MASTER

THE CONTAMINATION OF GROUNDWATER BY HEAVY METALS FROM THE LAND DISPOSAL OF FLY ASH

Final Report

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Abstract

This report provides information on laboratory and field research to assess the aquatic effects and extent of release, migration, and attenuation of trace metals from fly ash into subsurface soil environments for a typical disposal regime. Those metals analyzed for were arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc.

Laboratory studies indicated that the major effects of fly ash in water were pH alterations, which could be either acidic or basic, and comparatively high proportions of trace metals released from the ash surface, controlled largely by pH. Field studies confirmed the continued importance of pH in defining the attenuation of the metals by the soil but also suggested that pSO_4 , ionic strength, and soil chemical parameters, such as iron and manganese content, could not be ignored. Theoretical thermodynamic analysis in concert with field data indicated that both adsorption onto soil phases and precipitation of metal phases occurred, the dominant attenuation mechanism depending upon the specific metal and soil conditions.

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Section I

OBJECTIVES OF RESEARCH

The objectives of this research were threefold:

1. To document the behavior and note the effects of power plant fly ash on aqueous systems, especially the release of various heavy metal species.
2. To monitor the subsurface movement of trace species around an existing active ash disposal pond.
3. To characterize the mechanisms of interaction between dissolved leachate components and the soil medium in the field with respect to adsorption, precipitation, and soluble complex formation reactions.

Section II

SCOPE OF ACTIVITIES

II-1 Summary of Work Schedule

The work performed under this contract can be divided into three chronological periods corresponding to different methods of data acquisition and analysis. Initially, and for approximately 12 months, efforts focused on laboratory studies of the aqueous chemistry of power plant fly ash, especially solution effects of surface deposits. The next 12 months were devoted to field work on subsurface trace metal migration around an active disposal pond. The final period dealt with field data analysis primarily through the application of equilibrium calculations to the soil/solution leachate system. This analysis was facilitated through the use of the digital computer.

II-2 List of Publications

The following publications reported on the results of this research effort:

Theis, T.L., "The Potential Trace Metal Contamination of Water Resources Through the Land Disposal of Fly Ash," proc. 2nd National Conference on Complete Water Reuse, AIChE, 219-224 (May, 1975).

Theis, T.L., and J.J. Marley, "Sorptive Characteristics of Heavy Metals in Fly Ash-Soil Environments," proc. 31st Purdue Industrial Waste Conference, 312-324 (May, 1976).

Theis, T.L., and J.L. Wirth, "Sorptive Behavior of Trace Metals on Fly Ash in Aqueous System," Environmental Science and Technology, 11, 1096 (Nov., 1977).

Theis, T.L., J.D. Westrick, C.L. Hsu, and J.J. Marley, "Field Investigations of Trace Metals in Groundwater from Fly Ash Disposal," Journal of the Water Pollution Control Federation 50, 2457 (Nov. 1978).

Theis, T.L., and J.J. Marley, "Environmental Considerations for Power Plant Fly Ash Disposal," Journal of the Energy Division, ASCE, 105, No. EY1, Proc. paper 14286, 47-61, (Jan. 1979).

Theis, T.L., and R.O. Richter, "Chemical Speciation of Heavy Metals in Power Plant Ash Pond Leachate," Environmental Science and Technology, 13, 219 (Feb., 1979).

Section III

RESULTS AND DISCUSSION

III-1 Introduction

Recent studies have addressed the subject of the biogeochemical cycling of trace elements associated with coal within and in the vicinity of combustion or utilization processes (1,2,3,4,5,6). The principal industry of interest has understandably been the electric utilities and most of the above studies have centered on fossil fuel generating stations.

Within these systems there are two major sources of trace contaminants to the local environment, stack gases and fine metallic aerosols not removed by control equipment, and the ash residues of the combustion process. These residues are made up of particles collected by control equipment (fly ash) and left behind on furnace gratings (bottom ash). Most studies have shown those elements which display a volatile behavior (such as mercury) are lost primarily in stack gases while others are concentrated on the fly ash particles.

In 1975, approximately 36 million tons of fly ash were produced in the United States (7). The disposal of this material is normally achieved by temporary ponding (usually on site) followed by mining and subsequent depositions as fill material. Occasionally the ash is used as fill directly. Although large pressures exist for disposing of the material in more useful and creative ways, no consistent utilization trend is evident and, in fact, it appears that stockpiles of fly ash will continue to grow as reliance upon coal as a fuel source increases (8). Thus, large amounts of this material are brought into contact with soil and water environments.

It has been shown that fly ash consists of many small (0.01-100 μ diameter) glass-like particles of a generally spherical character (6) (9). During the combustion process many different metal oxides become concentrated on

the ash spheres forming a surface coating. The composition of this coating is highly variable from ash to ash and is primarily responsible for the alteration of aquatic solution conditions.

III-2 Laboratory Studies

The aim of the laboratory phase of this study was to define those chemical parameters of fly ash which are important in characterizing the release of trace metal contaminants into aqueous solution.

Natusch et al. (10), although finding evidence for certain crystalline compounds (such as mullite, hematite, and magnetite), have shown that the components of fly ash are largely amorphous to X-ray diffraction techniques. Fisher et al. (9), in a series of excellent photomicrographs, found evidence of crystal formation on the surface of ash particles but only after a period of aging. The amorphous character of fly ash surface suggests that certain chemical extractants could give some useful information about surface-sorbed trace metals.

Three extraction procedures were chosen for analysis of the ash materials. Dried pre-sieved (200 mesh) subsamples of eleven different fly ashes were subjected to a digestion procedure involving dissolution in hydrofluoric acid and aqua regia (according to the method of Bernas (11)). The values reported were taken to be total metals in the ash. A second extraction was made with ammonium oxalate (according to McKeague and Day, (12)). This procedure attacks only X-ray amorphous oxides of iron, aluminum, and manganese. A third extraction with hydroxylamine hydrochloride at pH = 3 (according to Chao (13)) was more selective for manganese oxides giving little iron and aluminum. Through a comparison of the trace metals released by these latter two extractions it was often possible to determine the oxide sink with which

they were associated. Further comparison with the digested portion allowed for an assessment of what could be termed an available fraction of metals for subsequent release in aquatic systems.

A second series of experiments involved washing various fly ashes in distilled water at pH's of 3, 6, 9, and 12. The procedure consisted of allowing a 200 gram/liter solution of each fly ash at each pH to equilibrate for 24 hours on a shaker table. pH adjustments were made with sodium hydroxide and perchloric acid as needed. At the end of the period samples were centrifuged, filtered through .45u and analyzed for trace metals released.

A final series of experiments designed to measure the quantity and form of mercury was made. This was necessitated by the volatile character of mercury. Shake tests similar to those described above only without pH adjustment were done in closed vessels to prevent escape of mercury vapor.

All metal analyses were performed using atomic absorption spectrophotometry.

