MASTER

COO-2727-3

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

Technical Progress Report
for the Period
June 1, 1975 - February 29, 1976

T.L. Theis and J.J. Marley
Department of Civil Engineering
University of Notre Dame
Notre Dame, Indiana 46556

NOTICE
This report was prepared as an account of work
sponsored by the United States Government. Neither
the United States nor the United States Energy
Research and Development Administration, nor any of
their employees, nor any of their contractors,
subcontractors, or their employees, makes any
warranty, express or implied, or assumes any legal
liability or responsibility for the accuracy, completeness,
or usefulness of any information, apparatus, product or
process disclosed, or represents that its use would not
infringe privately owned rights.

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE. It
has been reproduced from the best available
copy to permit the broadest possible avail-
February, 1976 ability.

Prepared for
The U.S. Energy Research and Development Administration
under Contract No. E(11-1)-2727

ED
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

This report summarizes significant findings for the period June 1, 1975 - February 29, 1976. In addition an estimate of activities to be performed for the period March 1, 1976 - May 31, 1976 is also given.

Major emphasis thus far has been placed on laboratory evaluations of heavy metal associations with fly ash. Data are presented showing that most fly ashes contain considerable amounts of As, Ca, Cd, Cr, Cu, Fe, Hg, Pb, and Zn. Desorption studies suggest that pH and the presence of various heavy metal sinks on the ash particle surface (notably hydrous iron oxides) play significant roles in the release of these metals into solution. Adsorption studies using natural ash leachate/soil systems and vertical soil columns give quantitative estimates (through the use of adsorption isotherms) of the degree of attenuation of the heavy metals. Results thus far verify the importance of solution pH and iron oxide concentration. In general the element cadmium shows the least tendency toward sorbing onto local solid phases while lead is sorbed to the greatest extent. Among soil types, organic peat was the most effective in removing metals while silica sand was least effective.

Future plans call for a gradual shifting of emphasis to field studies and groundwater quality model evaluation. Immediate laboratory plans call for continued investigation of various metal sinks surrounding the heavy metal/fly ash system.

I. INTRODUCTION

Progress to date is best viewed in light of the original proposal objectives, which were threefold:

1. to gather data from both the laboratory and field for purposes of assessing the impact of heavy metal leachates of fly ash on local water quality;
2. to investigate the mechanism of heavy metal attenuation in different soil systems; and
3. to evaluate a groundwater quality model for heavy metals to be used for managerial and predictive purposes.

The suggested time for conducting this research was two (2) years.

Roughly speaking, the first year was to be devoted primarily to laboratory research, while the second year was to involve the majority of the field research. Those metals investigated in whole or part are As, Ca, Cd, Cr, Cu, Fe, Hg, Pb and Zn.

II. LABORATORY RESEARCH

Much of the information contained in this section has already been submitted in the form of progress reports and publications. These documents are referred to in the text and listed in the bibliography. Not all of the information contained in them is reproduced in this report.

A. Fly Ash Characterization

Various properties of fly ash which are important relative to its traditional uses have been reported in the literature (1) (2). These include use as a pozzolanic additive to cement, brick manufacturing, road bed stabilizer, aggregate, etc. In general those parameters of greatest importance are size fraction distribution and lime content. In the United States, however, little more than 10% of the total ash produced (1975 estimate - 36 million tons) is used in this manner. The rest must be disposed of or temporarily stored for later use.

Relatively little information exists on those properties of fly ash which are of importance in an environmental sense. An initial phase of this investigation involved gathering several different fly ashes and subjecting them to a micro-elemental analysis. Results are given in Table 1, along with average natural crustal abundances of the elements in question. The trace element compositions of fly ash can be seen to be highly variable but in general greater than background levels. Because of the large specie-dependence of most transition metals with pH, a further characteristic of significance was found to be pH. Figure 1 gives concentration vs. pH information for two fly ashes, one a basic ash (#2 in Table 1), the other an acidic ash (#10 in Table 1). The major factors which control the pH properties of fly ash are leachable lime and iron contents. In general those fly ashes generated from "western" coals have large amounts of lime and low iron levels (thereby producing an alkaline reaction in water), while the opposite is true of mid-western and eastern coals (which tend to generate low pH environments in water). For most of the laboratory work, the two ashes in Figure 1 were chosen for in-depth studies described later in this report.

