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

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Abstract

Field studies were conducted at the fly ash disposal site of a 735 MW coal-fired power plant. Disposal consisted of ponding the ash followed by eventual removal and ultimate deposition as fill. Several sampling wells were made in order to monitor the groundwater quality. Trace metals analyzed for include As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, and Zn.

Results indicated that trace metals are released to the groundwater from the pond at generally low levels. Increased concentrations several times the normal levels were observed when the pond first began the filling cycle and again when maintenance procedures brought about a large fly ash loading in a short time.

Metals were found to accumulate in soils at the point of confluence of the pond seepage water with the natural groundwater which was high in dissolved carbonate. Deposition as carbonates and adsorption of metals onto the higher levels of hydrous iron and manganese oxides were considered responsible for this.

Effective control strategies, if deemed necessary, would include pH adjustment of pond water with lime or limestone, lining of ponds with natural or chemical materials, and relocation to a more environmentally suitable site.

Field Investigation of Trace Metals in Groundwater from Fly Ash Disposal

Introduction

The anticipated increased use of coal as an energy source has brought about several investigations on the environmental cycling of coal-related pollutants. Among these is the release of various toxic trace metals which are associated with coal during the combustion process. A portion of some of these metals exhibit a volatile behavior (such as mercury and to a lesser extent arsenic) and are emitted as vapors in stack gases. The more refractory metals, however, condense as oxides onto the particulate residue known as fly ash. The mode of formation of fly ash and its physical and chemical properties have been reviewed extensively elsewhere and will not be elaborated upon here (1)(2)(3)(4). It is composed chiefly of alumina, silica, lime, and iron oxides in an amorphous core. Figure 1 from the previous work of Theis et al. (4) gives typical ranges of the metallic components of several fly ashes. The extent of enrichment of many trace metals on fly ash is sometimes large, occasionally reaching 100 times the concentration originally found in the coal.

Fly ash is usually collected from the gas stream by precipitators or scrubbers. Approximately 40 million tons are produced in the United States annually; this quantity is likely to increase. Common disposal practice involves on-site ponding followed at appropriate intervals by mining and subsequent deposition of the material as fill. Large portions of the trace metals on fly ash have been shown to exist in a surface-sorbed form often associated with iron or manganese oxide reservoirs (4). As such, they must be considered as potentially able to be released into aqueous solution. The purpose of this study was to investigate in detail a ponded fly ash disposal site with particular emphasis placed on the extent, if any, of trace metal migration in groundwater from natural pond seepage.

Site Description

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 some 735 MW. Of special interest is a newly constructed 520 MW unit which went into service in 1974.

Figure 2 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 approximately 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 3. 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.

Experimental Procedures

a) Sampling Wells

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 2. 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.

b) Water Sampling and Analysis

An effort was made to adhere to a monthly sampling schedule. However, the unusually severe weather conditions during the winter 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) removal of approximately one liter of water from well and division into two equal aliquots,
- (3) immediate acidification to pH 5 of one aliquot to prevent oxidation of ferrous iron,
- (4) immediate measurement of temperature, pH, and oxidation reduction potential of the other aliquot,
- (5) filtration of both aliquots (.45 μ m),
- (6) 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 (5) were used.

Trace metals were analyzed by atomic absorption spectrophotometry with graphite furnace attachment (Perkin-Elmer model 305 with HGA-2100 and S-1 automated sampling system). A summary of all analyses and methods is given in Table 1. Analysis for mercury was discontinued shortly after the beginning of monitoring since levels were consistently beneath the detection limit (0.2 μ g/l). In general, ferrous iron determinations agreed closely with total iron due to the insolubility of iron III at the pH values encountered.

TABLE 1
ANALYTICAL METHODS FOR GROUNDWATER COMPONENTS

Specie	Method	Ref.
Na ⁺	atom. abs.	6
K ⁺	atom. abs.	6
Ca ⁺²	EDTA titrimetric	5
Total Hardness	EDTA titrimetric	5
Alkalinity	H ₂ SO ₄ titrimetric	5
SO ₄ ⁻²	turbidimetric	5
Cl ⁻	argentometric	5
PO ₄ ⁻³	ascorbic acid	5
Al	atom. abs.	7
As	atom. abs. - Ni	8
Cd	atom. abs.	7
Cr	atom. abs.	7
Cu	atom. abs.	7
Hg	flameless atom. abs.	9
Mn	atom. abs.	7
Ni	atom. abs.	7
Pb	atom abs.	7
Se	atom. abs. - Ni	8
Si	atom abs.	7
Zn	atom abs.	7
Fe ⁺²	bathophenanthroline	10
Fe _T	atom. abs.	7

c) Soil Analysis

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 1 (except for mercury) were determined again by atomic absorption.

