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EVALUATION OF SORBENTS FOR INDUSTRIAL SLUDGE LEACHATE TREATMENT

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related polluttional impacts on our environmental and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory, Cincinnati (IERL-Ci) assist in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report deals with the investigation of leachate contaminant control using sorbents. Ashes, clays, and refined materials were tested under laboratory and pilot-scale conditions to determine their capacity to remove leachate contaminants produced from three industrial sludges -- calcium fluoride, metal hydroxide, and petroleum. The report will provide useful data to government agencies and industries contemplating control of residue leachate from industrial sludge impoundment via sorbent contact.

For further information concerning this subject the Industrial Pollution Control Division should be contacted.

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ABSTRACT

A laboratory and outdoor pilot-scale investigation was conducted on the use of selected sorbents for removing leachate contaminants from three industrial sludges.

The laboratory results indicated that rather than a single sorbent, a combination of acidic and basic sorbents is required in a layered system for removal of all the measurable contaminants from the leachates. These combinations are illite, vermiculite, and a natural zeolite for the acidic leachate; illite, acidic fly ash for the neutral leachate, and illite, kaolinite, and a natural zeolite for the alkaline leachate. The sorbent capacities exhibited by the natural sorbents are comparable to those exhibited by refined sorbents.

The outdoor pilot study, which was limited to the treatment of the calcium fluoride sludge leachate, using lysimeters, some 80 times larger than the laboratory lysimeters, revealed that the sorbent effectiveness depends on the velocity of the leachate through the sorbents and the sorbent removal capacity for specific contaminants. Except for magnesium effective reductions of the measurable leachate constituents were achieved with the use of illite, acidic fly ash, and a zeolite in the weight ratio of 2:2:1.

Sorbent costs have been estimated for various combinations required for treating leachate from calcium fluoride sludge over a 10 year period of landfill operation. For the illite/acidic fly ash/zeolite combination and the illite/acidic fly ash/basic fly ash combination, costs are \$1.37 and \$0.45 per ton of sludge, respectively.

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SECTION 1

INTRODUCTION

The purpose of most waste treatment processes is to convert the pollutants to a gas, such as carbon dioxide, or to a solid that can be readily removed from the waste stream. In the latter instance, the end product is a sludge that must be disposed of in an environmentally acceptable manner. At present, ocean dumping and landfill are the two methods being utilized for the disposal of this sludge. However, ocean dumping is to be banned by congressional action in 1981; thus, landfill will be the remaining receptacle for these sludges.

The disposal of sludges by landfill can lead to heavy metal, toxic anion, and organic contamination of surface and ground waters by leachate from groundwater seepage or rainwater filtration through these sludges. In general, this contamination can be minimized by one of the following treatments:

- a. Chemical fixation of the sludge. This method applies physico-chemical principles to fix or stabilize the contaminants in the sludge so that they will not leach to the environment. Though the concept of this approach is most desirable, the process is expensive and leads to a significant increase in the volume of material that must be disposed of.
- b. Selective location of landfill site. This method requires that the landfill be located (at adequate distances) far enough from surface or ground waters to permit the natural clay components in the soil to attenuate the leachate pollutants. The cost of this method may be low in certain cases, but adequate sites are becoming scarce.
- c. Lining the landfill site. This method consists of lining the landfill with an impermeable membrane and collecting the leachate resulting from rainwater filtration through the sludge. The collected leachate is then given conventional physical-chemical treatment (i.e., activated carbon and alumina). Though this approach is widely used, it is expensive because the costly refined sorbents require regeneration facilities. This expense could be overcome if inexpensive sorbents such as clays in combination with fly ash could be used to treat the leachate.

The latter treatment method essentially simulates the natural process, but in a controlled manner. Furthermore, the method is appropriate for sandy areas where little attenuation of the leachate contaminants can be achieved.

A number of investigators have shown that the following pollutants in leachates and waste streams are attenuated by clay minerals, soils and waste products: organics (e.g., phenols², surfactants³, pyridine^{4,5} and other organics characterized by chemical oxygen demand (COD)⁶), pesticides (e.g. parathion⁷, DDT, dieldrin and heptachlor⁸), herbicides (e.g., paraquat⁹), heavy metals (e.g., lead, cadmium, mercury, zinc, manganese, copper¹⁰⁻¹⁴) and toxic anions (e.g., chromium VI, arsenic and selenium¹⁵). However, no-one has really explored the use of fly ash-clay sorbent mixtures to any great extent.

This investigation has been concerned with: (1) defining the clay/fly ash combinations that are most effective in removing the heavy metals, toxic anions, and organics present in leachates originating from industrial sludges; (2) examining the effect on contaminant removal of such factors as leachate pH and velocity through the sorbent, and (3) establishing a design approach for this treatment.

The sludges used in this study were a calcium fluoride sludge (of the type generated by the electronics and aircraft industries), a metal finishing sludge, and a petroleum sludge. These sludges were selected because their annual production is of significant magnitude to present disposal problems. The leachate from these sludges exhibited pH's that were neutral, basic, and acidic. Also, they were expected to contain a cross section of heavy metal hydroxides, cyanide, fluoride, and organics.

The sorbents selected for this study were acidic and basic fly ashes, vermiculite, illite, kaolinite, and a natural zeolite. Activated alumina and activated carbon, which are presently being used for the removal of cations, anions, and organics in industrial waste streams and potable water supplies, were included in the study for comparison purposes.

This investigation consisted of two phases: (1) continuation of the laboratory study described in a recent report by the U.S. Environmental Protection Agency (EPA)¹⁶ to define design parameters for treating industrial sludge leachates, and (2) an outdoor pilot-scale study designed to treat 530 liters of leachate. The pilot study was limited to calcium fluoride sludge leachate because the fluoride levels of this sludge range from 5 to 20 mg/l and there is currently no inexpensive treatment process to reduce the fluoride concentration to 1 mg/l or less.

SECTION 2

CONCLUSIONS

As a result of this study, an extremely promising, inexpensive system has been developed for the treatment of leachate arising from industrial sludges disposed of in landfills. The combinations of illite, vermiculite, and zeolite; illite, acidic fly ash, and a natural zeolite; and illite, kaolinite, and a natural zeolite have been found to be the most effective in a layered system for removing cations, anions, and organics in acid petroleum, neutral calcium fluoride, and basic metal finishing sludge leachates, respectively. The capacities exhibited by these sorbents for the removal of contaminants from these three leachates are comparable to those exhibited by activated alumina and activated carbon. The combinations of natural clay and fly ash are used because no single sorbent can remove all of the contaminants present in the industrial sludge leachates examined.

