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

Technical Progress Report
for the Period

June 1, 1976 - August 31, 1976

Thomas L. Theis
Department of Civil Engineering
University of Notre Dame
Notre Dame, Indiana 46556

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119

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I. Introduction

This document represents a summary report for the period June 1, 1976 - August 31, 1976 on grant E(11-1)-2727, "The Contamination of Groundwater by Heavy Metals from the Land Disposal of Fly Ash".

Previous reports (C00-2727-1, C00-2727-2, C00-2727-3) have established the organization of the project and have contained initial data. To summarize:

- 1) Commencement of the project began on June 1, 1975. The first 12 - 14 months have been devoted to initial laboratory studies aimed at defining the chemistry of trace metals on fly ash particles.
- 2) As of July, 1976 field studies of an actual ash disposal sight have begun. Preliminary results are given in this progress report.

II. Summary of Previous Laboratory Work

The major effort of the laboratory studies are conveniently gathered in a paper presented at the 31st Purdue Industrial Waste Conference in May, 1976 and appended to this report. The general laboratory approach in attempting to fractionate metals in fly ash was to submit several ashes to various chemical extractants, including complete HF-HNO₃ digestion, oxalate and hydroxylamine extraction, and variable pH washings at 3, 6, 9, and 12. Table 1 below summarizes part of these results for eleven different fly ash samples.

TABLE 1

Trace Metals in Fly Ash

(all values in ug/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	100-3100	515	933	24-1200	156	351	4.5-600	67	177
Selenium				88-213	150	*			

*Only two samples for Selenium

Through comparisons of the quantities of metals extracted it was possible to determine their approximate degree of surface concentration as given in Table 2. This determination is of considerable importance as it is the surface concentrated heavy metals which are likely to be the most chemically active. Those metals "locked" within the silica matrix of fly ash will be released only through long term weathering action.

TABLE 2
Surface Concentration of Trace Metals on Fly Ash
(expressed as % of total)

Metal	Range	Average
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

The wide range of the data among the ashes investigated is due primarily to the variable and quite complex geochemical matrix of the metals in the coal deposits. Sulfides, carbonates, and silicates could be expected to co-exist in variable proportions. Subsequent mining and preparation of the coal plus, of course, combustion in the power plant furnace will determine the location and form of metals on the fly ash particles.

Comparison of release patterns in the pH washings with the surface active "sink" of metals yields useful information in defining the degree of release, and subsequent contamination, from fly ash to the aquatic environment. Figure 1 expresses the average ratio of released to surface metals as a function of pH. Clearly release is favored by an acid pH. However, even in the neutral range a

FIGURE 1: Average Release of Trace Metals from the Surface of Eleven Fly Ashes as a function of pH.

significant degree of release of arsenic, selenium, cadmium, nickel, and lead takes place. Large arsenic release at extraordinarily high pH's occurs probably due to the lack of any available metals, especially iron, to cause its precipitation.

Soil sorption data given in the attached Appendix indicate that cadmium is poorly sorbed by most soil materials. Subsequent work for nickel and arsenic, although not reduced to final form, shows a similar trend. Lead is in general heavily sorbed by most soils.

Thus, from laboratory data it would appear that those metals in fly ash of particular concern would be arsenic, cadmium, nickel, and perhaps selenium. Cadmium dangers, however, may be attenuated somewhat because of its general geochemical sparsity and therefore, low levels in most fly ashes (see Table 1).

III. Field Studies

A. Field Site

Three field sites were initially selected for study. One is an active series of disposal ponds from a 600 MW power plant which are periodically mined, the second, an abandoned seepage pond which had been completely filled in, and the third, a smaller active site in which the fly ash is used as fill directly. Because of capital limitations, only one site could be studied in depth. The first site was chosen because of its active nature and similarity with most other ash disposal operations.

A schematic layout of the site is given in Figure 2. The location of sampling wells are also given and numbered. Fourteen wells were drilled initially. Four additional wells are currently in the process of being located.