Soil grain size analyses were made in accordance with ASTM D 422, Particle-Size Analysis of Soils (12). Grain size distribution curves for some soil samples recovered from depths 1.5 to 2 meters below ground surface are shown in Figure 3.

Coefficient of permeability was estimated using published correlations of effective grain size, D_{10} , and coefficient of permeability, k . (e.g., Leonards (13)). The D_{10} of these uniform sand soils is approximately 0.2 mm and the coefficient of permeability 0.1 cm/sec.

Results and Discussion

For the major portion of this study, only the first primary pond (in Figure 2) was actually being loaded with fly ash. Pond number 2 was allowed to dry for the eventual removal of the ash to the final fill site. Most of the data to be presented, then, has been generated by the seepage characteristics of the first pond.

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 4 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, depending upon other hydrologic factors. This effect is illustrated more clearly in Figure 5 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 2) were located as close as possible to this point. This information is important for two reasons. First, the extent of the pond influence determines the approximate path length of seepage water. This is important in determining the ultimate degree of attenuation of dissolved species. Secondly, the groundwater chemical characteristics change abruptly at this point. As will be seen, such a change can bring about significant alterations in trace metal forms.

An analysis of the fly ash from the plant is given in Table 2. This analysis is considered representative of the fly ash produced. It should be noted that most of the values given in Table 2 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.

Specie concentrations for most of the trace metals analyzed in the groundwater are given in Figures 6, 7, and 8 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 $\mu\text{g}/\text{l}$. 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 consideration. Figure 9 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

TABLE 2

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 $\mu\text{g/g}$

and the ash removed. Metal concentrations are uniformly low. Pond filling began at the end of September. Samples taken shortly thereafter (in October, Figure 6) 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 the 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.

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),

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

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

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

Figure 10 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 3. 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 4. 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

TABLE 3
 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 4
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

rarely composed more than two percent of the total sample and were normally much less.

Figure 11 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 of groundwater flow from the ponds. They appear to be much more uniform. The most prominent feature of Figure 11 is the elevated levels of metals at 150 meters (well 13) over other distances, particularly at the groundwater surface. Figure 12 presents this for a constant depth (groundwater interface) 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 the most dramatic rise in spite of its consistently low levels in the groundwater.

The reason for these increases is not obvious unless the hydrologic characteristics of the site are considered. An examination of Figures 4 and 5 reveal the "saddle point" for the meeting 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 depending upon pond cycling. Still, Table 3 shows the transition of water quality that occurs at this point. Carbonate minerals are not stable at the temperatures encountered in power plant furnaces and so fly ash leachates contain little dissolved inorganic carbon. Infusion of carbon dioxide from the atmosphere to the pond is a possibility but at the pH of the water (5.5-6.0) equilibrium C_T would be less than 1 mg/l. Under such conditions, the solubilities of all metals except arsenic and selenium would be expected to be controlled by their hydroxides. The concentrations measured, even at peak levels in Figures 6 and 7, are well within the calculated solubilities for cadmium, chromium, copper, lead, nickel, and zinc at the pH values encountered. Only iron (III) and oxidized forms of manganese would form precipitates.

Total inorganic carbon levels in the natural groundwater are more than 50 times the concentration in the pond seepage water. At these carbonate concentrations lead, zinc, cadmium and copper would be expected to precipitate giving higher levels in the soil. Nickel carbonate is naturally very soluble ($K_{so} = 1.3 \times 10^{-7}$ (14)), and should not precipitate.

Specific adsorption onto solid phases may also account for increased concentrations of metals in soil. Amorphous oxides of manganese and iron are present and probably exert a major influence. Concentrations are given in Table 5.

Parks (15) reports the zero point of charge of freshly precipitated iron hydroxide to be 8.5. Manganese dioxide has a ZPC of approximately 2.0. Thus, the major difference between these sorbing surfaces in the environment under discussion is that MnO_2 is negatively charged while $Fe(OH)_3$ has a net positive charge. Silica, which also would be negatively charged and is present to excess, sorbs comparatively little. James and Healy (16) attribute this to the low dielectric of silica which effectively inhibits overcoming the energy of solvation of hydrated metal ions.

Both arsenic and selenium possess an anionic chemistry under the conditions in the groundwater. They would be expected to adsorb readily onto the positive iron hydroxide surface. Other metals may adsorb into the MnO_2 which is present. Although it is not entirely clear, it would appear that the elevated levels of iron and manganese at well 13 are present naturally. However, these two oxides are major components of the surface of the fly ash also. In view of the high solubilities of the metals under conditions in the pond water, adsorption is the likely mechanism for the rapid attenuation of metal concentrations in the immediate vicinity of the pond. This was noted in Figures 6, 7, and 8. The fact that this mechanism is unable to control the large pulses of metals which arise from operational factors suggests a more complex phenomenon may be occurring in which kinetic factors become important.