Figure 1 indicates the relative distributions of the total metallic components among the fly ashes studied as determined by complete digestion. Not unexpectedly there is considerable variability, however, it is apparent that aluminum, iron, and silica are the major components. This confirms other literature reports which classify fly ash generally as an amorphous ferro-aluminosilicate mineral. Calcium concentrations, while high in some cases, are due primarily to surface deposits of calcium oxide. Trace element concentrations also display great variability but ranges are in agreement with other published reports. It appeared that ashes generated from "western" coals contained lower levels of trace metals.

Among the major effects which fly ash has on the aquatic environment are changes in pH. Figure 2 indicates some pH changes as functions of fly ash concentration. Near maximum pH change is attained within the concentration

FIGURE 1: Total Metal Analysis of the Fly Ashes. Bracketted Lines Represent Ranges, Dots Are Average Values (see Table 1 for further information).

FIGURE 2: Representative pH vs. Concentration Relationships for Fly Ash in Distilled Water.

range of 1-2 grams/liters. As shown, the change may be either basic or acidic. Only one of the ashes studied exhibited what could be considered a neutral reaction, and this ash had previously been ponded thereby having leached out pH altering substances. Several factors associated with the fly ashes were investigated to determine those most responsible for bringing about the pH change. Those properties which appeared to be most responsible were oxalate extractable (amorphous) iron and water soluble calcium (at pH = 3). Figure 3 shows equilibrium pH as a function of the oxalate-iron to calcium ratio. It can be surmised that oxalate iron is a measure of at least a portion of the acid content while soluble calcium, which is associated with the lime fraction, represents the basic components of fly ash.

The general reactions can be represented as:

The sigmoidal dotted line of Figure 3 is reminiscent of an acid-base titration curve and indeed the assembled data represent a composite description of such a system. From Figure 3 it appears that a ratio of 3 to 1 (Fe to Ca) is a rough delineation of the ultimate acidic or basic character of the fly ash.

It is important for comparative purposes to determine total metals as given in Figure 1. However, a more relevant consideration is the available fraction of these metals to the aquatic environment. Those metals locked within the silica matrix of the fly ash particles will be released only through the action of long term weathering processes while surface deposits will be more active chemically. For this reason selective extracts of the ashes were made.

Figure 4 summarizes the amounts of aluminum, iron, and manganese found for the oxalate and hydroxylamine extracts. Two factors are apparent, First, although a very large fraction of the fly ash consists of aluminum

FIGURE 3: Composite pH vs. Oxalate Iron-Soluble Calcium Ratio.

FIGURE 4: Ranges and Averages of Extractable Oxides of Iron, Aluminum, and Manganese for Oxalate and Hydroxylamine Washes.

and iron, only a portion is released by oxalate extraction. Also, in nearly all cases, the oxalate extractable aluminum was considerably less than the iron. Since these oxides have approximately the same sorbtive capacities, this factor tends to favor the role of iron over aluminum in controlling sorbed trace metals. Secondly, a comparison of hydroxylamine extracts with oxalate extracts indicates a general decrease for all three metals in the NH_2OH . However, this decrease is greatest for aluminum and iron and considerably less for manganese. Thus, there is a relative increase in the influence of manganese for the NH_2OH extracts. In spite of the small amounts of manganese compared with iron, its presence is important since the sorbtive capacity of MnO_2 is reported to be 15 - 30 times that of iron oxide.

Table 1 summarizes the trace metal digestive data contained in Figure 1 plus extracts with oxalate and hydroxylamine reagents. By noting relative increases or decreases of each metal in the chemical washings plus the absolute amounts of iron, aluminum, and manganese the primary surface deposit with which each trace metal is associated was inferred. This information is given in Table 2 for each fly ash and each trace metal studied.

In Table 2 blank spaces indicate an indeterminacy of the method while two sinks for the same metal indicate an inability to differentiate further. In spite of the wide ranges of values reported in Table 1, a clear and consistent pattern of association of trace metal with sink among all the fly ashes emerges. It is not surprising, in view of the abundance of iron associated with most fly ashes, that the amorphous oxides of iron should exert the primary controls on most of the metals and ashes studied. It is noteworthy, then, that cadmium, nickel, and to some extent lead exhibit a preference for the manganese portion of the surface coating on most of the ashes. Only in fly ash #2, where large amounts of amorphous surface oxides of aluminum were present, were the oxalate

TABLE 1

Trace Metals in Fly Ash(all values in $\mu\text{g/g}$ of fly ash)

Metal	HF - HNO_3			Oxalate			Hydroxylamine Hydrochloride		
	Range	Mean	Std. Deviation	Range	Mean	Std. Deviation	Range	Mean	Std. Deviation
Arsenic	6-1200	157	348	5-1000	146	302	0.5-12	4.5	4.2
Cadmium	5-20	8.1	3.9	0.1-2	1.0	0.6	0.1-11	2.0	3.4
Chromium	44-320	109	77	22-250	48	70	1.5-85	15	24
Copper	28-350	97	95	10-170	47	51	1.5-93	16	27
Lead	30-1120	157	320	2-55	12	15	1.0-58	11	17
Nickel	90-600	220	138	10-105	24	29	4.8-76	21	22
Zinc	100-3300	515	933	24-1200	156	351	4.5-600	67	177

TABLE 2

Major Surface Deposit Association for
Trace Metals on Fly Ash

Metal Fly Ash	As	Cd	Cr	Cu	Ni	Pb	Zn
1	Fe	Mn	Fe	Fe	Mn-Fe	Mn	Fe
2	Al	Mn	Al	Al	-	Mn	Al
3	Fe	-	Fe-Mn	Fe-Mn	Mn	Mn	Fe-Mn
4	Fe	Mn	Fe	Fe	Mn	Fe-Mn	Fe
5	Fe	-	Fe	Fe	Mn	Fe	Fe
6	Fe	Mn-Al	Fe	Fe	Fe-Mn	Fe	Fe
7	Fe	Mn	Fe	Fe	Mn	Fe	Fe
8	Fe	Mn	Fe	Fe	Mn	-	Fe
9	Fe	Mn	Fe	Fe-Mn	Fe-Mn	Mn	Fe-Mn
10	Fe	Mn	Fe	Fe	Mn	Mn	Fe
11	-	Mn	Fe	Fe	Mn	-	Fe

Key: Fe - Iron Oxides
 Al - Aluminum Oxides
 Mn - Manganese Oxides

extractable trace metals attributed to this sink. This ash had an unusually high amount of aluminum (20% by weight as Al).

The information contained in Table 2 is not meant to differentiate a specific mechanism such as adsorption or entrapment of the trace metals by metal oxides during combustion. The techniques used only imply an association between trace metal and oxide sink which could be expected to exert an influence on the behavior of the ash with respect to metal release patterns in aqueous solution. The amounts released are taken to be more realistic of the available fraction of metals over the short term than total metals as given by complete digestion.