B. Field Data

Sampling is performed approximately once per month. In general, the procedure involves immediate filtration (0.45 μ) and appropriate sample preservation in the field prior to transport. In the laboratory a complete chemical analysis

FIGURE 2: Site Layout

of the water is performed. Data for one sampling date, July 13, 1976, is presented in Table 3.

It cannot be emphasized too strongly at this time the tentative nature of the data contained in Table 3. There are, undoubtedly, certain anomolous points which may be due to procedure and analysis errors. These are being corrected with time. In general, respectable macroion charge balances could be performed if sodium and potassium levels were taken into account.

Analysis of such a large quantity of data (taken on a monthly basis) is difficult and time consuming. Correlation with groundwater flow patterns is being attempted but is hampered by the need for a good tracer study. In addition, flow patterns are strongly dependent on pond depth and status (i.e. empty or full). The feasibility of a tracer study is currently being investigated. Four new sampling wells are being drilled to aid in data interpretation.

Data display can be aided by computer graphical approaches and common two dimensional contour plots. A three dimensional view of the groundwater surface relative to the lake for 7/13/76 is given in Figure 3. The most westerly ash pond was, on this date, in the process of being mined and so no water was present. Contours of arsenic concentrations are superimposed on the site layout in Figure 4. This approach could be used for all the measurements in Table 3, but will probably be done only for those contaminants of greatest interest.

In spite of the complexity of the data, a preliminary analysis would appear to warrant the following observations:

- 1) There exists a general agreement between laboratory studies and trace metal migrations in the field. Chromium, copper, mercury, lead, and zinc were shown in laboratory studies to be released to an insignificant extent and/or be rapidly sorbed onto the soil phase. In the case of cadmium, the observation that its naturally low levels would tend to lessen its impact appears to be correct.
- 2) Similarly arsenic, nickel, and selenium levels are consistently

TABLE 3

Chemical Analysis of Groundwater
from Ash Disposal Site, 7/13/78

Well # Parameter	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Temperature (°C)	18	12	13	15	23	26	23	19	27	18	23	22	18	18
pH	7.4	9.4	9.4	7.5	8.2	8.9	8.2	8.2	9.1	6.6	9.0	7.8	8.6	7.0
E _H (mv)	+90	-180	-170	+20	+90	+60	+90	+100	+40	-30	+50	+110	+170	+100
Alkalinity (mg/l as CaCO ₃)	90	114	152	100	50	102	60	122	54	108	52	70	74	120
Cl ⁻ (mg/l)	20	20	30	40	25	20	25	25	20	18	25	25	3	3
SO ₄ ⁻² (mg/l)	660	1350	1700	1200	1100	975	950	360	1025	750	1100	870	760	40
Ca ⁺² (mg/l as CaCO ₃)	572	1052	1312	600	840	824	640	420	844	776	820	580	268	168
Mg ⁺² (mg/l as CaCO ₃)	60	48	12	100	20	48	152	28	16	40	8	56	68	56
P (ug/l as P)	60	420	330	90	150	240	420	360	270	30	390	60	120	210
Si (ug/l)	5.4	2.4	1.4	7.0	3.0	3.9	5.2	3.4	3.0	2.3	3.3	2.0	8.4	3.9
Al (ug/l)	1440	140	160	2220	720	490	1800	340	110	300	30	1015	220	165
As (ug/l)	400	1000	940	410	475	485	480	505	430	500	840	545	330	270
Cd (ug/l)	.12	.05	.06	.11	.10	.08	.01	.15	.09	.12	.08	.16	.09	.05
Cr (ug/l)	9.0	7.0	7.4	11.4	11.0	9.0	8.0	8.5	8.4	6.2	5.0	9.0	3.2	2.0
Cu (ug/l)	16	27	23	24	16	17	19	15	26	14	16	24	11	10
Fe _T (ug/l)	460	930	75	500	340	120	620	110	75	12000	45	580	90	270
Hg (ug/l)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mn (ug/l)	163	5	8	995	61	22	280	150	5	554	5	170	270	71
Ni (ug/l)	90	87	120	135	109	130	120	83	100	95	106	133	65	52
Pb (ug/l)	9	15	14	28	27	24	27	181	15	28	25	28	18	15
Se (ug/l)	108	510	640	270	430	360	310	120	380	320	450	300	100	60
Zn (ug/l)	75	8	10	30	16	10	30	100	9	77	7	35	59	30