TABLE 5
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

The extent of the accumulation of the trace metals in the soil around pond one can be assessed through a comparison with background soil levels. Well 13 contained the maximum or near maximum concentrations for each metal. Well 21 was located 500 meters from the pond and is considered representative of background conditions. Table 6 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 possible exception of arsenic. The high selenium concentrations even in the background samples are as yet unexplained. Further increases in soil metals are possible. The problem becomes an interesting one to model.

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 metal 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.

Summary

For the fly ash disposal site studied, it has been found that trace metals are released into the groundwater. Generally, the concentrations are low although they are sensitive to the ash loading rates and procedures. Rapid attenuation occurred for most metals very close to the pond itself. Many of the components of fly ash, especially iron and manganese oxides are effective metal scavengers once they are formed in the pond. These oxides are, however, unable to dampen

TABLE 6
 MAXIMUM INCREASE OF HEAVY METAL
 OVER BACKGROUND CONCENTRATIONS IN SOILS
 (all concentrations $\mu\text{g/g}$)

Metal	Boring 13	Boring 21 (background)	Average Crustal Abundance ($\mu\text{g/g}$)	$\text{Me}_{13}/\text{Me}_{21}$
As	55.0	3.83	1.8	13.36
Cd	0.66	0.30	0.2	2.20
Cr	17.0	12.8	100	1.33
Cu	13.4	15.4	40	0.87
Ni	14.9	17.6	80	0.85
Pb	20.7	9.50	13	2.18
Se	17.8	12.7	1	1.40
Zn	61.0	32.5	50	1.88

the curious peaks of metals which were observed and were related to the operation of the ponds and the power plant. This suggests that at sudden increases in ash concentrations there is either insufficient time or unfavorable local conditions (such as low pH) for the oxides to exert controls. If this is the case, simple pH adjustment in the pond to a more alkaline range should control metal release. Lime or limestone would be the chemicals of choice. Lime could elevate the pH bringing about precipitation of insoluble hydroxides of trace metals and promoting the formation of the sorbing hydrous oxides. Little excess sludge would be produced because of the low alkalinity of the pond water. Limestone would produce more sludge, but would also bring about the formation of insoluble metal carbonates prior to their release into the groundwater.

The behavior of trace metals in the groundwater once released is dependent upon the site hydrologic characteristics and the differences in water quality between seepage water and natural groundwater. In this study, metals were found to accumulate at the point where seepage and natural groundwater met due to precipitation of carbonates and adsorption onto the higher levels of hydrous iron and manganese oxides. Arsenic in particular displayed high increases over background levels.

If the accumulations of metals in soils is deemed to be a problem or if the filterable concentrations of metals in the water are considered too high even after remedial pH adjustment in the pond (for example, both nickel hydroxide and nickel carbonate are very soluble and the Ni^{+2} ion shows little tendency toward adsorbing onto local solid phases) then there may be no alternative except to limit the extent and quantity of pond seepage. Natural or chemical lining materials could be used for such a purpose although their presence makes the removal operation decidedly more difficult.

The ultimate answer to concern over heavy metal pollution from this type of non-point source lies in the proper siting of disposal facilities prior to their use.

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FIGURE 1: Total Metal Analysis of the Fly Ashes. Bracketted Lines Represent Ranges, Dots Are Average Values

FIGURE 2: Fly Ash Pond Site Layout
(approximate scale 3000:1)

FIGURE 3: Sieve Analyses for Representative Soil Samples from Disposal Site

FIGURE 4: Flow Lines Around Ash Pond Number One for Oct. 18, 1976 Sampling Day

3/18/77

15:47:20

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FIGURE 5: Three Dimensional View of Prevailing Groundwater Surface for Oct. 18, 1976. Lake is to the left.

FIGURE 6: Trace Metals as a Function of Distance for Pond 1, Oct. 18, 1976.

FIGURE 7: Trace Metals as a Function of Distance for Pond 1, Jan. 4, 1977.

FIGURE 8: Trace Metals as a Function of Distance for Pond 1, March 3, 1977.

FIGURE 9: Major Ionic Components in Groundwater for Pond 1, Jan. 4, 1977.

FIGURE 10: 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.

FIGURE 11: Depth Profiles of Trace Metals in Soil Around Pond 1 for Several Distances.

FIGURE 12: Trace Metals Concentrations in Soils at the Depth of the Groundwater Interface as a Function of Distance.