Since oxalate and/or hydroxylamine washes make soluble only the surface metals associated with the ash, an estimation of the degree of surface concentration for each metal can be made through comparison with the more complete hydrofluoric-strong acid digestion. Data are summarized in Table 3.

Kaakinen *et. al.*, (3) have suggested that the melting and boiling points of the metallic oxides correspond to the overall degree of enrichment in particulate residues of power plants, those oxides which are more volatile displaying the greater enrichment. Undoubtedly the furnace environment ultimately favors formation of the oxides of the metals in question. In addition, the mineralogical associations of the trace metals prior to combustion could be expected to affect the distribution of elements within and around the ash particles also. The geochemical composition of the ores in coal seams is likely very complex. In view of the general abundance of sulfur, silicon, and carbonate it would appear that the pyrites, silicates, and carbonates of the metals are present. Carbonates could be expected to decompose to the respective metal oxide at relatively low temperatures ($<500^{\circ}\text{C}$). The boiling point of the metal sulfides is generally somewhat higher (800°C - 1350°C) although these too are unstable in the presence of oxygen. Metal silicates, while more

TABLE 3

Surface Concentration of Trace Metals on Fly Ash

(expressed as percent of total)

Metal	Range	Ave
Arsenic	65-100	93
Cadmium	<2-58	25
Chromium	15-84	44
Copper	25-75	48
Lead	5-40	8
Nickel	5-42	11
Zinc	10-70	30

volatile than the oxides, are nevertheless quite stable in the temperature range of power plant furnaces (1400 - 1600°C) and would not be expected to volatilize to any appreciable extent. Thus it is suggested that the relative amounts of trace metals within and on the surface of ash particles is due primarily to the distribution of the metal among the various mineral forms prior to combustion.

The consistently high degree of surface concentration of arsenic with iron can be explained by noting its probable existence as an arsenical pyrite. Both sulfides of arsenic and iron are volatile and thus could be expected to condense on the surface of cooling ash particles. In contrast Garrels and Christ (14) point out that manganese could be expected to exist as an oxide since MnS forms only under extreme conditions of high sulfur and low oxygen availability. As such, it is very non-volatile (m.p. 1705°C) and could be expected to be more distributed throughout the ash. Chemical extraction in this study found an average of 24% of the manganese on the surface.

Further clarification of the short term release of trace metals was obtained by subjecting the fly ashes to variable pH washings. Table 4 presents these data again in terms of ranges and averages. These data are summarized graphically in Figure 5. Here the desorption at each pH has been normalized by making a ratio of average amount released to total average amount on the surface as determined by chemical extraction and given in Table 1. In Figure 5 it is possible to discern the relative tendencies of the metals to desorb from their respective sinks. The U-shaped curves generated are suggestive of a solubility controlled reaction, the extent of solubilization of the oxides determining the degree of desorption of trace metals from the fly ash surface. This is not completely the case, however; for instance, zinc, which is quite soluble in the solutions generated, is nevertheless very poorly desorbed in the neutral pH range. Lead is relatively insoluble and yet is released to a greater extent

TABLE 4

Metal Release at Various pH(all values $\mu\text{g/g}$ of fly ash)

Metal \ pH	3		6		9		12	
	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.
Arsenic	3 -325	51.9	0.1-8.0	1.0	0.1-4.8	0.80	1.0-650	72.9
Cadmium	<.1-5.5	1.1	< .1-2.75	.41	< .1- .9	0.15	< .1-.75	.18
Chromium	1.5-23.5	9.4	< .1-8	1.9	< .1-7.5	2.0	.5-10	2.4
Copper	5 -52	15.6	< .1-1.75	.82	< .1-1.0	.36	.5- 1.5	.59
Lead	0.5-60	9.1	< .5-5.5	1.4	< .5-3.0	.73	<.5- 3.0	.91
Nickel	1.8-35	11.7	.1-6.5	3.6	< .1-2.5	.50	.1- 1.2	.61
Zinc	5.8-112	25.7	0.1-75	8.3	< .1- .9	.26	<.1-16	1.7

FIGURE 5: Average Release of Heavy Metals from Fly Ash in Water as a Fraction of the Surface Available Metals vs. pH. Fly Ash Concentration Equal to 200 g/l (see Table 4 for absolute values).

than other more soluble species. In several instances the absolute concentrations measured were in fact in excess of simple solubility predictions. Large amounts of both chloride and sulfate are typically released by fly ash and it is probable that soluble inorganic complexes are formed.

The choice of 200 grams of ash per liter of solution for these experiments is arbitrary. It represents a middle concentration between small amounts of ash which find their way into watercourses (as, for example, in lake sediment sealing operations) and large disposal ponds where the concentration could be much higher. Values in Table 4 and Figure 5 have been normalized per weight of ash. Although the amount of metals released per unit weight could be expected to vary somewhat with concentration, the effect should become less pronounced as concentration increases. Maximum pH effects were shown previously to be at 1 - 2 grams per liter of fly ash.

The case of arsenic is somewhat distinct since it possesses an anionic chemistry under the conditions present. As such it forms predipitates with many trace metals, especially iron (solubility product of $\text{FeAsO}_4 \cdot 1.8 \times 10^{-20}$ (19)). The sudden jump at pH 12 in arsenic release is probably due to the unavailability of free metal ions to cause its precipitation.

Experimental work with mercury was difficult because of its presence in many cases as the elemental vapor. This problem was alleviated by allowing the fly ash water mixture to equilibrate in a closed system. Using flameless analysis by atomic absorption the amount and form (Hg^0 or Hg^{+2}) of mercury released could be determined. This was done by noting the absorption initially in the absence of a reducing agent (SnCl_2) giving the volatile form of mercury followed by the absorption after SnCl_2 addition which yielded total mercury. The difference was attributed to inorganic mercuric ion. Results are shown in Figure 6 for each of the ashes studied. Regardless of form, only very small amounts of mercury are released in the duration of the studies. In comparison with the total amounts given in Figure 1 it can be concluded that very little

FIGURE 6: Release of Mercury from Fly Ash According to Chemical Form. Numbers Above Columns Refer to Equilibrium pH.

of the mercury is surface concentrated. This finding is consistent with those of Klein et al., (1) who determined that most of the mercury in coal is lost out the stack. Both forms of mercury were detected in solution, however no correlation with ash properties, such as pH, could be found.

III-3 Field Studies

Field studies were conducted at the coal-fired Michigan City Generating Station of the Northern Indiana Public Service Company. This station has a generating capacity of 735 MW. Of special interest is a newly constructed 520 MW unit which went into service in 1974.