FIGURE 3: Three-Dimensional View of Piezometric Surface at Study Site for 7/13/76.
Horizontal Scale is Approximately 1:4000, Vertical Scale 1:200.

the highest found among trace metals and appear to be capable of migrating the furthest (as indicated by data for wells #13 and 14) from the disposal site. Even at well 14, the furthest from the ponds (at the edge of the property limits of the power plant), arsenic levels are over 5 times drinking water standards while selenium is 6 times the standard. Among additional wells to be drilled will be two further distant off the power plant property.

3) In most of the samples taken, the chemical matrix is such that sulfate ion is clearly the dominant specie. This is consistent with the history of high sulfur coal used at the power plant. Sulfate ion complexes with most of the trace metals are of an intermediate strength with stability constants on the order of 10^2 . However, in view of the large sulfate concentrations, the sulfate complexes could be expected to predominate as the major soluble metal ion species. Exceptions, of course, would be arsenic and selenium which possess anionic chemistries under the conditions of this groundwater environment. This factor is a probable reason for their relatively unrestrained migration. The major attenuating mechanism is precipitation by other metals, most likely iron.

C. Chemical Models

At the present time many computer models exist for describing environmental systems. The use of these models as applied to the systems at hand can facilitate matters in two ways:

- 1) As analytical aids, computer simulations can determine the relative concentration of all soluble and sorbed species. In a multi-ligand-cation-surface system such as leachates in groundwater this is an accurate way to assess the equilibrium state. So called "chemical equilibrium" models can be used for this purpose.
- 2) To describe the dynamic interactions among all components of a system, mathematical computer simulations are essentially the only way to approach

the problem. By noting the extent of agreement between such models and the actual field data obtained, such models can be calibrated and used in the future planning of trace metal disposal on land. These models are usually referred to as the "transport" type.

The extent to which these two models can be combined for application to the systems under study is currently being reviewed. Models such as those described are available at a nominal cost and once operating can be modified as needed.

IV Future Studies

At the present time, several aspects of heavy metal contamination from fly ash disposal remain unclear. The precise extent of metal migration from the site of disposal for certain metals, arsenic, nickel, and selenium, is not yet known. For the other metals it is uncertain if their low levels result from rapid attenuation or simply low inputs for the fly ash under study.

The movement of groundwater at the present monitoring site is complex and not yet adequately described. As indicated, the pattern of pond usage strongly influences subsurface water movement.

Speciation and its subsequent effect on trace metal attenuation mechanisms has not as yet been examined fully enough. It is clear that sulfate ion dominates the chemical matrix in the immediate vicinity of this high sulfur fly ash. The extent to which this determines the degree of attenuation should be further investigated.

There exists a wide spread belief that the problem of trace metal movements and reactions in groundwater can be modeled satisfactorily. This may be true, however, there are relatively few groundwater models available at the present time. Many of these have no provision for trace metal movements and those which have such an input either ignore their complex chemistry or have not been calibrated on the trace metals of interest in this study. It is felt that a considerable effort is yet required toward this end.

Finally, it is felt that an effort should be made to monitor at least one other "different" field site to give a greater degree of general validity to the findings of this study. Such a site might be one with chemical or natural liners on ponds such that a direct flow through system exists, or a site which uses predominantly a low sulfur coal, or perhaps an active fill site with no ponding.