Both pH control of the leachate and the order that the natural clays and fly ashes are used in a layered bed influence the removal of the cations, anions, and organics in the industrial sludge leachates. Acidic sorbents such as illite, kaolinite, and acidic fly ash, which can initially induce slightly acidic conditions into the leachate, are placed at the top of the layered system followed by those sorbents that can induce slightly alkaline conditions in the leachate. This results in the removal of the anions before the cations. Slightly acidic conditions (greater than pH 6) and slightly alkaline conditions (less than pH 9) favor the removal of anions and cations, respectively. Organics are effectively treated under both acidic and basic conditions.

Alkaline conditions at the base of the bed are desirable, since they favor the removal of both the cations in the leachate and the heavy metal cations initially leached from specific sorbents at leachate conditions below pH 6. Either zeolite or basic fly ash is effective in controlling this initial leaching of heavy metal ions by the acidic sorbents.

In the design of a sorbent system, the total amount of a specific cation, anion, or organics removed is indicated by the sorbent removal capacity. This property is influenced by pH and the concentration of the contaminant in the leachate. The volume of leachate that can be treated with maximum removal is regulated by the velocity of the leachate through the sorbent bed. This leachate velocity can be regulated by sorbent bed height (which defines leachate volumetric flow rate through the sorbent bed under specified hydraulic conditions), by varying the amount of inert material added to the clays to regulate their permeability, or by varying

the particle size of the sorbents in the bed.

The illite, acidic fly ash, and zeolite combination in the weight ratio of 2:2:1 was found to be effective for treating the measurable contaminants (except magnesium) in calcium fluoride sludge leachate on a pilot scale. The copper and fluoride ions, which are considered toxic, were reduced to concentration levels generally acceptable for potable water supplies. A calcium ion concentration of over 300 mg/l in leachate was reduced to 80 mg/l; a copper ion concentration of 0.12 mg/l was reduced to 0.04 mg/l; the fluoride ion concentration was reduced from 15 to 1 mg/l; the total cyanide was reduced from 0.37 to about 0.06 mg/l, and the COD was reduced from about 45 to 15 mg/l. The magnesium ion concentration was only reduced from 76 to about 53 mg/l. In addition, except for magnesium and COD, the resulting effluent concentration was found to be independent of influent concentrations. Thus, variations in the concentrations of the contaminants in a leachate should not influence the effectiveness of a treatment system containing the natural clay/fly ash sorbent combinations.

Sorbent cost for the illite, acidic fly ash, and zeolite combination in the weight ratio of 2:2:1 required for the treatment of the leachate during a 10-year period of landfill operation was estimated to be \$1.37/ton of sludge disposed of in the landfill. This cost is based on an annual rainfall of 102 cm (40 in) and assumes that all the precipitation that falls on the landfill becomes leachate. This cost may be reduced to only \$0.45/ton of sludge disposed of in the landfill if the illite, acidic fly ash, and basic fly ash combination in the weight ratio of 2:2:1 is used. Based on the laboratory lysimeter results, the illite, acidic fly ash, and basic fly ash combination appears promising for the treatment of the measurable contaminants except for the calcium ion in the calcium fluoride sludge leachate. This combination was not evaluated on a pilot scale because of the limited time available under this grant.

SECTION 3

RECOMMENDATIONS

As a result of these studies, three additional investigations are indicated:

1. A project should be undertaken with the cooperation of State and Federal agencies and industry to demonstrate the use of fly ash/clay sorbent combinations for treatment of industrial sludge leachates under actual field conditions. Test cells containing the sludge should be constructed in the field. Both the use of a sorbent bed and a liner containing the sorbent combination should be evaluated. The most economical system should be defined for control of fluoride, cyanide, and heavy metal pollution of ground and surface waters by leachate from the operation of regionalized landfills or specific industrial sites. This system should be available for inspection by other potential users. But before this project is initiated, a pilot scale evaluation of the illite/acidic fly ash/basic fly ash sorbent combination for the treatment of leachate containing fluorides, cyanides, and heavy metals should be carried out, since the sorbent cost associated with the use of this combination is significantly less than that associated with a zeolite combination.
2. The leachate from additional industrial sludges should be examined in the laboratory lysimeters to define the best sorbent combinations for treating nickel, in neutral and basic leachates and iron, lead, chromium, cadmium, mercury and arsenic in acidic, neutral and basic leachates. The concentrations of all of these constituents were below measurable levels in the leachates that were examined. In addition, the maximum velocity of leachate through the sorbents should be defined to provide the most effective removal of all of the above constituents. These results would provide data for potential users to set up pilot-scale studies to obtain the engineering data necessary for field use.
3. A project should be undertaken to demonstrate the use of this technology in the field on leachate being generated in an existing industrial landfill. Means to collect the leachate for treatment would be required. Analysis of the leachate would be carried out to identify the constituents so that the sorbent combinations that could be used to treat the leachate could be selected. Laboratory lysimeter studies would be utilized to identify the sorbents and their capacity for removing the cations and anions not encountered in the present study. Test sorbent beds would then be set up in the field to identify the most promising sorbent combination and obtain the engineering design parameters for full scale treatment of the leachate from the landfill.

SECTION 4

MATERIALS AND METHODS

The preparation of the industrial sludge leachates and the analytical procedures utilized in this study are discussed in the final report¹⁶ covering the first phase of this study.

LABORATORY LYSIMETER STUDIES

Laboratory lysimeter studies were conducted using 500 g of each sorbent material. Since "pure" clay lysimeters did not exhibit adequate permeability characteristics, illite, kaolinite, vermiculite, and zeolite were prepared as a mixture consisting of 80 percent inert Ottawa sand and 20 percent clay. This ratio was arrived at after a series of studies established that this figure would permit adequate flows of leachate through these sorbents.

Lysimeters used in the laboratory were constructed of plexiglass tubing (6.2-cm ID, 0.6-cm wall thickness, 90-cm length) supported in a vertical position. The laboratory arrangement of the lysimeters is shown in Figure 1. A 164-micron pore size corundum disc (6.10-cm diameter, 0.6-cm thickness) was placed in each column directly over the drain hole to prevent clogging of the outlet and also to support the sorbent material. The column was packed with the preweighed sorbent, with 3 to 4 cm of Ottawa sand below and above the sorbent to prevent disturbing the geometry of the sorbent column during addition of leachate or water. The packed column was then slowly wetted with leachate to allow total saturation and to force all entrapped air in the soil voids out of the column packing. After a saturation period of at least 24 hours, the column was filled with leachate to the level of an overflow drain that had been tapped into the top side of the column in order to maintain a constant head condition. Leachate was fed to the top of the column through a valved manifold that distributed the leachate simultaneously to 10 lysimeters, from a central reservoir. The central reservoir, a 100 liter polyethylene carboy, delivered the leachate to the manifold system by means of a gravity syphon feed arrangement. Any overflow from the constant head drains was collected and pumped back up to the central reservoir. All tubing in the system was made of Tygon tubing 9.5 mm ID (3/8 in). A constant hydraulic head was maintained in the lysimeters at all times, and the volume of leachate passing through the columns was continuously monitored. Samples of leachate effluent were analyzed at predetermined intervals for pH and the concentrations of all measurable constituents remaining in the effluent. This procedure was continued until breakthrough for all measurable contaminants had occurred or until excessively low