Figure 7 gives a schematic site layout of the ash ponding facilities located on site (numbers refer to the sample wells and borings which were made as part of this study). The system consists of two sets of ash ponds, each containing a primary and a secondary settling unit. Each primary pond has a volume of 62,000 cubic meters (16.5 million gallons). Under normal operating conditions, each set of ponds are used in an alternate fashion, i.e. while one primary pond is being filled the other is allowed to dry for the removal operation. Pond water overflow is recycled during the ash sluicing process. Each pond cycle is from 6 to 9 months in duration. These ash ponds were constructed and put into operation concurrently with the latest plant expansion (early 1974).

The site is located within a dunal region adjacent to Lake Michigan. Pond elevations, when full, are 9.6 meters (31.5 ft.) above the lake datum. The area is underlain by a clean, porous sand of considerable uniformity. Sieve analyses made from several of the borings on site are shown in Figure 8. The effective size varied between 0.16 to 0.18 mm and the coefficient of uniformity was approximately 1.5.

During this study, the Michigan City Generating Station burned coal mined in southern Illinois. Quantities of fly ash produced varied but averaged 340-400 tons/day.

FIGURE 7: Fly Ash Pond Site Layout
 (approximate scale 3000:1)

FIGURE 8: Sieve Analyses for Representative Soil Samples from Disposal Site

A series of twenty-one 2-inch sampling wells were installed during the year in and around the power plant site. These are located in Figure 7. As a rule, wells were drilled to a depth of 1.5 to 2.5 meters (5 - 8 ft.) beneath the groundwater table. The well casings are PVC pipe which is slotted for the portion beneath the water level. Wells were capped and sealed between sampling periods. In addition, soil samples were taken at each half meter depth and saved for later analysis.

An effort was made to adhere to a monthly sampling schedule. However, the unusually severe weather conditions during the winter of 1976-77 made the site inaccessible for long periods of time and so this schedule was necessarily compromised. A typical sampling regime consisted of the following steps:

- (1) measurement of groundwater surface elevation,
- (2) initial pumping of the well to remove standing water,
- (3) removal of approximately one liter of new water from well and division into two equal aliquots,
- (4) immediate acidification to pH 5 (using acetic acid) of one aliquot to prevent oxidation of ferrous iron,
- (5) immediate measurement of temperature, pH, and oxidation reduction potential of the other aliquot,
- (6) filtration of both aliquots (.45 μ m),
- (7) further acidification of the first aliquot to pH -1 with perchloric acid.

Samples were transported back to the laboratory and stored under refrigeration prior to analysis. The unacidified sample was analyzed immediately for alkalinity, chloride, orthophosphate, calcium, and total hardness. Procedures as given in Standard Methods (15) were used.

Trace metals were determined on the acidified aliquot by flameless atomic absorption. A summary of all analyses and methods is given in Table 5.

Analysis for mercury was discontinued shortly after the beginning of monitoring

TABLE 5
ANALYTICAL METHODS FOR GROUNDWATER COMPONENTS

Species	Method	Ref.
Na ⁺	atom. abs.	16
K ⁺	atom. abs.	16
Ca ⁺²	EDTA titrimetric	15
Total Hardness	EDTA titrimetric	15
Alkalinity	H ₂ SO ₄ titrimetric	15
SO ₄ ⁻²	turbidimetric	15
Cl ⁻	argentometric	15
PO ₄ ⁻³	ascorbic acid	15
Al	atom. abs.	17
As	atom. abs. - Ni	18
Cd	atom. abs.	17
Cr	atom. abs.	17
Cu	atom. abs.	17
Hg	atom. abs.	19
Mn	atom. abs.	17
Ni	atom. abs.	17
Pb	atom. abs.	17
Se	atom. abs. - Ni	18
Si	atom. abs.	17
Zn	atom. abs.	17
Fe ⁺²	bathophenanthroline	20
Fe _T	atom. abs.	17

since levels were consistently beneath the detection limit ($0.2 \mu\text{g/l}$).

In general, ferrous iron determinations agreed closely with total iron due to the insolubility of iron III at the pH values encountered.

Soil samples obtained during the drilling of wells were analyzed for total component concentrations according to the method of Bernas (11). In this procedure, the sample is digested under heat and pressure in aqua regia/HF and analyzed. Those trace metals given in Table 5 were determined again by atomic absorption.

Soil grain size analyses were made in accordance with ASTM D 422, Particle-Size Analysis of Soils (21). Grain size distribution curves for some soil samples recovered from depths 1.5 to 2 meters below ground surface are shown in Figure 8.

Coefficient of permeability was estimated using published correlations of effective grain size, D_{10} , and coefficient of permeability, k (e.g. Leonards (22)). The D_{10} of these uniform sand soils is approximately 0.2 mm and the coefficient of permeability 0.1 cm/sec.

The hydrologic characteristics of the disposal site are of considerable importance in assessing the movement of dissolved constituents in the groundwater. The seepage of water from the ponds alters the flow of groundwater in a significant fashion in the general vicinity. Figure 9 shows typical flow lines around pond one. The prevailing groundwater flow is, of course, toward the lake. The pond, however, brings about a counter flow which extends outward a distance of 100-150 meters. This effect is illustrated more clearly in Figure 10 which gives a three dimensional view of the groundwater surface when the pond is full. It is possible to see a "saddle point" where the pond flow and the natural groundwater flow meet. Well numbers 18 and 13 (Figure 7) were located as close as possible to this point. This information is important for two reasons. First, the extent of the pond influence determines

FIGURE 9: Flow Lines Around Ash Pond Number One for Oct. 18, 1976 Sampling Day

3/18/77

15:47:20

GKAFL3C

FIGURE 10: Three Dimensional View of Prevailing Groundwater Surface for Oct. 18, 1976. Lake is to the left.

the approximate path length of seepage water. This is important in determining the ultimate degree of attenuation of dissolved species. Secondly, the ground-water chemical characteristics change abruptly at this point. As will be seen, such a change can bring about significant alterations in trace metal forms.

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:

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

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 (22) and correlation with the type of

soil deposit. 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. (23). 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 decreases.

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 $122,000 \text{ ft}^3/\text{day}$ (.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 $870,400 \text{ ft}^3/\text{day}$ (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 (see Fig. 15). 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 11 for seepage rate as a function of time within the pond cycle. The curve is only approximate but accurate at significant points.

An analysis of the fly ash from the plant is given in Table 6. This analysis is considered representative of the fly ash produced. It should be noted that most of the values given in Table 6 are toward the upper end of the ranges given in Figure 1. As might be expected, this ash exhibits an acid reaction in water. The pH measured in the pond was consistently between 5.5 and 6.0.