APPENDIX

Sorbitive Characteristics of Heavy Metals
in Fly Ash - Soil Environments

by

Thomas L. Theis*
John L. Wirth+
Richard O. Richter+
Jerry J. Marley**

Department of Civil Engineering
University of Notre Dame
Notre Dame, Indiana 46556

Presented at the 31st Purdue Industrial Waste
Conference, West Lafayette, Indiana

* Assistant Professor
+ Graduate Student
** Associate Professor

Abstract

Sorbitive Characteristics of Heavy Metals in Fly Ash - Soil Environments

Thomas L. Theis, John L. Wirth, Richard O. Richter, Jerry J. Marley

Eleven different fly ashes from coal-fired power plants were subjected to various degrees of extraction for determination of their heavy metal chemistry. Extractants included complete HF-HNO₃ digestion, oxalate and hydroxylamine extraction, and variable pH washings. In separate tests, adsorption isotherms for the metals studied were determined for several different soils.

Results show that trace metals are associated with surface coatings of amorphous iron and aluminum oxides and MnO₂. Oxalate and/or hydroxylamine extraction gives a good measure of the amount of each trace metal which is "available" for release to the aqueous environment. Cadmium was most readily desorbed over the pH range 3-12 followed by lead, chromium, copper, and zinc. Mercury behaved anomalously due to its presence of the elemental (vapor) form. Adsorption experiments on soils indicated increasing sorption with increasing pH. An organic peat had the greatest capacity followed by bentonite clay, a calcite sand and clean silica sand. Cadmium was adsorbed the least. Zinc was absorbed to an intermediate extent and chromium and copper were adsorbed to the greatest extent.

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 and selenium) 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 (17). The disposal of this material is normally achieved by temporary ponding (usually on site) followed by mining and subsequent deposition 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, and confirmed by electron micrographs in this study, that fly ash consists of many small (0.5-100 μ diameter) glass-like particles of a remarkably spherical character (9). During the combustion process many different metal oxides condense on the cooling 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.

In examining the problems of trace metal chemistry in fly ash, it is important to be aware of the existence of various metal "pools" to which the trace metals may be sorbed. While the thermodynamic properties of most individual trace metals have been aptly described, their anticipated behavior may nevertheless be at considerable variance with that actually displayed in the presence of these sorptive reservoirs. It has been shown that amorphous iron and aluminum oxides, manganese dioxide, and various types of organics possess high affinities for many trace metals (10, 11, 12). Although most fly ashes contain little volatile matter, as will be seen they do have high levels of iron, aluminum and manganese associated with them.

The aims of the current phase of this study were twofold:

- 1.) to define those chemical parameters of fly ash which are important in characterizing the release of trace metal contaminants into solution, and
- 2.) to examine attenuation effects once trace metals are released into the soil/groundwater environment.

EXPERIMENTAL

Experimentation was divided into two portions reflective of the objectives given above. Initially, fly ashes from eleven different power stations were gathered and subjected to several types of extractants. This was done in order to determine the sorptive characteristics of the trace metals on the surface of the fly ash and as a means of assessing the available fraction of each metal compared with the total amount present. The extraction procedures were as follows:

- 1.) distilled water to determine relevant pH and mercury release data
- 2.) hydrofluoric acid-nitric acid digestion for total metal analysis, (according to the method of Bernas¹³),

- 3.) nitric acid digestion,
- 4.) oxalate wash as a measure of those metals associated with amorphous iron and aluminum oxides (according to Williams et al¹⁴),
- 5.) hydroxylamine hydrochloride wash for manganese extractable metals (according to Chao¹⁵), and
- 6.) washings with distilled water at pH's 3, 6, 9, and 12.

Simultaneously, sorption experiments for trace metals in fly ash leachates onto different soils were also performed. The general procedure consisted of leaching a fly ash with distilled water overnight, adjusting the pH for reduction of iron levels (which were normally too excessive for the type of experiments performed), filtration (0.45 μ), addition of desired amounts of trace metals (as their nitrates), adjustment of pH to the desired level, and mixing with a known amount of previously dried soil matter. Reaction vessels were agitated for 12-15 hours, filtered and analyzed for residual trace metal concentrations. Data were typically expressed as adsorption isotherms. Those soil types investigated were a clean silica sand, bentonite clay, organic peat, and a natural sand with calcium and iron impurities.