Previous investigators (4)(5) have presented information showing higher concentrations of trace metals associated with smaller size fractions of fly ash. Thus those characteristics of fly ash which are important relative to trace metal contamination of water resources are initial trace metal concentrations, acid-base characteristics (lime and iron contents), ~~concentration~~ of the fly ash in the aquatic system, and size fraction distribution of the ash.

TABLE 1 (modified after Theis (3))
Micro-Elemental Analysis of Several Fly Ashes
(metal concentrations given in $\mu\text{g/g}$)

Fly Ash	pH Character	As	Ca	Cd	Cr	Cu	Fe	Hg	Pb	Zn
1.) Toledo Edison	Weakly Acidic	240	-	0.6	18	14	-	0.25	9.5	41
2.) Gary (NIPSCO)	Alkaline	370	72,800	1.5	40	24	15,000	0.12	42	50
3.) Chicago (Comm. Ed.)	Alkaline	250	50,000	1.5	40	64	20,000	0.16	46	50
4.) Detroit (Det. Ed.)	Acidic	440	2,000	1.3	30	31	14,500	0.10	20	42
5.) Tanners Creek #4	Acidic	370	23,000	2.0	54	88	28,000	0.10	27	140
6.) Tanners Creek #3	Alkaline	480	5,800	-	23	22	12,000	0.12	11	30
7.) Mishawaka (I & M)	Neutral	80	8,000	2.8	38	24	21,000	0.32	11	84
8.) Bay Shore	Alkaline	390	4,800	-	39	46	16,500	0.02	28	40
9.) West Olive (Cons. Power)	Acidic	470	3,500	-	34	17	20,500	0.04	24	47
10.) Michigan City (NIPSCO)	Acidic	275	17,000	11.2	64	113	41,500	0.18	625	1130
11.) Michigan City (Low Sulfur)	Alkaline	460	22,000	1.0	33	15	17,000	-	13	125
12.) Breed (I & M)	Acidic	540	400	0.1	11	18	12,500	0.01	7	50
Avg. Crustal Abundance	-	1.8	-	0.2	100	40	-	0.06	13	50

B. Sorption Studies

The mechanism which most readily explains the behavior of metal leachates of fly ash in groundwater/soil environments is a sorptive one. In addition to being a "macroscopic" phenomenon (i.e., one which allows for the interaction of a variety of intermolecular forces), adoption of this view facilitates mathematical treatments of the data.

The problem of trace metal contamination of groundwaters and soils can be broken down into two aspects. Initially the metal specie must desorb from the ash particle. Once in the aquatic system, it is subsequently adsorbed onto local solid phases. One aspect of the laboratory studies has been to investigate these phenomena separately, elucidating factors of importance for each step.

1. Desorption Studies

Natural leachates of the two fly ashes of Figure 1 (#10 and 2 of Table 1) are given in Table 2 at concentrations of 200 g/l. These values were obtained by suspending the fly ash in distilled water for one hour, allowing it to settle and filtering (.45 μ) the supernatant. Analyses were by atomic absorption spectrophotometry except for calcium which was done by EDTA titration.