Species concentrations for most of the trace metals analyzed in the groundwater are given in Figures 12, 13, and 14 for three separate sampling days. Data are presented as distance profiles using the wells outlined previously. The groundwater surface elevation is also presented. The initial concentrations of metals in the pond were found to vary widely. It is assumed that these were mainly functions of fly ash loading rate. For all three sampling days, metals generally decreased rapidly with distance from the pond. This is true also for wells 2 and 3 which are not plotted due to unwanted congestion in the Figures. Certain of the metals were consistently low. Cadmium was not plotted since its concentration in the groundwater was generally less than 5 $\mu\text{g/l}$. Chromium was also very low. Sampling days on October 18 and January 4 also show certain similarities in that virtually all the metals displayed sharp peaks at about 115 meters from the pond (well 18), which decreased at greater distances. No such peak was found on the March 3 date. These observations are difficult to explain unless the cycle and loading rates of the ash pond are taken into

TABLE 6

COMPOSITION OF FLY ASH AT MICHIGAN CITY

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 $\mu\text{g/g}$

FIGURE #1

FIGURE 12: Trace Metals as a Function of Distance for Pond 1, Oct. 18, 1976.

FIGURE 13: Trace Metals as a Function of Distance for Pond 1, Jan. 4, 1977.

FIGURE 14: Trace Metals as a Function of Distance for Pond 1, March 3, 1977.

consideration. Figure 15 shows concentrations as a function of time for several of the metals analyzed. A sequence of significant events is also presented. From the beginning of monitoring (July, 1976) to the end of September, pond one was allowed to dry and the ash removed. Metal concentrations are uniformly low. Pond filling began at the end of September. Samples taken shortly thereafter (in October, Figure 12) at well 18 show increases in filterable metals. Maintenance needs within the power station reduced the generating capacity by a considerable amount for several weeks during the next sampling interval. Unit 12 in particular is rated at 520 MW. Plant records of sluice water quantities to pond one reflect the decreased activity. During the period October through December an average of 1.40 MGD was pumped to the pond as compared with an average of 2.85 MGD for periods when all units are on line. Plant capacity returned to normal on December 12, 1976. The next sampling day was January 4. Coincidentally, the interval between each activity (pond filling initiated and return of units 12 and 3) and sampling day was approximately the same -- 21 -- 23 days. It appears that groundwater concentrations of trace metals are significantly affected by normal plant operations. In the case of the pond filling, fly ash concentrations at the bottom before the water volume has reached pond capacity are larger than normal. The return to service of such a large amount of generating capacity brings about a similar increase in ash concentration. The effect in either case is similar. The uniformly low levels of trace metals for the March 3 sample date could perhaps be considered more indicative of a steady-state operation of the disposal system.

The phenomenon described is further supported by an analysis of the time of travel of groundwater from well 10 adjacent to the pond to well 18, a distance of approximately 90 meters. |

FIGURE 15: Trace Metal Concentration at Well 18 (115 Meters from Pond 1) as a Function of Time. Scale at bottom depicts significant events which affected trace metal levels.

The travel time can be estimated using Darcy's law and Dupuits assumption that the hydraulic gradient is equal to the slope of the free surface.

Writing Darcy's law

$$\bar{v} = \frac{-kc'}{n}$$

where: $\bar{v}$ = seepage velocity

k = coefficient of permeability

i = hydraulic gradient

n = porosity

and substituting measured and previously determined values, ($k = 0.1$ cm/sec, $i = 2.5 \times 10^{-2}$ and $n = 0.5$ for the medium sand),

$$\bar{v} = \frac{10^{-3} \frac{\text{cm}}{\text{sec}} \times 2.5 \times 10^{-2}}{0.5} \times \frac{8.64 \times 10^4 \text{ sec}}{\text{day}}$$

$$\bar{v} = 4.3 \text{ meter/day}$$

$$\text{Travel time is then } \frac{90}{4.3 \text{ m/day}} = 21 \text{ days}$$

When this analysis is applied to the concentrations of metals measured in the ash leachate with time (Figure 15) it is possible to estimate the total amounts of metals leaving the system via subsurface leaching. A generalized representation is given in Figure 16 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 this bringing online of generating units which had been undergoing maintenance.

FIGURE 16

Figure 17 gives some of the major ionic species present in the groundwater on January 4. Results for other days were similar. The confluence of pond seepage water with natural groundwater is clearly indicated. The dominant anion shifts from sulfate to carbonate. These values are given more precisely in Table 7. Similar data exist for other sampling days. It should be noted that there were large amounts of both iron and manganese present in the natural groundwater outside of the influence of the ponds.

In order to analyze the data further, it is necessary to consider the results of the chemical analysis of soil samples. As indicated previously, soils were sieved yielding several size fractions. Each of these was analyzed for metals. Total metals, then, were computed by taking the weighted average of individual fractions. For all soil samples tested, the greatest concentration of metals was consistently associated with the smallest size fraction. Specific data for a sample taken from well 18 at the approximate level of the groundwater are given in Table 8. Although this trend is interesting and is to be expected for cases where adsorption is occurring, it is nevertheless of limited significance with respect to the total metals found in any sample. It was indicated previously that the D_{10} size was 0.16 to 0.18 mm. The smaller size fractions rarely composed more than two percent of the total sample and were normally much less.

Figure 18 shows total metal concentrations in soils as a function of depth for several distances from pond one. Most of the metals display elevated soil concentrations at or beneath the groundwater level suggestive of bulk transport. Profiles at 340 meters are outside of the area of influence for groundwater flow from the ponds. They appear to be much more uniform. The most prominent feature of Figure 18 is the elevated levels of metals at 150 meters (well 13) over other distances, particularly at the groundwater surface. Figure 19 presents this for a constant depth (groundwater interference)

TABLE 7

MACRO-IONIC COMPOSITION OF WATER
AT WELLS 18, 13, and 15 (1-4-77)
(all values mg/l)

Specie	Well 18	Well 13	Well 15
Na ⁺	52	7.5	16.0
K ⁺	24	8.2	13.6
Ca ⁺²	424	96	166
Mg ⁺²	41	17	25
Alk(as CaCO ₃)	8	80	478
SO ₄ ⁻²	1250	210	28
Cl ⁻	65	2.5	7.5
Fe	2.25	0.14	-
Mn	1.48	0.03	0.60
Si	4.60	2.85	9.0
pH	7.0	6.9	6.5

TABLE 8

TYPICAL DISTRIBUTION OF METALS WITH SOIL GRAIN SIZE

Boring 18 at Groundwater Interface
(all values $\mu\text{g/g}$ dry wt)

Size Range (mm)	As	Cd	Cr	Cu	Ni	Pb	Se	Zn
>.841	6.3	0.10	36.7	28.1	40.6	25.1	26.1	65.4
.425 - .841	4.8	0.14	12.7	15.5	25.0	8.6	19.1	28.7
.250 - .425	3.4	0.11	13.6	12.6	20.0	8.6	12.0	26.7
.149 - .250	3.9	0.32	10.2	12.6	36.5	9.9	15.8	30.8
.075 - .149	6.0	0.09	76.5	19.4	16.8	16.4	22.3	65.6
<.075	15.0	0.33	105.3	106.5	49.5	77.7	30.0	353.3

FIGURE 17: Major Ionic Components in Groundwater for Pond 1, Jan. 4, 1977.

