Such a model must be capable of describing both hydrodynamic transport and chemical reactivity of a component in the system. Present groundwater flow models do not appear applicable to such a system predominantly because of their lack of a suitable description of the chemical reactions involved.

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