



Project Summary

Migration of Hazardous Substances through Soils

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Factorially designed column and batch leaching studies were conducted on samples of various industrial wastes, flue gas desulfurization sludges, and coal fly ash to determine the effect of leaching solution composition on release of hazardous substances from waste samples, and the effect of soil properties and leaching solution composition on subsequent migration through soils.

The wastes studied came from:

- Electroplating
- Secondary Zinc Refining
- Inorganic Pigment
- Zinc-Carbon Battery
- Titanium Dioxide Pigment
- Nickel-Cadmium Battery
- Hydrofluoric Acid
- Water-Based Paint
- White Phosphorus
- Chlorine Production
- Oil Re-refining
- Flue-Gas Desulfurization
- Coal Fly Ash

Seven different soils and two leaching solutions (water and municipal landfill leachate) were used.

Waste characteristics, such as pH and total metal content, were marginally useful predictors of metal concentrations in water or municipal solid waste (MSW) landfill leachate extracts of the waste. However, no satisfactory substitute for leaching tests, whether by batch or column procedure, was found. Waste and extract characteristics such as pH, electrical conductivity, and metal content were useful predictors of metal movement in soils. Leaching solution composition was highly significant. MSW leachate solubilized greater amounts of metals from all wastes than did distilled water, and metals contained in MSW leachate moved

more rapidly through soils than those contained in water.

Serial batch extractions gave leaching data that were quite similar to data obtained from the slower and less convenient column leaching procedure. Both procedures require long-term extraction because some waste do not begin to release significant amounts of metals until several void volumes of leaching solution have been passed.

The results of the project have been documented in three reports published by the U.S. Army. These reports are identified as Parts II, III, and IV. Part I was an unpublished interim report that was later incorporated into the larger Part II report. The complete citations are given at the end of this Project Summary.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Industrial processes and air and water pollution abatement systems produce solid wastes that, when placed in landfills, can release hazardous substances that can move through soils and find their way into groundwater. Hazardous substances in the wastes studied included elements such as arsenic, beryllium, boron, cadmium, chromium, copper, fluoride, lead, mercury, nickel, selenium and zinc. Other elements essential to plant growth, such as phosphorus, sodium, and magnesium may occur in toxic concentrations or may influence attenuation of toxic elements by soil. Important factors to be weighed when considering land disposal are knowledge of the way wastes behave in the disposal



environment, and how hazardous materials in leachates from landfills move in soils. The broad objective of this study was to answer such questions for selected wastes. The study would serve as a guide for future research and help to identify wastes that may require special care in disposal. Another objective for this study was to develop techniques that would be applied to the evaluation of leaching behavior of wastes at specific sites. This work was conducted before final regulations were issued under the Resource Conservation and Recovery Act (RCRA). Under current regulations many of the wastes studied would be banned from land disposal unless properly treated to reduce their toxicity and mobility.

Determination of the Leachability of Metals from Five Industrial Wastes and their Movement Within Soil

The first phase of the study involved sampling five different industrial wastes and then determining composition and tendency to solubilize when extracted with distilled water or municipal landfill leachate. The distilled water was used to simulate rain or groundwater, and the landfill leachate was used to simulate the leachate produced when MSW and industrial wastes are disposed of together. Samples of wastes from industries such as electroplating, nickel-cadmium battery, inorganic pigment, water-based paint, and chlorine production, were studied using batch extractions and continuous flow columns.

The effect of pH on solubility of each of the wastes was determined from single batch studies with waste to distilled water ratios of 40 g of dry waste/400 mL water and 80 g dry waste/400 mL water. The pH of each combination was adjusted to 5, 7, or 9. Alkaline conditions favored immobilization of sample metals used, except for chromium, which was mobilized at alkaline and acid condition, but relatively immobile at neutrality. The test indicated that pH was the most important factor in determining solubility of Cd, Cu, Ni and Zn, which were about 100 times more soluble at pH 5.0 than they were at pH 7.0.

Serial batch extractions were conducted by mixing waste with distilled water at a ratio of 20 g waste/300 mL water and 1 kg waste/2000 mL water and stirring for 72 hr. Samples were filtered, and the filtrates were analyzed for metals by Atomic Absorption Spectrometry (AAS). The process was then repeated by recovering the residue, and adding 200 ml of water to it.

A total of seven extractions were conducted at 20 g waste to 200 mL water.

Heavy metal solubilization remained relatively uniform throughout the seven extractions. The first extractions removed significant quantities of ions other than heavy metals. But after four extractions pH and conductivity became relatively stable.

Serial batch extractions with landfill leachate were conducted in a similar fashion. All five of the wastes were subjected to single batch extractions with water at 3 different pH levels and to serial batch extractions with both water and municipal landfill leachates at (waste to water) ratios of 20 g to 200 mL and 1 kg of waste to 2000 ml. Minor variations in procedure were employed for different wastes. Landfill leachate solubilized more metals than the distilled water did.