FIGURE 18: Depth Profiles of Trace Metals in Soil Around Pond 1 for Several Distances.

FIGURE 19: Trace Metals Concentrations in Soils at the Depth of the Groundwater Interface as a Function of Distance.

as a function of distance. All metals show elevations at a distance of 150 meters from the pond with the exception of nickel and copper. Arsenic shows a rather large rise in view of its consistently low levels in the groundwater.

The reasons for these increases are not obvious unless both the hydrologic characteristics of the site and chemical interactions are considered. An examination of Figures 9 and 10 reveal the "saddle point" for the meetings of the two groundwater flows to be very close to well 13 which is 150 meters from pond one. This point will naturally move back and forth during the year and depend upon pond cycling. There are significant changes in both soil composition and water quality (see Figure 14) that occur near this point. Tables 8 and 9 give specific data which illustrate this change. In general, there are two attenuation mechanisms which can act to decrease soluble metal concentrations in the water: precipitate formation of an insoluble compound and adsorption onto local solid phases. The data of Tables 8 and 9 suggest that both may be occurring in the groundwater. This is further explored in section III-4.

The extent of the accumulation of the trace metals in the soil around the pond can be assessed through a comparison with background soil levels. Well 13 contained the maximum of near maximum concentrations for each metal. Well 21 was located 500 meters from the pond and is considered representative of background conditions. Table 10 gives ratios of metals in well 13 over background as well as average crustal abundances as reported in the literature. It is evident that accumulation of metals through precipitation and adsorption over background is occurring. If the increases shown are attributed to ash pond seepage, this has taken place over a period of two and a half years. It is not clear that the higher levels which exist are excessive in view of natural abundances with the exceptions of arsenic and cadmium. The high

TABLE 9
SOIL IRON AND MANGANESE
CONCENTRATIONS AT GROUNDWATER
INTERFACE (ug/g dry wt.)

Location	Mn	Fe
#10	22.3	1510
#18	36.0	2710
#13	57.3	3230
#15	52.1	3180
#21	33.0	2120

TABLE 10
MAXIMUM INCREASE OF HEAVY METAL
OVER BACKGROUND CONCENTRATIONS IN SOILS
(all concentrations $\mu\text{g/g}$)

Metal	Boring 13	Boring 21 (background)	$\text{Me}_{13}/\text{Me}_{21}$	Average Crustal Abundance ($\mu\text{g/g}$)	Source
As	55.0	3.83	2.4	1.8	18
Cd	0.66	0.30	2.20	0.2	19
Cr	17.0	12.8	1.33	100	18
Cu	13.4	15.4	0.87	40	19
Ni	14.9	17.6	0.85	80	20
Pb	20.7	9.50	2.18	13	18
Se	17.8	12.7	1.40	1	21
Zn	61.0	32.5	1.88	50	19

selenium concentrations even in the background samples are as yet unexplained. Further increases in soil metals are possible.

The matter of metal concentrations which flow directly into the lake from the pond is one which must be addressed further. Analysis is difficult because of the site layout which leaves room for only one boring line between the ponds and the lake. At this time, it appears reasonable to assume attenuation patterns on the lake side of the pond similar to those observed and described previously for the opposite side. Metal concentrations attenuate rapidly, however short term perturbations may create momentary large concentrations entering the lake water.

Control Strategies

If control of ionic constituents in ash pond leachates is deemed necessary, there are basically four alternatives which are available:

- 1) conversion to a dry handling and disposal system,
- 2) installation of chemical or natural lining materials,
- 3) addition of appropriate chemicals to sluice water, and
- 4) selective mixing of fly ash types to minimize metal release.

Some utilities, often by direct or anticipated order of regulatory agencies, use a dry ash handling system or have installed lining materials in ponds thereby greatly reducing or eliminating seepage. These alternatives can complicate ash disposal procedures. In the case of dry handling, provision must be made for resuspension of particles due to wind currents. Once an acceptable site is selected, the area should be properly graded and maintained to minimize drainage. Chemical lining materials are expensive and sometimes subject to degradation. Natural lining materials, such as clays, are cheaper. Both types will complicate ash handling procedures in areas where there is a space limitation (such as the case study in this report) by slowing considerably the drying of ash prior to its removal and ultimate deposition. Clay liners

in particular may need replacing at regular intervals.

The addition of appropriate chemicals directly to ash sluice waters can effectively control metal release by forming insoluble compounds which precipitate in the ash pond. Lime, CaO , is the chemical of choice and is effective in promoting the formation of insoluble hydroxides. Since ash pond waters are generally low in dissolved carbonate, the addition of soda ash, Na_2CO_3 , may prove more effective by forming metal carbonates which are generally more insoluble than respective hydroxides.

The final alternative of selective mixing of fly ashes to minimize ionic leaching becomes a real possibility due to the increasingly common practice of burning two or more distinctly different types of coal, with high and low sulfur contents, to reduce SO_2 emissions. Generally, high sulfur coals are also high in heavy metal impurities associated with iron pyrites while low sulfur coals have fewer metals. In addition, if the low sulfur coal is of "western" origin, the resulting fly ash will often have high amounts of water soluble lime thereby causing an alkaline reaction as noted previously. Thus, an effect similar to alternative three, the direct addition of chemicals, can be realized.

Some indication of the effectiveness of this approach is given in Table II. Beginning in May of 1977, the Michigan City Generating Station began burning an approximate fifty-fifty mixture of high sulfur Illinois and low sulfur Wyoming coal in order to meet prevailing SO_2 emission standards. Table II summarizes average metal concentrations measured in the leaching field before and after this time. In addition, the average pH of the pond water rose from 5.8 to 8.3, and the alkalinity rose from 8 mg/l as CaCO_3 to 96 mg/l as CaCO_3 . In all cases except arsenic and selenium, the average metals found were lower, in some case by large amounts. It was previously shown (Figure 5) that arsenic release from fly ash increases with pH.

TABLE 11

Average Metal Concentrations in Groundwater
Before and After May, 1977
(all values in $\mu\text{g}/\text{l}$)

Metal	Sept. '76 - April '77	May '77 - Nov. '77
As	77.7	88.8
Cd	2.3	2.0
Cr	9.0	4.4
Cu	69.3	48.4
Ni	124.5	58.3
Pb	101.0	98.3
Se	38.8	40.7
Zn	54.7	4.6

Selenium, possessing a somewhat similar anionic chemistry, would be expected to behave analogously.

III-4 Modeling Studies

Once a leachate containing various substances enters the soil environment, it is desirable to know the types and extent of interaction which occur between leachate and soil particles, that is, the "natural attenuation capacity" of a specific soil component for a given leachate constituent. In the case of dissolved ions, these interactions will take the form of precipitation of a discrete solid phase or adsorption onto particle surfaces. Soluble complexes, if they are formed to an appreciable degree, will also affect these mechanisms.