TABLE 2
Heavy Metal Leachates of Fly Ash (200 g/l)

Metal	Concentration, $\mu\text{g/l}$	
	Fly Ash #10 (acid)	Fly Ash #2 (alkaline)
As	12500	43
Ca	6.2×10^5	1.22×10^6
Cd	1300	40
Cr	1000	200
Cu	5100	50
Fe	1.7×10^4	2100
Pb	2000	900
Zn	2.3×10^4	80

Certain features of Table 2 are obvious. The more acid the environment, the greater the solubilization of the heavy metals. In addition, the high lime level of the alkaline ash and high iron level of the acid ash are reflected in their respective values. Table 2 gives gross values which one might anticipate in ash pond or fill environments. It does not, however, suggest a mechanism of release of the metals. Previous investigators (5)(6) have indicated the major form of most metals on dry ash particles are the respective oxides. Thus the marked effect of pH on metal release is to be expected. However in view of the high iron content of many ashes, and its tendency to strongly adsorb other metal oxides (7)(8) it would seem imprudent to ignore the potential influence of this factor.

Figure 2 gives more information on this aspect. Here the pH of the leaching solutions was artificially controlled prior to and during fly ash addition. For the acid ash, desorption occurred at pH's 3, 4, 5, 6 and 7 while for the alkaline ash the pH's were 8, 9, 10, 11 and 12. Results are expressed as fraction of total metal desorbed (C/C_0). It is interesting to note the relative degree of desorption of the metals for these two different ashes. On first appearance it seems that the desorption of the metals is controlled primarily by natural solubility considerations. However if one compares fraction desorbed vs. pH with the natural solubility vs. pH (see Theis, Reference 3, Figure 5), it is evident that while this mechanism may be operative for fly ash #2, for fly ash #10 the fraction desorbed decreases long before solubility limits are exceeded for Cd, Cu, Cr, Pb, and Zn. This strongly suggests that desorption of trace metals is dependent upon relative degree of release

from an associated trace metal sink. In this case, amorphous iron oxide appears to limit metal desorption since it is the least soluble of all the metals in question (except oxides of mercury). However other sinks cannot be ruled out, particularly surface adsorbed manganese dioxide, aluminum oxides and various forms of silica. In addition, certain metal concentrations given in Table 2 are present in considerable excess of simple solubility -- such as lead and iron -- raising the probability of supracolloidal phases or the formation of soluble complexes. A large portion of the laboratory work in the final three months of the first year will be devoted to further investigations along these lines.

Desorption studies such as those reported on above for mercury have been anomalous. Further investigations are shown in Figure 3, which shows speciation of mercury forms released according to elemental (vapor) or ionic character. Most of the ashes examined showed little release of mercury for the duration of the tests (one day of continual agitation). Several, however, did show a sizable fraction of their mercury released in the elemental state. As such this mercury is volatile and much of it could be expected to disappear from ash disposal sites before entering the groundwater environment. The pH of the solution (given in Figure 3) appeared to have little influence on either the amount or form of mercury released. It should also be noted that, even for ash #6, the total amount of mercury released was less than 1% of the total amount contained in the ash.

Mercury Released, Nanograms/Cram of Fly Ash

Figure 3 Mercury Release from Fly Ash Speciated According to Elemental (open spaces) and Ionic (lined). Numbers Above Refer to pH of Solution.

2. Adsorption Studies

Once released into the soil/water environment, the metals will be strongly or weakly attracted by the soil matter present. Adsorption studies have been divided into two parts: soil column studies, and equilibrium adsorption studies. Soil columns allow for the variability of soil systems, experimentation with a relatively simple geometry (of use in model verification), and introduction of a flow (time) parameter.

Equilibrium adsorption studies give greater accuracy and flexibility of experimental mode while allowing a more rigorous mathematical treatment of the data.