All metal analyses were performed using atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Figure 1 indicates the relative distributions of the total metallic components among the fly ashes studied. 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. In general (although there were major exceptions),

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 around the concentration 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 soluble calcium at pH = 3. Figure 3 shows equilibrium pH as a function of the oxalate-iron calcium ratio. It can be surmised that oxalate iron is a measure of the acid content while soluble calcium, which is associated with the lime fraction, represents the basic component of fly ash. 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 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 (steps 4 and 5 previously). Two factors are apparent. First, although a very large fraction of the fly ash consists of aluminum 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 sorptive 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 may nonetheless be important since the sorptive capacity of MnO_2 is approximately 15 times that of iron oxide.

An added complication is the fact that it is difficult to determine in each case whether the three sinks behave independently or are themselves sorbed onto one other. Analysis of subsequent data was facilitated by defining the iron, aluminum, or manganese deposits as the primary, not absolute, sink for each trace metal, an approach which is more consistent with probable reality in any case.

Figures 5 through 11 illustrate average amounts and ranges of trace metals found in each type of extractant. Total metals determined by HF-HNO_3 digestion are included for comparative purposes. Then follow HNO_3 (alone) digestion, oxalate and hydroxylamine extracts, and washings at pH's 3, 6, 9, and 12. Differences between HF-HNO_3 and HNO_3 alone digestions give an approximation of the amount of metals on the surface of the particle.

From the data, it appears that arsenic is strongly concentrated on the surface of the fly ash, copper, chromium, zinc, and cadmium are concentrated to an intermediate extent, while mercury and lead are contained primarily within the ash matrix. This is summarized in Table 1.

TABLE 1

% of Total Metal Found on the
Surface of Fly Ash (Average Values)

Metal	%
As	93
Cd	25
Cr	44
Cu	48
Hg	0.74
Pb	8
Zn	32

Further comparisons of oxalate and/or NH_2OH extracts with HNO_3 digestion suggest the actual amount of a given trace metal which is available to solution while variable pH washings give some indication of the short term release associated with each metal specie.

Experimental work with arsenic and mercury was hampered, in the former case by unexplained contamination from available nitric acid (sulfuric acid was substituted for digestion) and in the latter case by the anomalous behavior of mercury in solution. The special case of mercury will be taken up later.

Further analysis of the information in Figures 5-11 can yield some interesting information about trace metal behavior. By noting relative increases or decreases of each metal in the oxalate and NH_2OH extracts, and the absolute amounts of iron, aluminum, and manganese, it is possible to determine the primary surface deposit with which each metal is associated. This information is tabulated below for each fly ash studied.

TABLE 2

Major Surface Deposit Association for
Trace Metals on Fly Ash

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

Key: Fe - Amorphous Iron Oxides

Al - Amorphous Aluminum Oxides

Mn - MnO₂

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, and to some extent lead, exhibit a preference for the manganese portion of the surface coating. Aluminum oxides were major sinks only when the oxalate extractable aluminum was greater than the extractable iron, a situation which occurred only once.

The identification of the surface associations of the heavy metals on fly ash is an important step in understanding their behavior in aqueous solution.