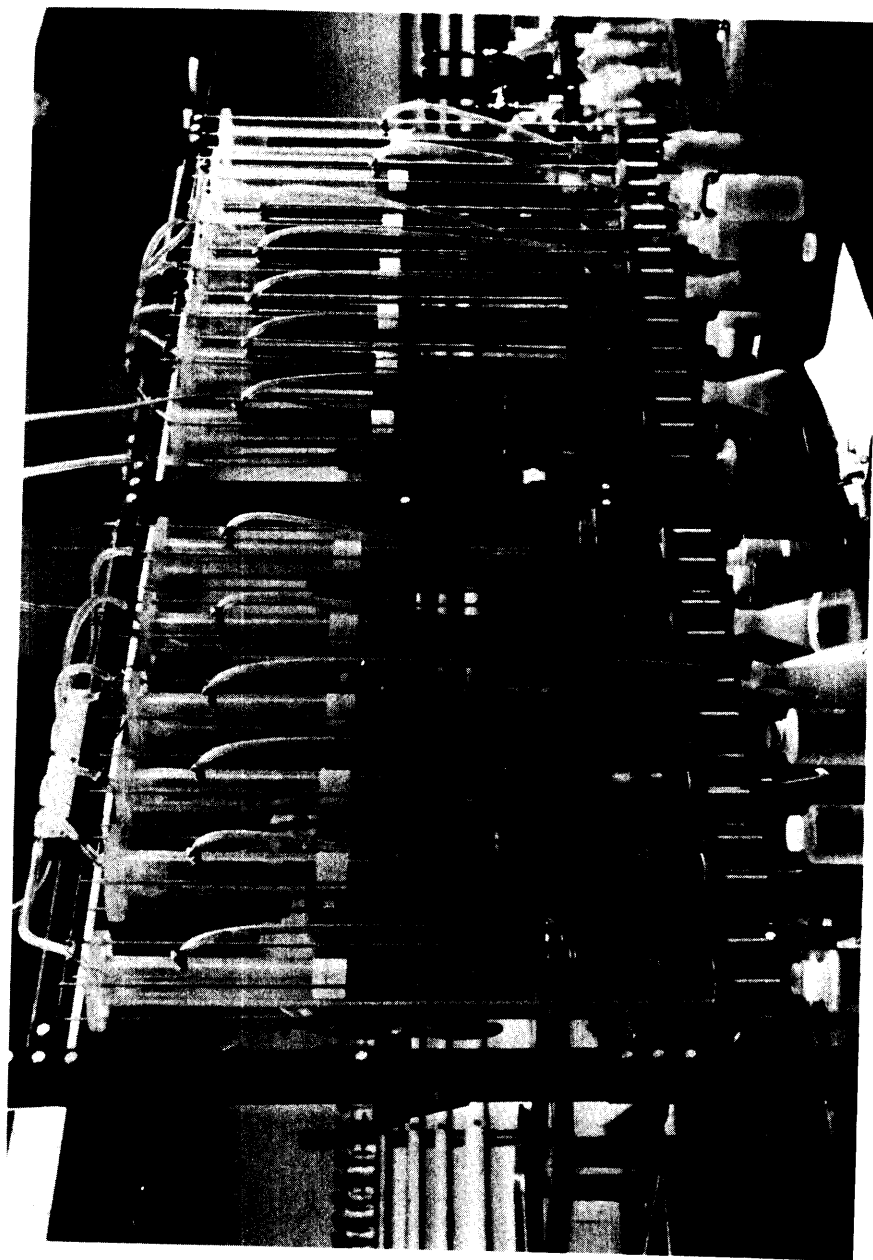


Figure 1. Laboratory arrangement of lysimeters.

permeabilities were encountered. Breakthrough was defined as that condition when the concentration of the species of concern in the collected effluent sample approached or exceeded that in the influent. After breakthrough was achieved, water was continually passed through the spent sorbent bed until the cations, anions and organics removed by the sorbents were below measurable levels in the effluent. The sorbent capacity exhibited by each sorbent represents the total amount of specific cation, anion, or organic retained by the sorbent after extensive water washing.

PILOT STUDIES

To evaluate the use of the clay/fly ash combination for the treatment of industrial sludge leachates on a pilot scale, two large vertical lysimeters were set up outdoors. This outdoor system consisted of an agitator, filtration column, storage tank, and constant head lysimeter. (See Figure 2).

Calcium fluoride sludge was collected from the same source over a period of a year to take advantage of changes in production schedules and processes that could lead to compositional changes in the leachate. In this manner, the effect of compositional changes on the removal efficiency of the natural clay/fly ash sorbent combinations could be studied.

The preparation of sludge leachate for the outdoor study was as follows: A sample of each batch of sludge was dried at 103°C to constant weight to determine its moisture content. The unaltered sludge was then mixed with water in a ratio of 2.5 ml water/g of dried sludge and mechanically stirred for 24 hours. The resulting mixture was then filtered through a multimedia filter bed. The filter bed, which was housed in a stainless steel column, consisted of 5 layers of filter sand and gravel: The top layer was uniform medium gravel with $D_{50} = 19.1$ mm (particle sizes are such that 50 percent passed through a sieve with a spacing of 19.1 mm) and a thickness of 7.6 cm; the second layer from the top was a fine gravel with $D_{85} = 16.8$ mm and $D_{15} = 14.2$ mm, and a thickness of 7.6 cm; the third layer was a coarse sand with $D_{85} = 6.3$ mm and $D_{15} = 5.1$ mm, and a thickness of 10.2 cm; the fourth layer was medium sand with $D_{85} = 1.47$ mm and $D_{15} = 1.2$ mm, and a thickness of 10.2 cm; and the bottom layer was #20 - #30 Ottawa sand with $D_{50} = 0.715$ mm and a thickness of 22.9 cm. This arrangement of gravel and sand in the filter bed was based on the results of a series of measurements using different sizes of gravel and sand to provide an effluent whose suspended particles would not clog the bed.