Four soil-types are being used in this phase of laboratory work: a clean silica sand, a courser sand (with greater oxidic iron level), bentonite clay, and an acid organic peat. These soils cover a broad spectrum of soil properties and were selected in order to give maximum range of usable information while preserving opportunities to form viable mechanistic inferences from the data.

a. Column Adsorption Studies

As outlined in the original proposal, several vertical soil leaching columns have been constructed and are being used to determine the relative degree of attenuation of the metals on different types of soil matter. Typical results are shown in Figures 4 and 5. Such plots are reminiscent of ion exchange breakthrough curves. They give a direct indication of the relative effectiveness of different soil types on adsorption of metals. By comparing graphs, the effectiveness of a given soil on the attenuation of different metals can be seen. For instance, an organic peat has the greatest capacity for adsorption for cadmium,

Concentration_{out} / Concentration_{in} C/C_0

iron, and lead. Among these metals, however, it appears that it is most effective in removing lead, then iron, and last cadmium. Tabularized sorption capacities based upon these studies are currently being developed.

The basic shape of the curves obtained for these soil columns suggests a steady-state approach to the adsorption/flow situation is not unrealistic. This is of use in the model development stage (objective #3). This aspect will be further explored later.

Other aspects of the column studies involve the use of variable flow rates to determine the degree of adsorptive equilibrium attained in these systems. As will be seen subsequently, the simplest way to obtain quantitative information on soil-metal systems is through the use of the adsorption isotherm.

b. Adsorption Isotherms

Figures 6 and 7 illustrate adsorption isotherm data for pH = 3, fly ash #10 (of Table 1) (other plots are given in the second progress report (10) for the period 10/1/75 - 12/31/76). Three soil types are shown: silica sand, organic peat, and bentonite clay. Use of these soils represents a wide range of adsorptive capacities and allows for the separation of certain effects, e.g., weak surface bonding (ottawa sand) from organic complex formation (organic peat). The isotherms are of the Freundlich type which follow the general equation:

$$\frac{C_o - C}{M} = k C^{1/n}$$

where C_o = initial concentration of metal ion,
 C = equilibrium concentration of metal ion,
 M = amount of soil material,
 k, n = constants.

The logarithm of this equation gives a straight line relationship. In general, the y-axis intercept is a measure of the sorptive capacity of a given soil for a certain metal, while the slope of the line is inversely proportional to the reaction "intensity" (or enthalpy). A great deal of qualitative as well as quantitative information can be obtained from arranging the data in this fashion. For instance, a vertical line (such as for cadmium on ottawa sand) indicates essentially no reaction of any kind taking place while a more horizontal line (such as for cadmium and organic peat) indicates a high reaction enthalpy suggestive of a more irreversible chemisorption effect. Quantitatively, the constants determined can be used to rank adsorptive characteristics of individual metals on individual soils and can generate water quality data in equilibrium groundwater models.

Thus far isotherms of the type indicated have been determined for all metals on all soils, except the sand with oxidic iron impurity, at pH = 3 and pH = 7. Further tests at other pH values and with variable amounts of amorphous iron oxide added will be performed in the remainder of the first budget year.

Difficulties have been experienced in studies of this type with detection limits of the atomic absorption procedure employed in most metal ion analyses. This limitation yields data which is sometimes of questionable accuracy and applicability. This is being overcome through: 1). the use of "spiked" solutions of ash leachates with somewhat higher (although not unrealistic) concentrations of trace metals, and 2). the acquisition of a graphite furnace attachment to the AA unit used to give greater sensitivity and detection limits.

3. Model Development

Groundwater quality model development for trace metal contaminants is now beginning. At present several existing formulations are being reviewed to assess their suitability to the system being studied. The model envisioned will consist of two aspects:

- 1). natural groundwater dispersion,
- 2). trace metal attenuation on soil matter.

These two components will be superimposed upon one another. The literature contains several types of models which describe the hydraulics of groundwater flow (1 above), but very few addressing the subsequent sorption of trace constituents. Model development is further considered in the renewal proposal.

III. FIELD RESEARCH

Several local ash disposal sites have been examined. These are indicated in Table 3.