In this portion of the study, data previously presented will be analyzed with the aid of a chemical equilibrium calculations so as to provide a realistic assessment of the subsurface reactions which various heavy metals have undergone since the initial construction of the facilities. Although the interactions among several soil and leachate components may be chemically rather complex, and are, of course, specific to the site studied, they are considered typical of the reactions which occur in a subsurface leaching zone.

Analysis of soil and leachate data was facilitated through application of the computer model REDEQL2 (24). It was assumed that equilibrium conditions are reasonable approximations for relatively slow moving groundwater systems over long time periods. The model is capable of thermodynamically speciating a chemical system given a set of input data. This includes complex formation, oxidation-reduction, precipitation-dissolution, and surface sorption reactions. The adsorption routine used was that of the solvent-ion interaction model which requires specification of specific chemical free energies of adsorption of a given sorbate-sorbent combination apart from coulombic or solvation effects (25). These were either determined in the laboratory, found in the literature, or estimated.

The general procedure for the application of the program was to input total concentrations of heavy metals and sorbing metal oxides plus the chemical composition of the leachate as determined analytically on soil fractions and well samples. In this manner, a present day assessment of the past contributions of various attenuation mechanisms at each boring could be made. The geometry of the borings around pond 1 provide a convenient distance parameter from which to determine the effects of changing soil and leachate properties.

An examination of the analyses from a typical volume of soil and water from the leaching zone (boring 18) reveals that less than one percent of the total for any metal exists in a soluble form, the rest being associated in some manner with the solid phase. These results are given in Table 12. For a system such as this one in which soil accumulations of metals are a recent event, it is likely that they are present as a surface form which is chemically sensitive to even slight changes in solution chemistry. This could be expected to affect the partitioning of a metal between solution and solid phases.

In this study, the major sorbing sinks for heavy metals were assumed to be oxides of iron, manganese, and silica. The total amounts of iron and manganese found in the leaching field around pond 1 are given in Table 13. In situ determinations of the oxide properties were not made, rather the representative values given in Table 14 for all three oxides were used. Combination of the information in Tables 13 and 14 yielded oxide data which were specific for the location of each boring in the leaching field. As indicated previously, adsorption data for each metal and oxide combination apart from electrostatic and solvation effects (ΔG_{chem}^0) must be given. Values used in this study are given in Table 15.

As a measure of the degree of correspondence between field and computer data, the total soluble measured metal concentrations were compared with those predicted. Results are given in Figure 20. Points falling within the

TABLE 12

Particulate and Soluble Metals in
Soil-Water System at Michigan City^a

Metal	Particulate ($\mu\text{g/g}$)	Soluble ($\mu\text{g/g}$)	Z Soluble ^b
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

^a Data for 10-18-76 sampling date at Well #18.
Data for other wells and dates do not differ
substantially.

^b Computed using an average void ratio of 0.5.

TABLE 13

Total Iron and Manganese
Values Around Pond 1
($\mu\text{g/g}$)

Boring	Fe	Mn
2	2820	30.8
3	3360	41.1
10	1680	22.3
18	2470	36.2
13	2930	57.3
15	2690	52.1

TABLE 14

Oxide Properties Used in This Study^a

	ZPC	γ_s	ϵ^c
αFeOOH	5.5^{11}	85^{11}	14^{12}
MnO_x	2.25^{13}	280^{14}	32^{12}
SiO_2	2.0^{12}	0.013^{11}	4.3^{12}

^a Superscripts refer to references in bibliography^b Specific surface area, m^2/g ^c Dielectric

TABLE 15
Specific Chemical Free Energies
Used in This Study^a
(kcal/mole)

	αFeOOH	MnO_2	SiO_2
Cd	-6.0 ²⁹	-4.85 ²⁷	-6.54 ²⁸
Cr	-5.4 ^b	-4.85 ²⁷	-7.00 ²⁵
Cu	-5.4 ^b	-5.17 ²⁸	-7.98 ²⁷
Ni	-6.0 ^b	-4.25 ²⁸	-6.54 ²⁶
Pb	-5.4 ^b	-4.85 ²⁷	-6.50 ²⁷
Zn	-7.4 ²⁹	-4.85 ²⁸	-6.54 ²⁸

^a Superscripts refer to reference numbers in bibliography.

^b Estimated

dotted lines are within 0.5 log units of the actual concentration. Points falling below the line indicate greater solubility predicted than measured. The modeling of chromium is seen to give results generally higher than measured. It is possible that the chemical free energy of adsorption for this metal onto iron oxide was underestimated thus accounting for the discrepancy. It may, however, be due to a lack of agreement about the speciation of chromium. Modeling studies suggest that conditions favor the formation of Cr (III); however the reduction reaction from Cr (VI), which is likely present in the pond waters, would be expected to be slow in the pH range of interest, thus the equilibrium modeling of this metal may be limited by kinetic considerations. Most other points below the line of Figure 20 are predictions for boring 15 which was outside the leaching field. The soil chemistry characterization here is not considered as thorough as at other locations.

The computer simulated speciation of specific metals as a function of distance is given in Figure 21 (a) through (d) for chromium, copper, lead, and zinc, respectively. The results for cadmium and nickel were qualitatively similar to zinc. Leachate data for one sampling date were used, however, the speciation pattern changed very little for other sampling dates. For most metals free aquo and sulfato complexes are seen to dominate in the pond liquor. The hydroxo complex of chromium III is the major soluble form for this metal. When the leachate stream enters the soil environment several reactions occur. Zinc, cadmium, and nickel are attenuated predominantly by adsorption onto the iron oxide, manganese oxide playing a lesser role. In contrast, the solubilities of chromium, copper, and lead are controlled by discrete precipitates while adsorption is of diminished importance. Leachate conditions favor the formation of lead and chromium hydroxides in the immediate pond area. Copper precipitates as the basic carbonate, malachite, in spite of

FIGURE 21 (a): Metal Speciation Around Pond #1 vs. Distance, Chromium.

FIGURE 21(b): Metal Speciation Around Pond #1 vs. Distance, Copper

FIGURE 21 (c): Metal Speciation Around Pond #1 vs. Distance, Lead.

FIGURE 21 (d): Metal Speciation Around Pond #1 vs. Distance, Zinc.

the low alkalinities. When inorganic carbon concentrations increase due to the presence of natural groundwater, the model predicts lead carbonate will form. In all cases, soluble metals are considerably lower than the solid phase concentrations in accord with the measurements given in Table 12.