The outdoor lysimeters were constructed of PVC pipe (40.6 cm OD) 4.8 mm wall thickness and 1.52 m length supported by lucite plates in a vertical position. The general configuration and features of the field lysimeter are similar to those of the laboratory lysimeters described earlier. The use of identical lysimeters provided a measure of the reproducibility of the sorbent system. Both lysimeters were packed with enough preweighed sorbent to treat 530 liters of leachate. Five to 10 cm of Ottawa sand was placed below and above the sorbents to prevent disturbing the

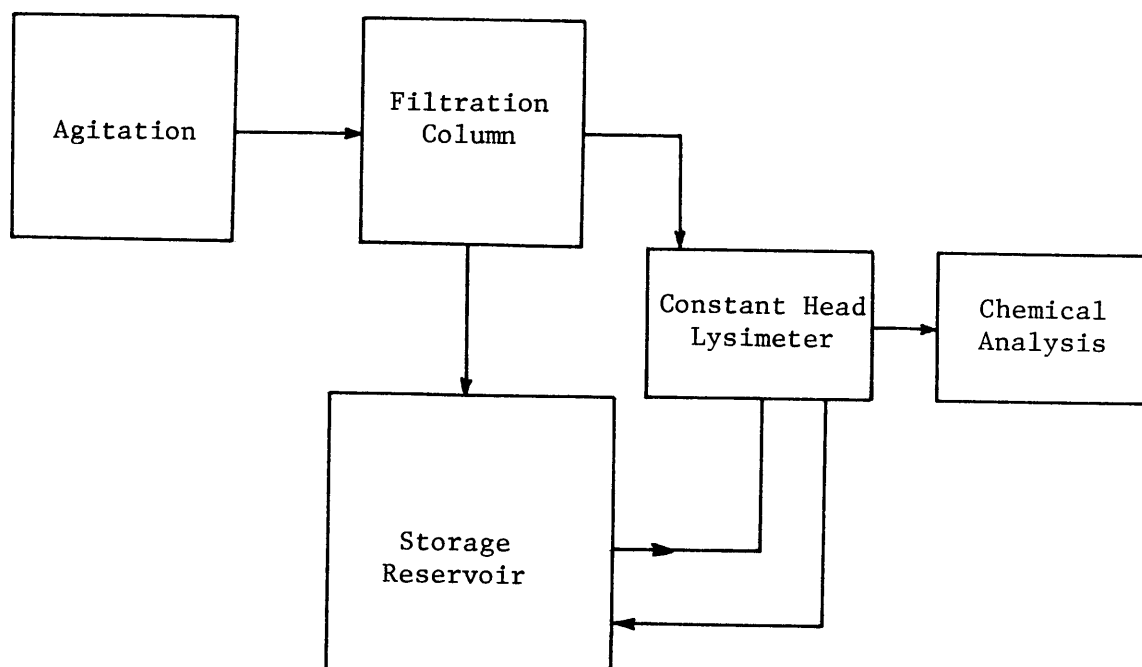


Figure 2. Schematic diagram of pilot scale study.

geometry of the sorbents during addition of leachate. Leachate was fed to the top of the column through a valved manifold that distributed it to both lysimeters simultaneously from the storage reservoir. The lysimeters were designed for constant hydraulic head. Thus overflow from the constant head drain was collected and pumped back to the storage reservoir. All tubing in the system was made of Tygon tubing (9.5 mm ID). The volume effluent was monitored as a function of time, and samples of leachate effluent were analyzed at intervals to determine the concentration of all measurable constituents remaining in the effluent after a known volume of leachate had passed through the column. This procedure was continued for three different calcium fluoride sludge leachates collected from the same source at different times.

A stainless steel, 200 liter tank equipped with drainage outlet was used as the storage reservoir. This tank was located between the filter bed and field lysimeters to serve as both a reservoir and an overflow receiver.

SECTION 5

RESULTS AND DISCUSSION

LABORATORY STUDIES

Leachates from the petroleum, calcium fluoride, and metal finishing sludges, prepared and analyzed (Table 1) according to procedures described elsewhere¹⁶, were passed through individual lysimeters that contained one of the following sorbents: acidic fly ash, basic fly ash, zeolite, vermiculite, illite, kaolinite, activated alumina, and activated carbon. The volume of effluent from each of these lysimeters was monitored, and effluent samples were analyzed for pH, calcium, copper, magnesium, zinc, nickel, cadmium, chromium, lead, fluoride, total cyanide and organics. This monitoring and analysis were carried out through repeated washings of the spent sorbents until no measurable contaminants appeared in the wash effluent.

Effect of Sorbents on Lysimeter Effluent pH

Monitoring results showed that in general, the pH of the lysimeter effluent from the three sludge leachates was initially influenced by the sorbents. Considerable variations were observed in the pH of the effluents collected initially (Figures 3, 4, and 5). However, as the leachate was passed through the sorbents in the lysimeters, effluent pH eventually became the same as that of the influent. The effluent from the illite lysimeter is a particularly good example of this effect (Figures 3, 4, and 5). Thus the pH at which the removals of the cations, anions, and organics in the industrial sludge leachates occur is influenced initially by the sorbents and finally by the leachate.

Effects of Leachate pH

Leachate pH and Sorbent Removal Capacity --

The pH of the industrial sludge leachate was found to influence the different sorbent capacities for the removal of the cations, anions and organics present in these leachates.

Calcium, Copper, and Magnesium-- Based on the removal capacities shown in Tables 2, 3, and 4, the three most promising sorbents for a specific leachate constituent were compared (Table 5). As the pH was raised, increases occurred in the removals of calcium, copper, and magnesium ions.

For example, the zeolite, acidic fly ash, and kaolinite sorbent removal capacities for copper are 5.2, 2.4, and 0 $\mu\text{g/g}$, respectively, in the presence

TABLE 1: CONCENTRATIONS OF SPECIFIC CATION, ANIONS, AND ORGANICS IN THE
THREE INDUSTRIAL SLUDGE LEACHATES (m/l)

| Measured* pollutant | Acidic petroleum sludge leachate | Neutral calcium fluoride sludge leachate | Basic metal finishing sludge leachate |
|------------------------|-------------------------------------|--|---|
| Ca | 34-50 | 180-318 | 31-38 |
| Cu | 0.09-0.17 | 0.10-0.16 | 0.45-0.53 |
| Mg | 27-50 | 4.8-21 | 24-26 |
| Ni | --- + | ----- | ----- |
| Zn | 0.13-0.17 | ----- | ----- |
| F | 0.95-1.2 | 6.7-11.6 | 1.2-1.5 |
| Total CN | 0.20-1.2 | ----- | ----- |
| COD | 251-340 | 44-49 | 45-50 |

* Fe, Cd, Cr, and Pb contents were analyzed, but found to be below measurable levels.

+ Dashed line indicated amounts below measurable levels.