TABLE 3
Potential Disposal Sites for Monitoring

Location	Type of Ash	Method of Disposal
Univ. of Notre Dame	Weakly Acidic	Direct Fill
Twin Branch (Mishawaka, IN)	Neutral	Fill
Michigan City	Strongly Acidic	Pond
Bailey (Burns Harbor, IN)	Weakly Acidic	Pond
Mitchell (Gary, IN)	Strongly Alkaline	Pond
Schahfer (DeMotte, IN)	Alkaline	Pond

During the Spring of 1976 test wells and soil borings will be made at each of these sites. Based upon these analyses plus other geographic and hydrologic factors two sites will be chosen for intensive monitoring. The nature of this monitoring program is further outlined in the renewal proposal.

IV. ANTICIPATED RESULTS FOR THE PERIOD 3/1/76 - 5/31/76

During this period it is expected that major project emphasis will gradually shift from laboratory to field work, although the original timetable called for laboratory work to progress through the summer. Those aspects of the problem which will be researched in the laboratory during this period include:

1. further development of isotherm data primarily through the use of "spiked" heavy metal leachates,
2. a more intensive examination of fly ash sinks for heavy metals and factors which control release into solution,
3. initial stages of model development for predictive purposes.

Major field work will include:

1. Test well drilling at several sites, and
2. selection of two sites for intensive monitoring, and location of well points at these sites. Establishment of a sampling regime.

V. TIME REQUIREMENTS

For the major portion of the first year of this study, a breakdown of time spent (%) by principal investigators is indicated below:

Duty	Principal Investigator (T.L. Theis)	Co-Principal Investigator (J.J. Marley)
Supervision of Research	40%	50%
Performance of Research	10%	-
Interpretation of Results	20%	40%
Consultation with Experts	10%	10%
Writing Reports	20%	-

These percentages represent 25% of total time of principal investigator (release time in contact-10%) and 10% of the total time of co-principal investigator (release time specified-10%).

VI. REFERENCES

1. Minnick, L.F., "Investigations Relating to the Use of Fly Ash as a Pozzolan Material and as an Admixture in Portland Cement Concrete," Proc. of the American Society of Testing Materials, 54, 1129 (1954).
2. Minnick, L.J., "Stabilization of Waste Materials Including Fly Ash, Sulfur Oxide Scrubber Sludges, and Sewage Sludges," Proc. of the 2nd National Conference on Complete Water Reuse, AIChE, EPA (in press).
3. Theis, T.L., "The Potential Trace Metal Contamination of Water Resources through the Disposal of Fly Ash," Proc. of the 2nd National Conference on Complete Water Reuse, AIChE, EPA (in press).
4. Davison, R.L., Natusch, D.F.S., Wallace, J.R., and Evans, C.A., "Trace Elements in Fly Ash," Environmental Science and Technology, 8, 13, 1107 (1974).
5. Natusch, D.F.S., Evans, C.A., Hopke, P.K., Loh, A., and Linton, R., "Characterization of Trace Elements in Coal Fly Ash," paper presented at the International Conference on Heavy Metals in the Environment, Toronto, October 27-31 (1975).
6. Kaakinen, J.W., Jorden, R.M., Lawasani, M.H., and West, R.E., "Trace Element Behavior in a Coal-Fired Power Plant," Environmental Science and Technology, 9, 9, 862 (1975).
7. Jenne, E.A., "Controls on Mn, Fe, Ca, Ni, Cu, and Zn Concentrations in Soils and Water: The Significant Role of Hydrous Mn and Fe Oxides," in Trace Inorganics in Water, Adv. in Chemistry Series #73, ed. Robert F. Gould, American Chemical Society Publication (1968).
8. Jenne, E.A., and Wahlberg, J.S., "Role of Certain Stream-Sediment Components in Radioion Sorption," Geological Survey Professional Paper 433-F, U.S. Government Printing Office, Washington, D.C. (1968).
9. & 10. Theis, T.L., and Marley, J.J., "The Contamination of Groundwater by Heavy Metals from the Land Disposal of Fly Ash," Progress Reports #COO-2727-1 and COO-2727-2, Energy Research and Development Administration Contract No. E(11-1)-2727 (1975-76).