It is interesting to examine the effects which leachate and soil variables have on the soluble metals in solution. Figure 22 (a) and (b) show predicted soluble metal concentration as a function of sulfate and carbonate in solution, respectively. Sulfate ion, SO_4^{-2} , forms weak complexes with all of the metals studied, however since it is a common component of aqueous power plant waste streams, the effect of these complexes on attenuation in the soil should not be ignored. A typical sulfate concentration in the leaching field is indicated in Figure 22 (a). In this system it appears that sulfate has no appreciable solubilizing effect although concentrations only slightly higher, above approximately 10^{-2} moles per liter, could be expected to increase the proportion of soluble metals. Thus, although the presence of high sulfate alone may be comparatively unobjectionable in these waters, the accompanying effect of heavy metal solubilization could be more serious. Chromium is relatively unaffected by sulfate due to the dominance of hydroxo complexes at this pH (7.0).

The effect of carbonate on the solubility of the metals in Figure 22 (b) is less obvious. Chromium (III) does not form a stable carbonate and so is not affected. The carbonates of nickel and cadmium do not form under the conditions present, and zinc carbonate affects soluble zinc at total carbonate concentrations approaching 10^{-1} M. Carbonate interacts with both lead and copper by forming both soluble complexes and precipitates. Above 10^{-4} M total carbonate, copper precipitates as malachite while soluble lead actually increases due to the formation of a carbonate complex, $[\text{PbCO}_3]^0$. At higher carbonate levels lead carbonate begins to precipitate while soluble

FIGURE 22(a): Predicted Variation of Total Soluble Metals With Sulfate.

FIGURE 22(b): Predicted Variation of Total Soluble Metals With Carbonate as the Determining Parameter.

copper increases as the negatively charged $\text{Cu}(\text{CO}_3)_2^{-2}$ complex forms.

The effect of solution pH is shown in Figure 23. This variable brings about the most noticeable changes in soluble metals, affecting both the extent of adsorption and degree of precipitation. In general, higher pH results in less adsorption and less precipitation. Chromium solubility increases at pH values above 7.5 due to the formation of soluble hydroxo complexes such as $\text{Cr}(\text{OH})_4^-$, and in fact, the line for chromium in Figure 23 represents a hydroxide solubility diagram. It should be noted for the other metals that the dominant attenuation mechanisms change as solution conditions change, thus, for example, lead sulfate exerts the major control on lead solubility at pH 5 while the stoichiometry of the copper precipitate changes from malachite to cupric hydroxide, $\text{Cu}(\text{OH})_2$, at pH 9.

The changes in soluble metals as the quantities of soil components vary are shown in Figure 24(a), (b), and (c) for silica, manganese oxide, and iron oxide respectively. Silica exerts only minor effects at very high surface areas per unit volume. In the model, this is due primarily to the low dielectric of silica which brings about a correspondingly high oppositional energy of solvation for adsorption of the metal cations. The effects of both iron and manganese are more pronounced. Surface areas of manganese approaching 10^{-2} ha/l begin to exert an influence due to the large sorptive capacity of this oxide; however, the amounts measured in the field were generally insufficient to bring about this effect so that manganese oxide adsorptive controls are secondary to adsorption onto iron oxide. Figure 24(c) indicates that major effects due to iron become apparent at surface area concentrations higher than manganese. Field measurements suggest that this oxide is present in quantities sufficient to control cadmium, nickel, and zinc (Figure 21 (d)). In comparing Figures 24 (b) and (c) the observation can be made that manganese oxide, if present in large enough quantities, is capable

FIGURE 23: Sensitivity of Predicted Total Soluble Metals as pH Varies.

• FIGURE 24 (a): Sensitivity of Predicted Total Soluble Metals to Changes in Sorbing Surface Area, Silica.

FIGURE 24(b): Sensitivity of Predicted Total Soluble Metals to Changes in Sorbing Surface Area, Manganese Oxide.

FIGURE 24(c): Sensitivity of Predicted Total Soluble Metals to Changes in Sorbing Surface Area, Iron Oxide.

of becoming the dominant sink for all the metals studied while iron oxide has only a minor influence over those metals which form discrete precipitates, that is copper, chromium, and lead.

The results imply some interesting possibilities with respect to heavy metal containment in ponded fly ash disposal sites. The removal of chromium, copper, and lead through a precipitation mechanism depends upon the solution chemistry of the leachate/soil system and so it could be expected to be operative for all times as long as conditions are favorable. Unless the metal oxides in the soil are replenished, however, it is to be expected that the adsorptive capacity of the system could eventually be exhausted depending upon the quantities present initially, and those metals which are controlled through this mechanism (in this study, cadmium, nickel and zinc) may migrate more freely.

In either case, the partitioning of metals between the soluble and particulate phases is strongly influenced by solution pH and to a lesser extent by complex forming ligands such as sulfate and carbonate. This offers an explanation for the relatively wide variation in soluble metals shown in Figure 2 and previously related to chemical perturbations moving through the system.

The comparatively large sorptive capacity of manganese oxide is especially noteworthy and may warrant consideration as a control procedure for seepage type ponds such as the one studied. For this site, it is unclear whether the iron and manganese oxides found at various locations were present naturally or are being deposited from the fly ash. In the latter case, it is possible that certain fly ashes are capable of providing this ameliorating effect, a factor which should probably be taken into account when assessing various control procedures. The purposeful use of these

oxides for heavy metal attenuation would depend upon maintaining an oxidizing soil environment. Our studies of ash disposal ponds have shown rather consistently that oxidizing conditions prevail in the active leaching zone.

In reviewing these results, it must be stressed that many of the trends indicated are derived from the anticipated thermodynamic behavior of the various components in the system. They are, however, based upon field measurements and are in general accord with observations made of heavy metal partitioning in the soil/water environment. It is felt that the information presented is a reasonable assessment of the attenuation mechanisms which are operative. This study suggests that the subsurface reactions between heavy metal leachate constituents and soil components are generally complex. Nevertheless, knowledge of these reactions are viewed as important in the overall evaluation of the pollutorial potential of a leachate/soil system.

Section IV

CONCLUSIONS

The following major conclusions are drawn from this research:

- 1) Among the most important reactions of fly ash in water are those which alter solution pH. The effect may be either acidic or basic. The ratio of ammonium oxalate extractable iron to water soluble calcium at pH = 3 was found to be a good indicator of acid or base behavior with a ratio of 3 an approximate measure of a neutral ash.
- 2) Generally large proportions of trace metals contained on the surface of fly ash are capable of being released into aqueous solution. The extent of release is strongly pH dependent, with most metals showing higher release at lower pH values. An exception is arsenic which displays high release at both low and high pH.
- 3) Field studies confirm the migration of the metals in aqueous ash extracts in the subsurface soil environment. The quantities of metals present appeared to be dependent on the mass loading regime to the fly ash pond, with peak concentrations occurring at those times of sudden increases of fly ash produced in the power plant.
- 4) Soils are capable of attenuating the chemical contaminants in the fly ash leachate through both adsorption and precipitation reactions. In this study those properties in the system which were found to greatly influence the extent of metal removal were pH, pSO_4 , ionic strength, and soil iron and manganese contents. Rather than single out one or more metals of potential significance, it is suggested that a system in question be evaluated through the use of these and similar parameters.

Section V

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