The sorption capacities of all three of the sinks identified in this study become less with decreasing pH. This is shown in Figures 12 through 16 for the release of Cd, Cr, Cu, Pb, and Zn. Values are expressed as the fraction of metal released from the "available" amount found associated with surface deposits of Al, Fe, and Mn. Figure 17 is a composite of the average release values for all the metals. Both cadmium and lead, those metals associated with MnO_2 , display the greatest degree of release with cadmium exhibiting considerably greater desorptive tendencies at all pH values. Cr, Cu, and Zn also displayed similar properties. With the exception of cadmium, which is naturally very soluble, none of the other metals showed any correlation with its solubility-governing properties. Figure 18 shows the free aqueous and monohydroxyl complexes of the metals as a function of pH. Since in most environments it is the hydroxide which controls the solubility of these species, these lines represent the left hand portion of the respective solubility diagrams. A ranking of solubilities, then, would be $\text{Cd} > \text{Zn} > \text{Cr} > \text{Cu} > \text{Pb}$. Ranking of desorptive tendencies (from Figure 16) were $\text{Cd} > \text{Pb} > \text{Cr} > \text{Cu} > \text{Zn}$. Other considerations which could have an influence are total surface concentration of each metal and any inorganic complexes which are formed. This latter factor appears very likely since in many cases, total soluble metal ion released was in excess of solubility relationships. These factors also aid in explaining the wide variations observed in sorptive behavior from fly ash to fly ash.

Experimental work with mercury was difficult due to its presence in many cases as the elemental vapor. Highly oxidative digestion procedures were satisfactory since oxidation to non-volatile Hg^{+2} was promoted (see Figure 10). Extractions with oxalate, NH_2OH , or at various pH values were questionable because of the escape of Hg^0 . This was alleviated in one set of experiments in which the fly ash solution was allowed to go to its natural pH in a closed system. Using cold vapor analysis by atomic absorption the amount and form (Hg^0 or Hg^{+2}) of released mercury could be determined. Results are given in

Figure 19 for each of the ashes studied. As indicated earlier, little of the total mercury is surface concentrated and from Figure 19 it appears that relatively little of this is available for release (at least in the short term). In many of the fly ashes the mercury appeared as Hg^0 , although there was no pattern such as with pll. These findings are consistent with the naturally low solubility of mercuric ion (see Figure 18), and the previously cited work of others who found most of the mercury in power plants is lost out the stack.

As described previously, most fly ash disposal areas consist of ponds or landfills. Once a metal ion is released into the aquatic environment it comes into contact with the existing soil system. Of concern are the sorptive tendencies of individual metals on the soil and the long term attenuation of concentration with distance. The former phenomenon, sorption onto soil matter, was addressed via the generation of adsorption isotherms as described under the section on experimental methods. It should be emphasized that natural ash leachate was used. Thus the gross effect of ionic strength and inorganic complex formation is contained in the data collected.

Figures 20 through 23 show several of the isotherms obtained plotted in the Freundlich manner. In working with trace metals two problems exist which limit critical examination of their properties in solution. These are solubility limitations which yield some upper concentration, and analytical sensitivity which gives a lower concentration limit. Care was exercised in adsorption experiments to include only soluble species of metals. Data were occasionally erratic but in general plots of the quality shown were obtained.

Figures 20 and 21 illustrate adsorption onto calcite sand and bentonite, respectively. pH adjustment with the sand was difficult due to its high buffering tendency in the neutral pH range. Figure 22 displays the general effect of pll on sorption capacity. Shown is cadmium onto organic peat however the trend, that of increasing sorptive capacity with increasing pH, was found in all cases. Figure 23 contains a comparison of the capacity of the four soils studied. Again, although

cadmium is shown, the ranking of organic peat > bentonite > calcite sand >> silica sand was found to hold for all metals studied.

The y-axis intercept at Log concentration = 0 gives a good reference parameter for determining the relative ranking of various metal-soil-pH combinations. This information is present for all systems studied in Table 3.