Columns of waste were leached to determine solubilization rates by using six columns with distilled water and six columns with landfill leachate as solvents for each waste. Wastes were packed into 37 ml mm glass tubing, that was equipped for upflows of solvent at a flow rate of 0.5 to 1.5 soil pore volumes per day.

The waste leaching columns were connected to soil columns to study the metal migration through soils in a continuous flow system. Samples of five soils were collected and analyzed. They were:

- Kalkaska - a yellowish brown, rapidly permeable sandy Spodosol from Michigan;
- Davidson - a reddish clayey, moderately permeable Ultisol from North Carolina;
- Anthony - a dark brown, permeable, sandy Entisol from Arizona;
- Chalmers - a dark gray, fine, loamy, slowly permeable Mollisol from Indiana; and
- Nicholson - a yellowish brown, fine, slowly permeable Alfisol from Kentucky.

All five soils were tested in preliminary batch attenuation studies to measure their ability to remove metals from water and landfill leachate that had been in contact with wastes. Davidson soil, the most retentive, and Kalkaska, the least retentive, were selected for use in the column attenuation studies.

An attempt was made to achieve a flow rate of 0.5 to 1.5 pore volumes of leachate through each soil column each day. It was difficult to achieve similar flow rates and contact times however because the physical properties of the soils were different. The soils were packed into columns with an inside diameter of 3.3 cm but the heights of the columns were varied from

10 cm for the Davidson to 21.4 cm for the Kalkaska. Other aspects of column design such as the head (depth) of waste leachate and the use of stop cocks were varied in the attempt to equalize flow rates and give each soil equivalent contact with the waste leachate.

The solubilization studies showed that substantial concentrations of cadmium and copper were released by water from the electroplating waste. In addition, chromium was released by the landfill leachate. Very high concentrations of nickel and cadmium were released by water and MSW leachate from nickel-cadmium battery waste. Nickel and Cd moved rapidly in soils. The inorganic pigment waste released only small quantities of cadmium, chromium and lead for each solvent used, but the concentration in the soil column leachate exceeded drinking water standards. Water-base paint released only mercury sporadically and at very low concentration. Mercury was also the only metal found, though at low concentration, in leachate from chlorine production brine waste when landfill leachate was the solvent. Although relative positions of the soils in the ranking varied, depending on which metals and extracts were examined, Kalkaska and Anthony were consistently poor attenuators and Chalmers and Davidson were consistently very good attenuators. Davidson soil removed more metals from the waste leachate than did other soils with comparable pH even when the other soils had higher clay contents, cation exchange capacity, and surface areas per unit weight. The Davidson had a high iron oxide content.

Flue-Gas Desulfurization and Fly-Ash Wastes

The second part of the study examined the way that wastes from coal-burning power plants react in the soil environment. Samples of flue-gas desulfurization (FGD) sludge and/or fly-ash (FA) were collected from nine power-generating plants that burn coal from different sources and/or use different scrubbing materials. Six FGD wastes and three FA wastes were characterized primarily by their heavy metal, fluoride and boron content, as well as their tendency to solubilize. They were also analyzed for chloride, total residue, volatile residue, filterable residue, and nonfilterable residue in order to characterize the waste and help explain how waste composition affects the migration of elements in soils. The FGD samples were collected as liquid sludge with high solids contents and FA was collected as a dry powder. To determine the composition of the waste, portions were dried, digested

in aqua regia, the digestates filtered, diluted and then analyzed for arsenic, beryllium, boron, cadmium, chromium, copper, fluoride, lead, mercury, nickel, selenium, and zinc. Iron was also determined to further characterize the wastes. The FGD waste contained high concentrations of boron and fluoride, and moderate amounts of arsenic, chromium, copper, lead, nickel, and zinc. Concentrations of beryllium, cadmium, mercury, and selenium were low to very low. In addition to the elements in the solid portion, the liquid portion was found to contain a large amount of dissolved salts. A high concentration of calcium, potassium, and sodium were found in the supernatant liquor. This is significant because these could interfere with soil attenuation of metals.

The dry fly ash powder was mixed with water at ratios of 20 g solids to 200 parts water and 40 g solids to 200 ml water. The slurries were stirred for 24 hr, filtered, the pH measured, and the liquid analyzed by atomic absorption spectrophotometry and/or argon plasma emission spectrophotometry.

The pH was found to be an important factor in determining the solubility of metals of interest. For instance, change in pH between 5 and 9 did not change the solubility of boron, but fluoride solubility increased as pH increased.

Three of the soils used in previous batch soil attenuation studies, Chalmers, Davidson, and Nicholson, were used in the soil column attenuation studies with FGD and FA wastes. In addition to these, a sample was collected from an unidentified clayey fill in Kentucky and from a clayey, saline soil from the Dugway Proving Grounds in Utah. The Dugway sample was chosen specifically to determine the effect of salt accumulation on a soil's capacity to absorb metals from a percolating liquid.