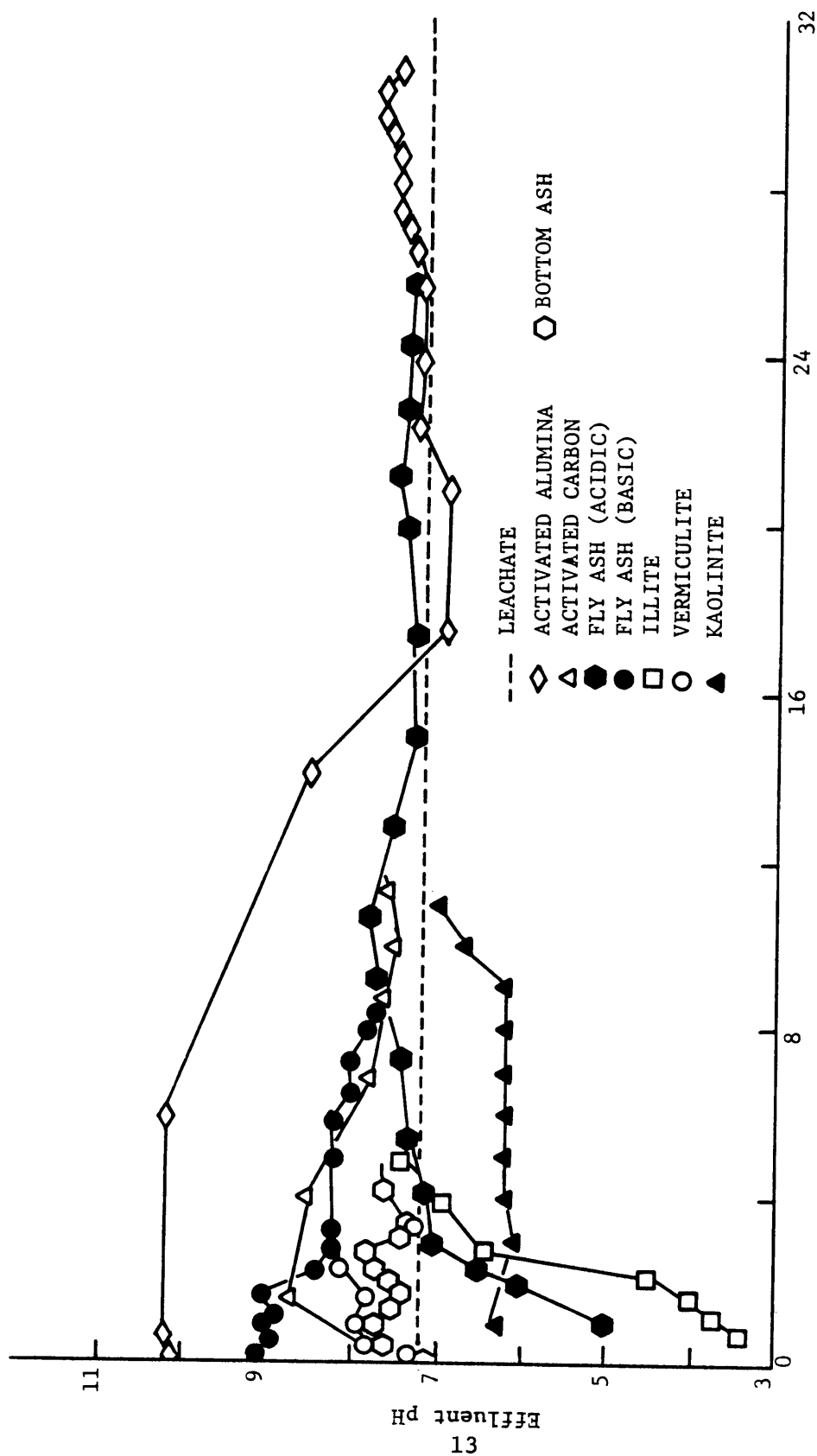


Figure 3. Lysimeter effluent pH for calcium fluoride sludge leachate.

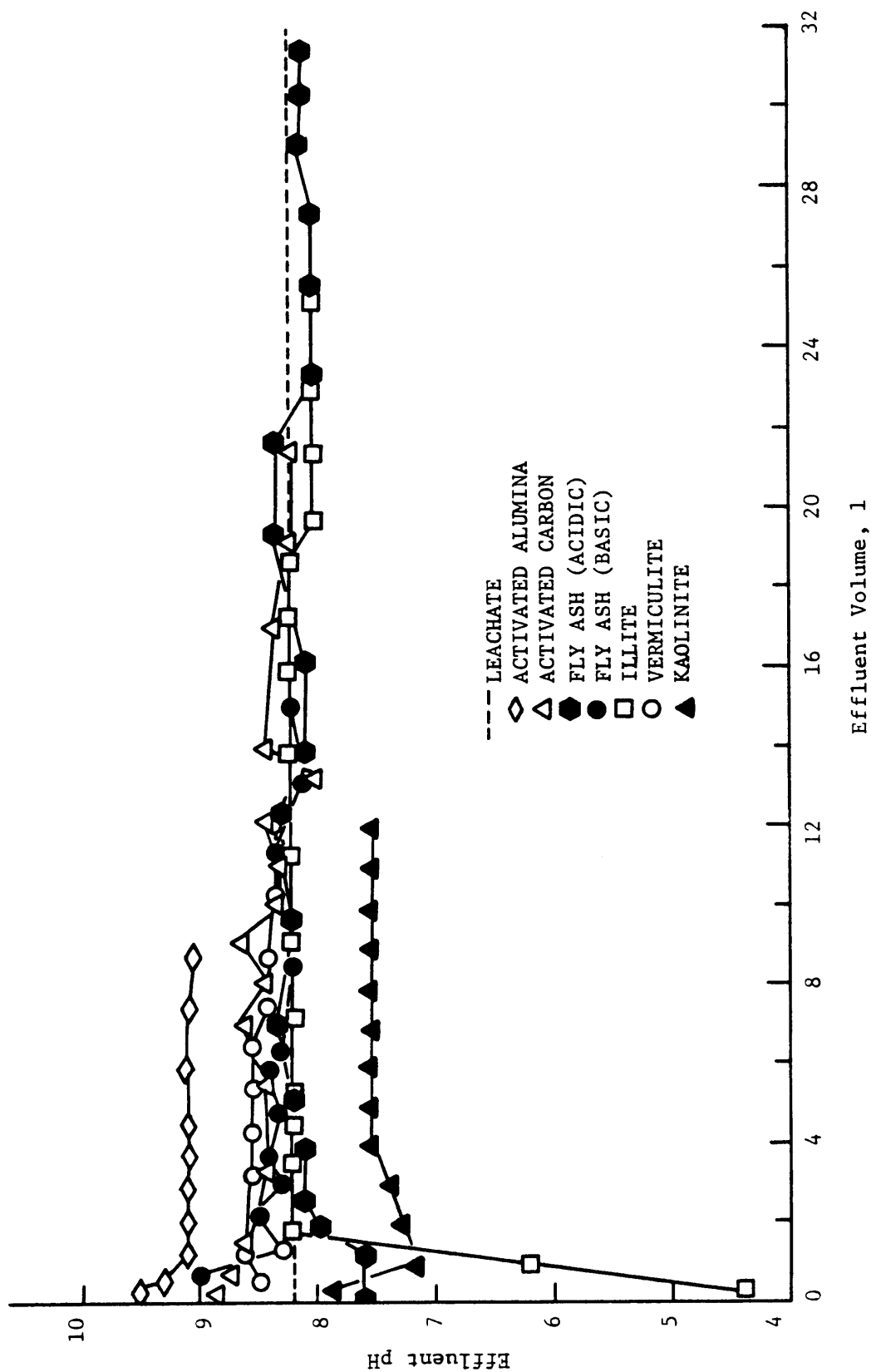


Figure 4. Lysimeter effluent pH for metal finishing sludge leachate.