TABLE 3
Log q at Log C=0 for all Systems Studied

Metal	pH	Silica Sand	Calcite Sand	Bentonite	Organic Peat
Cd	3	N.A.	-	-4.85	-4.8
	4	N.A.	-	-4.85	-3.9
	5	-7.8	-5.6	-4.80	-3.6
	7	-6.7	-4.7	-4.35	-3.2
Cr	3	N.A.	-	-4.25	-3.9
	4	-6.2	-	-3.85	-3.5
	5	-5.0	-4.4	-2.8	-4.4
Cu	3	N.A.	-	-4.6	-3.6
	4	N.A.	-	-3.9	-3.2
	5	-6.7	-5.0	-4.2*	-3.5
Pb	3	N.A.	-	-5.1	-4.5
	4	N.A.	-	-4.0*	-4.2*
Zn	3	N.A.	-	-4.7	-5.5
	4	N.A.	-	-4.7	-4.4
	5	N.A.	-5.8	-4.35	-4.1
	7	-6.3*	-3.2	-4.0	-3.3

N.A. = No adsorption measurable

blank= not able to be run

* = estimate

Several features of Table 3 should be pointed out. The more negative the number, the less the adsorptive capacity of the soil. Several runs with silica sand at low pH values could not be accurately determined, i.e. so little of the metal was adsorbed that concentration differences could not be detected. As indicated, the calcite sand could not be adjusted to pH's below 5 because of buffering. Unfortunately, many of the metals become severely solubility limited in the neutral to alkaline pH range so that isotherms above pH 5 (7 for cadmium and zinc) were difficult to determine. This was a particularly acute problem for lead, which is the least soluble of the metals studied.

In spite of these difficulties, some very useful kinds of information are contained in Table 3. The ranking of soil sorption capacity (organic peat > bentonite > calcite sand > silica sand) and effect of pH mentioned previously are seen to be generally valid for all metals studied. pH appeared to have the least effect on the bentonite systems. This is consistent with the known isoelectric point of expanding three layer clays of around 2.0. The clay is negatively charged throughout the pH range studied. Those effects which are present are probably due to changes in metal ion speciation with pH. Hydroxo complexes would be expected to bond to surface oxide grouping on clays. Zinc and cadmium display the least effect with pH and exist predominantly as the doubly charged ion in the range 3-7. In contrast, organic peat contains many ionizable organic functional groups with pK values from 3 to 6. Thus one would expect pH to have a large effect on the sorptive characteristics of this material.

The relatively large capacity of the calcite sand as compared to the silica sand is most likely due to surface iron oxide impurities. The calcite sand was used since it was felt to be more representative of the soil type typically encountered around power plant sites which are located along major waterways.

It is interesting to note that cadmium, which was most readily desorbed from ash particles appears to be least adsorbed to the soil systems. A more complete ranking of metals in order of adsorptive tendencies is $\text{Cr} \geq \text{Cu} > \text{Zn} > \text{Cd}$.

lead is perhaps closer to cadmium and zinc in its sorptive tendencies, but the paucity of data available does not appear to warrant a definitive conclusion.

CONCLUSIONS

A useful method of differentiating surface from total heavy metals associated with fly ash is selective extraction for those metal oxide sinks (Fe, Al, Mn) with which the heavy metals have become associated. This association is important in defining the release of the metals in aqueous environments. This desorption, as well as subsequent adsorption onto local soil matter is pH dependent -- lower pH values favoring greater release or less adsorption in the system. Another aspect of trace metal chemistry is solubility, which generally decreases with increasing pH.

In view of this pH dependency, it would appear that the more critical case of potential contamination of water resources is that of the acid fly ashes, i.e. those where iron oxide deposits control the pH of the system. The problem could be reduced by maintaining the ash in a neutral or alkaline environment, although at extremely high pH values (~12) the desorptive tendency of most metals increased slightly. Even at neutral pH values, soluble complexes may increase the concentration of a given metal in excess of solubility. The average percentage of metals released for all fly ashes studied from their surface sinks at pH = 9 were cadmium - 17%, lead - 8%, chromium - 6%, copper - 1%, and zinc less than 1%. Another important factor is the absolute amount of metal on the surface. For instance, even though copper is released very little at neutral pH's, surface concentrations up to 200 µg/g of fly ash were found.