Solubilization and soil attenuation were studied in continuous flow columns similar to the column leaching procedure used in studies of solubilization of selected elements from industrial wastes with water and landfill leachates as solvents, and the attenuation of these elements from percolating leachates by soil. Serial batch solubilization studies of FGD and FA wastes were not conducted. It was concluded that a highly soluble salt content could diminish a soil's capacity to attenuate some elements from waste leachates. It was also shown that soils with the characteristics of Chalmers, Nicholson, the Kentucky soil, or the Dugway soil, would be relatively unchanged in permeability by FGD and FA wastes similar to those used in

this study. Permeability of samples of Davidson was increased significantly by the waste leachates.

Boron and fluoride concentrations were generally higher in the waste leachate than were other elements of interest, but they were successfully removed by the soils. Significant concentrations of arsenic found in waste leachates was effectively removed by all soils except Dugway. The high soluble salt content of Dugway apparently interfered with adsorption of contaminants by soil.

Development of a Serial Batch Extraction Method and Application to the Accelerated Testing of Seven Industrial Wastes

An important goal for conducting waste leaching and soil adsorption tests in the laboratory is to simulate field conditions. While studying the leachability of industrial wastes and the attenuation of ions that occurred when the leachate passed through soil, it was observed that serial batch and continuous column studies gave similar results. Column studies are slower and more cumbersome. Some of the field conditions to be simulated include the dynamic changes that occur in both leachate and soils through the progression of leaching and adsorption. Leaching of the most soluble ions in the waste takes place first, followed by other ions in order of their solubility as leaching progresses. The soils change chemically and physically as ions are exchanged during the movement of leachates through them.

The graded serial batch extraction procedure was developed. Seven industrial wastes and three clayey soils were used in this study. Seven extracts for each of the 7 industrial wastes were applied to the three soils. The three soils were Chalmers, Davidson, and Nicholson. The industrial wastes included the following: zinc-carbon battery manufacturing, titanium dioxide pigment production, hydrofluoric acid manufacturing, white phosphorus production, oil re-refining, and two from zinc secondary-refining (cinders and scrubber-waste). The volume of extraction liquid used was varied to simulate the variability in time of leaching the waste under field conditions. The soil batches were graded in size to allow for analyzing samples of the extracts after each step while maintaining a constant ratio of waste extract to soil.

Both before and after contact with the soils, the resulting solutions were analyzed for pH, conductivity, and concentrations of the elements of concern.

This analysis facilitated calculation of distribution coefficients, penetration factors, the fraction of each ion retained on the soils, the amount flushed off of a soil by the passage of a later extract, and the yield of an ion per unit weight of soil. The effect of soil-to-waste ratio on these values and the limitations and applicability of empirical equations and prediction models are discussed in the report.

Conclusions

- Waste characteristics were only marginally useful as predictors of metals concentrating in water or MSW extracts of the waste; leaching tests are needed to predict characteristics of leachate from MSW landfills containing industrial wastes.
- Characteristics such as pH, electrical conductivity, and metal content of waste and extracts were useful predictors of metal movement in soils.
- MSW leachate solubilized greater amounts of metals than water did and the metals moved more readily through soils.
- Of the soils used in absorption or column studies, the Davidson removed the greatest amount of metals, apparently because of its relatively high iron oxide content.
- The FGD and FA waste contain toxic elements that may solubilize and create adverse impacts on soil, and their relatively high dissolved solids contents in supernatants may cause mineralization of groundwater.
- The state-of-knowledge is inadequate to allow formulation of a prediction model that would include all of the factors that control movement of metals in soil.
- The serial batch extraction procedure provides a method for making quick assessment of a site for disposal of given wastes where soil properties vary with depth, and where alternative site management techniques are to be considered.

This Project Summary is based on three separate parts of a report submitted in partial fulfillment of Interagency Agreement EPA-IAG-D4-0443 between the U.S. Environmental Protection Agency and the U.S. Army Dugway Proving Ground. The Principal Investigator was Martin J. Houle of the Chemical Laboratory Division, U.S. Army Dugway Proving Ground. Michael H. Roulier was the EPA Project Officer.

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Michael H. Rouller is the EPA Project Officer (see below).

The titles for the complete report (except Part I) are listed below. Part I is an unpublished interim report that was incorporated into the Part II report.

"Migration of Hazardous Substances through Soil: Part II-Determination of the Leachability of Metals from Five Industrial Wastes and their Movement within Soil," (Order No. AD-A 158990; Cost: \$31.00).

"Migration of Hazardous Substances through Soil: Part III-Flue-Gas Desulfurization and Fly-Ash Wastes," (Order No. AD-A 182108; Cost: \$45.00).

"Migration of Hazardous Substances through Soil: Part IV-Development of a Serial Batch Extraction Method and Application to the Accelerated Testing of Seven Industrial Wastes," (Order No. AD-A 191856; Cost: \$53.00).

The above reports are available (cost subject to change) only from:

National Technical Information Service

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