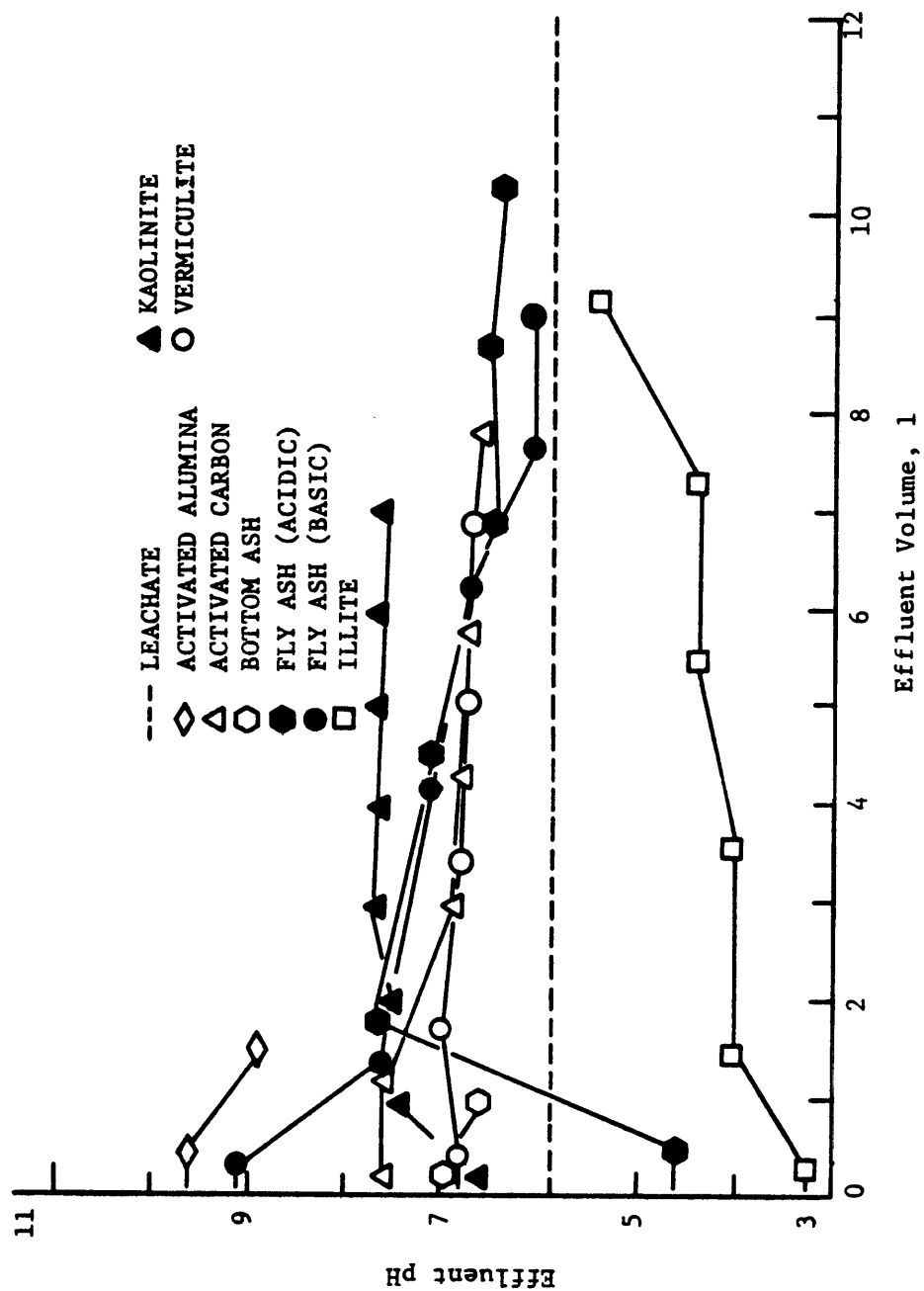


Figure 5. Lysimeter effluent pH for petroleum sludge leachate.

of acidic leachate (Table 5). But these figures become 8.2, 2.1 and 6.7 $\mu\text{g/g}$ in the presence of neutral leachate, and 85.4, 13.0, and 23.7 $\mu\text{g/g}$ with basic leachate. Griffin, et al.¹² have also reported similar results. In their study, which was limited to kaolinite and montmorillonite, removals of copper, cadmium, and zinc increased as the pH of the leachate progressed from acidic to alkaline conditions. Maximum removals were obtained at a pH of about 8.

The reason for the zero sorbent capacities exhibited by the illite and zeolite for the calcium and magnesium in the neutral leachate is not understood at this time (Table 5).

Zinc, Nickel, Iron, Cadmium, Chromium, and Lead--The influence of leachate pH on the different sorbent removal capacities for zinc, nickel, iron, cadmium, chromium and lead could not be established in this study. Unfortunately, measurable concentrations of zinc and nickel were encountered only in the acidic and basic leachates, respectively, whereas the concentrations of iron, cadmium, chromium and lead were all below measurable levels in the three types of leachates examined.

Fluoride--The sorbent removal capacities for fluoride are also dependent on leachate pH, but they are the reverse of those encountered with cations. In the case of fluoride, sorbent capacities increase as the pH of the leachate decreases from alkaline to acidic. For example, the sorbent capacities for illite, acidic fly ash, and kaolinite are 2.2, 0, and 2.6 $\mu\text{g/g}$, respectively, for removal of fluoride in the basic leachate, these increase to 9.3, 8.7, and 3.5 $\mu\text{g/g}$ for the acidic leachate (Table 5). Griffin et al.¹² also showed this to be the case for the anion $\text{HAsO}_4^{=}$ using kaolinite and montmorillonite. Maximum removal of this anion was achieved under acidic conditions (about pH 6).

Organics--Organics removal also appears to be pH dependent. The sorbent removal capacities for the COD in both acidic and basic leachates are significantly higher than those achieved with the neutral leachate (Table 5). However, a trend in the change of sorbent capacity with pH is difficult to identify in our study, since the concentration of organics in the acidic leachate is significantly higher than that measured in the basic leachate (Table 1). But Lub and Baker⁴ did report maximum sorption of pyridine by sodium kaolinite and sodium montmorillonite in a pH range of 4.0 to 5.5. Thus it appears that both the pH and the organics concentration influence the removal of organics from the acidic leachate.