Another control strategy is the selective lining of ash ponds with a highly adsorptive soil material. Bentonite would probably be preferred over an organic soil even though it possesses less adsorptive capacity because of its low permeability. It should be emphasized, however, that the lining of ash ponds is only a temporary control since the ash must eventually be removed and placed in a more permanent fill-type location. Control in these areas may be considerably

more difficult unless steps are taken to place an impermeable cover over the ash fill.

Special mention should be made of cadmium because of its inert character in aqueous solution. Several of the findings of this study suggest that more sophisticated control methods may be needed to prevent its migration from ash sites. Significant amounts of the total cadmium in fly ash are located on the surface, it is readily desorbed even at higher pH values, it is poorly adsorbed onto most soil matter, and it is naturally very soluble. Fortunately it is not geochemically abundant.

Finally it is apparent from the wide spread of the data that fly ash exhibits a large degree of variation from place to place with regard to trace metal release. Average values are included in this report, however, they should be interpreted and used with care. Where a problem exists or is suspected to exist, individual experimentation with the ash and other environmental variables (eg. type of water, soil) should be undertaken and a separate assessment should be made.

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Figure 1: Total Metal Analysis of Fly Ash (average and range of values for ashes studied) as Determined by HF-HNO₃ digestion.

Figure 2: Equilibrium pH of Distilled Water as a Function of Fly Ash Concentration for Several Ashes.

Figure 3: Equilibrium pH for Fly Ash Concentration = 200g/l as a function of Oxalate/Iron-Soluble Calcium Ratio.

Figure 4: Comparison of Oxalate and Hydroxylamine Extracts of Iron, Aluminum, and Manganese.

CHROMIUM CONCENTRATION, $\mu\text{g/g}$ of Fly Ash

Figure 2: Comparison of Chromium released from Fly Ash for different Antacids.

ARSENIC CONCENTRATION, $\mu\text{g/g}$ of Fly Ash

Figure 3: Comparison of Arsenic released from Fly Ash for different Antacids.

COPPER CONCENTRATION, $\mu\text{g/g}$ of Fly Ash

Figure 4: Comparison of Copper released from Fly Ash for different Antacids.

CADMIUM CONCENTRATION, $\mu\text{g/g}$ of Fly Ash

Figure 5: Comparison of Cadmium released from Fly Ash for different Antacids.

Figure 12: Comparison of Zinc Released from Fly Ash for Different Digestions.

Figure 13: Comparison of Mercury Released from Fly Ash for Different Digestions.

Figure 14: Comparison of Lead Released from Fly Ash for Different Digestions.

Figure 11: Fraction of Cadmium Released from the Surface of Fly Ash as a Function of pH.

Figure 12: Fraction of Chromium Released from the Surface of Fly Ash as a Function of pH.

Figure 13: Fraction of Copper Released from the Surface of Fly Ash as a Function of pH.

Figure 15a Fraction of Lead Released from the Surface of Fly Ash as a Function of pH.

Figure 15b Fraction of Zinc Released from the Surface of Fly Ash as a Function of pH.

Figure 17: Composite of Figures 12 through 16
Showing Average Fraction of Metals Released from
the Surface of the Fly Ash as a Function of pH.

Figure 18: Solubilities of the Trace Metals Studied as a Function of pH (free aqueous and monohydroxo complexes only).

Figure 19: Quantities of Mercury Released from Each of the Fly Ashes Studied. Open Space Represents Elemental (Hg^0), Shaded Region Represents Ionic (Hg^{+2}). Numbers Above Each Column Are the pH of the Solution.

Figure 20. Representative Adsorption Isotherms for Various Metals on Calcite Sand at pH = 5.

Figure 21. Representative Adsorption Isotherms for Various Metals on Bentonite at pH = 4.

Figure 22. Representative Adsorption Isotherms for Cadmium on Organic Peat Showing the Effect of pH.

Figure 23. Representative Adsorption Isotherms for Cadmium at pH = 7 Showing the Relative Adsorptive Capacities of Soil Types.