Leachate pH and Leaching of Ions from Specific Sorbents--

The leachate pH in the lysimeter also influences the leaching of ions from specific sorbents. When the leachate in the lysimeter was initially acidic, as indicated by its initial effluent pH, the concentration of a specific ion in the effluent was found to exceed the concentration of this ion in the influent. But as the effluent pH approached 6 (and above), the leaching of the specific ion ceased, and in some cases, the sorbent actually began to remove the specific ion that was leached from it under more acidic conditions. As shown in Table 6, for example, when the pH of the effluent approached 6, as indicated by the final effluent pH, the illite and acidic fly ash either ceased to leach copper or began to remove it. The removal of

TABLE 2. NET SORBENT REMOVAL CAPACITIES
FOR TREATING ACIDIC PETROLEUM SLUDGE LEACHATE
($\mu\text{g/g}$)*

| Pollutant | Acidic fly ash | Basic fly ash | Zeolite | Vermiculite | Illite | Kaolinite | Activated Alumina | Activated Carbon |
|-----------------|-------------------|------------------|---------|-------------|--------|-----------|----------------------|---------------------|
| Ca | 0 | 0 | 1,390 | 686 | 721 | 10.5 | 200 | 128 |
| Cu | 2.4 | 1.9 | 5.2 | 1.1 | 0 | 0 | 0.35 | 0 |
| Mg | 0 | 102 | 746 | 67 | 110 | 595 | 107 | 8.6 |
| Zn | 1.6 | 1.7 | 10.8 | 4.5 | 0 | 0 | 0.40 | 1.1 |
| F ⁻ | 8.7 | 6.2 | 4.1 | 0 | 9.3 | 3.5 | 3.4 | 1.2 |
| CN ⁻ | 2.7 | 2.5 | 4.7 | 7.6 | 12.1 | 3.1 | 0 | 2.4 |
| COD | 3,818 | 3,998 | 468 | 6,654 | 4,807 | 541 | 411 | 3,000 |
| TOC | 1,468 | 737 | 170 | 2,545 | 2,175 | 191 | 176 | 1,270 |

* μg of contaminant removed/g of sorbent used.

+ Cl⁻, Cd, Cr, Fe, Ni, and Pb were measured and found in low concentrations.

TABLE 3. NET SORBENT REMOVAL CAPACITIES
FOR TREATING NEUTRAL CALCIUM FLUORIDE SLUDGE LEACHATE
($\mu\text{g/g}$)*

| Pollutant | Acidic fly ash | Basic fly ash | Zeolite | Vermiculite | Illite | Kaolinite | Activated Alumina | Activated Carbon |
|----------------|----------------|---------------|---------|-------------|--------|-----------|-------------------|------------------|
| Ca | 261 | 0 | 5,054 | 0 | 0 | 857 | 6,140 | 357 |
| Cu | 2.1 | 0.36 | 8.2 | 0 | 0 | 6.7 | 2.9 | 2.0 |
| Mg | 230 | 155 | 0 | 0 | 0 | 0 | 214 | 3.0 |
| F ⁻ | 102 | 51.8 | 27.7 | 0 | 175 | 132 | 348 | 0 |
| COD | 690 | 203 | 171 | 0 | 108 | 185 | 0 | 956 |
| TOC | 153 | 44.7 | 93 | 0 | 26.1 | 71 | 0 | 325 |

* μg of contaminant removed/g of sorbent used.

+ Cl^- , CN^- , Cd, Cr, Cu, Fe, Ni, Pb, and Zn were measured and found in low concentrations.

TABLE 4. NET SORBENT REMOVAL CAPACITIES
FOR TREATING BASIC METAL FINISHING SLUDGE LEACHATE
($\mu\text{g/g}$)*

| Pollutant | Acidic fly ash | Basic fly ash | Zeolite | Vermiculite | Illite | Kaolinite | Activated Alumina | Activated Carbon |
|----------------|-------------------|------------------|---------|-------------|--------|-----------|----------------------|---------------------|
| Ca | 87.3 | 97.8 | 1,240 | 819 | 1,280 | 735 | 737 | 212 |
| Cu | 13.0 | 6.1 | 85.4 | 15.2 | 43.1 | 23.7 | 6.2 | 16.8 |
| Mg | 296 | 176 | 1,328 | 344 | 1,122 | 494 | 495 | 188 |
| Ni | 3.8 | 1.7 | 13.5 | 2.3 | 5.1 | 4.6 | 2.3 | 4.7 |
| F ⁻ | 0 | 0 | 2.1 | 0 | 2.2 | 2.6 | 11.4 | 0 |
| COD | 1,080 | 259 | 0 | 618 | 1,744 | 0 | 0 | 1,476 |
| TOC | 430 | 115 | 0 | 244 | 729 | 0 | 0 | 589 |

* μg of contaminant removed/g of sorbent used.

+ Cl^- , CN^- , Cd, Cr, Fe, Pb, and Zn were measured and found in low concentrations.

TABLE 5. NATURAL SORBENTS AND THEIR CAPACITY FOR REMOVAL
OF SPECIFIC CONTAMINANTS IN ACIDIC, NEUTRAL, AND BASIC LEACHATES

| Ion | Acidic leachate (petroleum sludge) Sorbent Capacity ($\mu\text{g/g}$)* | | Neutral leachate (calcium fluoride) Sorbent Capacity ($\mu\text{g/g}$)* | | Basic leachate (metal finishing sludge) Sorbent Capacity ($\mu\text{g/g}$)* | |
|-------|---|-------|--|-------|--|-------|
| | | | | | | |
| Ca | Zeolite | 1,390 | Zeolite | 5,054 | Illite | 1,280 |
| | Illite | 721 | Kaolinite | 857 | Zeolite | 1,240 |
| | Kaolinite | 10.5 | Illite | 0 | Kaolinite | 733 |
| Cu | Zeolite | 5.2 | Zeolite | 8.2 | Zeolite | 85 |
| | Acidic F.A. | 2.4 | Kaolinite | 6.7 | Kaolinite | 24 |
| | Kaolinite | 0 | Acidic F.A. | 2.1 | Acidic F.A. | 13 |
| Mg | Zeolite | 746 | Basic F.A. | 155 | Zeolite | 1,328 |
| | Illite | 110 | Zeolite | 0 | Illite | 1,122 |
| | Basic F.A. | 1.7 | Illite | 0 | Basic F.A. | 176 |
| Zn | Zeolite | 10.8 | - | - | - | - |
| | Vermiculite | 4.5 | - | - | - | - |
| | Basic F.A. | 1.7 | - | - | - | - |
| Ni | | | | | Zeolite | 13.5 |
| | | | | | Illite | 5.1 |
| | | | | | Acidic F.A. | 3.8 |
| F | Illite | 9.3 | Illite | 175 | Kaolinite | 2.6 |
| | Acidic F.A. | 8.7 | Kaolinite | 132 | Illite | 2.2 |
| | Kaolinite | 3.5 | Acidic F.A. | 102 | Acidic F.A. | 0 |
| Total | | | | | | |
| CN | Illite | 12.1 | - | - | - | - |
| | Vermiculite | 7.6 | - | - | - | - |
| | Acidic F.A. | 2.7 | - | - | - | - |
| COD | Vermiculite | 6,654 | Acidic F.A. | 690 | Illite | 1,744 |
| | Illite | 4,807 | Illite | 108 | Acidic F.A. | 1,080 |
| | Acidic F.A. | 3,818 | Vermiculite | 0 | Vermiculite | 244 |

* μg of contaminant removed/g of sorbent used.

copper is indicated when its concentration in the effluent falls below the influent concentration. This same behavior was observed with the zinc ion (Table 6). Similar results for fly ash have been recently reported by Theis and Wirth.¹⁷ Their work, which was carried out under batch condition on a laboratory scale showed that the average leaching of the heavy metals (zinc, copper, nickel, chromium, lead, and cadmium) from the sorbents was minimal at a pH 6 and above.

Thus, the results show that regulation of the leachate pH is essential for optimum removal of anions, cations, and organics while minimizing the leaching of specific ions from the sorbents. Initial control of leachate pH so that it is slightly acidic favors the removal of anions and organics while minimizing the leaching of specific ions. Further adjustment of the leachate pH so that it is slightly alkaline favors the removal of cations.

Effects of Leachate Contaminants

The concentration of the contaminants in the leachate also appears to influence the sorbent removal capacity. As the contaminant concentration increases, the sorbent removal capacity also increases. The large zeolite, acidic fly ash, and kaolinite sorbent removal capacities for copper (85, 13, and 24 $\mu\text{g/g}$) obtained with the basic leachate (Table 5) could be due both to the influence of pH and to the relatively high concentration of copper ion found in this leachate. Copper concentrations range from 0.45 to 0.53 mg/l in the basic leachate compared to only 0.09 to 0.17 and 0.10 to 0.16 mg/l in the acidic and neutral leachates, respectively (Table 1). This effect of contaminant concentration on sorbent removal capacity is also seen with the other cations and the fluoride anion. The highest concentrations of calcium and fluoride are encountered in the neutral leachate (Table 1). The zeolite sorbent capacity for calcium in the neutral leachate is 5,054 $\mu\text{g/g}$ (Table 3) as opposed to only 1,240 $\mu\text{g/g}$ in the basic leachate (Table 4), even though alkaline conditions favor the removal of cations. Similarly, the illite sorbent capacity for the fluoride is 175 $\mu\text{g/g}$ in the neutral leachate (Table 3) as opposed to 9.3 and 2.2 $\mu\text{g/g}$ in the acidic and basic leachates (Tables 2 and 4), respectively.

The influence of the concentration of a specific constituent in the leachate on the sorbent removal capacities is as expected. If it is assumed that an equilibrium relationship exists between the bound and unbound ions in the leachate, the higher the ion concentration is in the leachate, the greater the tendency will be for binding. As a result, greater amounts of the ion will be removed from the leachate in the presence of a given amount of sorbent.

Effects of Leachate Velocity Through the Sorbent Bed

The leachate velocity through the sorbent bed in the lysimeters was also found to influence the removal of cations, anions, and organics in the leachates. The velocity does not affect the total amount of contaminant that can be removed by a sorbent (sorbent removal capacity), but it does define the volume of leachate that can be treated with maximum contaminant removal.

TABLE 6. RELATIONSHIP OF COPPER AND ZINC CONCENTRATION TO LEACHATE pH

| Sorbent | Type of Sludge Leachate | Effluent pH | | Cu Concentration, mg/l | | Zn Concentration, mg/l | |
|-------------------|-----------------------------|----------------|-------|---------------------------|---------------------------|---------------------------|---------------------------|
| | | Initial | Final | Influent | Effluent Initial Final | Influent | Effluent Initial Final |
| Illite | Acidic petroleum | 3.0 | 6.0 | 0.18 | 0.80 0.18 | 0.12 | 0.40 0.12 |
| | Neutral calcium fluoride | 3.8 | 7.2 | 0.10 | 3.1 0.10 | - | - - |
| | Alkaline metal finishing | 4.5 | 8.2 | 0.53 | 1.0 0.30 | - | - - |
| Acidic Fly Ash | Acidic petroleum | 4.5 | 6.2 | 0.18 | 0.38 0.05 | 0.12 | 0.40 0.02 |
| | Neutral calcium fluoride | 5.0 | 7.2 | 0.10 | 3.0 0.05 | - | - - |

For example, different leachate velocities were obtained when neutral calcium fluoride sludge leachate was passed through four lysimeters that contained different amounts of illite. The fluoride and COD concentrations remaining in the effluent were monitored until breakthrough was achieved. The results are shown in Figures 6 and 7, where the fractions of fluoride and COD remaining in the lysimeter effluent are plotted against the volume of leachate treated per gram of illite used. These figures show that as the velocity of the leachate decreases, the removal efficiency of the sorbent increases. For example, when the leachate velocity is reduced from 0.140 cm./min. to 0.049 cm./min., the fraction of fluoride remaining in the effluent after 20 l of effluent has been collected has been reduced from 0.50 to 0.02.

The sorbent removal capacities, however, are not influenced by the velocity of the leachate through the sorbent bed. For example, velocity was found to have no significant effect on the sorbent removal capacity exhibited by illite for fluoride and COD removals (Table 7).

TABLE 7. SORBENT CAPACITY EXHIBITED BY ILLITE
FOR REMOVAL OF FLUORIDE AND COD
AT DIFFERENT LEACHATE VELOCITIES THROUGH SORBENTS

| Leachate velocity through the bed (cm/min) | Sorbent capacity for fluoride ($\mu\text{g/g}$) | Sorbent capacity for COD ($\mu\text{g/g}$) |
|---|--|---|
| 0.140 | 190 | 185 |
| 0.138 | 186 | 192 |
| 0.079 | 179 | 198 |
| 0.042 | 175 | 216 |

An examination of the curves in Figure 6 reveals that the optimum velocity for treating the largest volume of leachate with maximum fluoride removal is less than 0.049 cm/min. The curve representing operation at the optimum leachate velocity should allow the greatest volume of leachate to be treated with a sharp rise in fraction of fluoride in effluent (C/C_0) to breakthrough.

Natural versus Refined Sorbents

The most effective natural sorbents for the removal of each cation, anion, or organic present in measurable quantities in the acidic, neutral, and basic leachates are listed in Table 8. No single sorbent can remove all the measurable constituents present in the three leachates. A combination of illite, vermiculite, and natural zeolite is the most effective for treating the acidic leachate. Illite, acidic fly ash, and zeolite or basic fly ash are the most effective combinations for treating the neutral leachate. Illite, kaolinite, and zeolite are the most effective for treating the basic leachate.

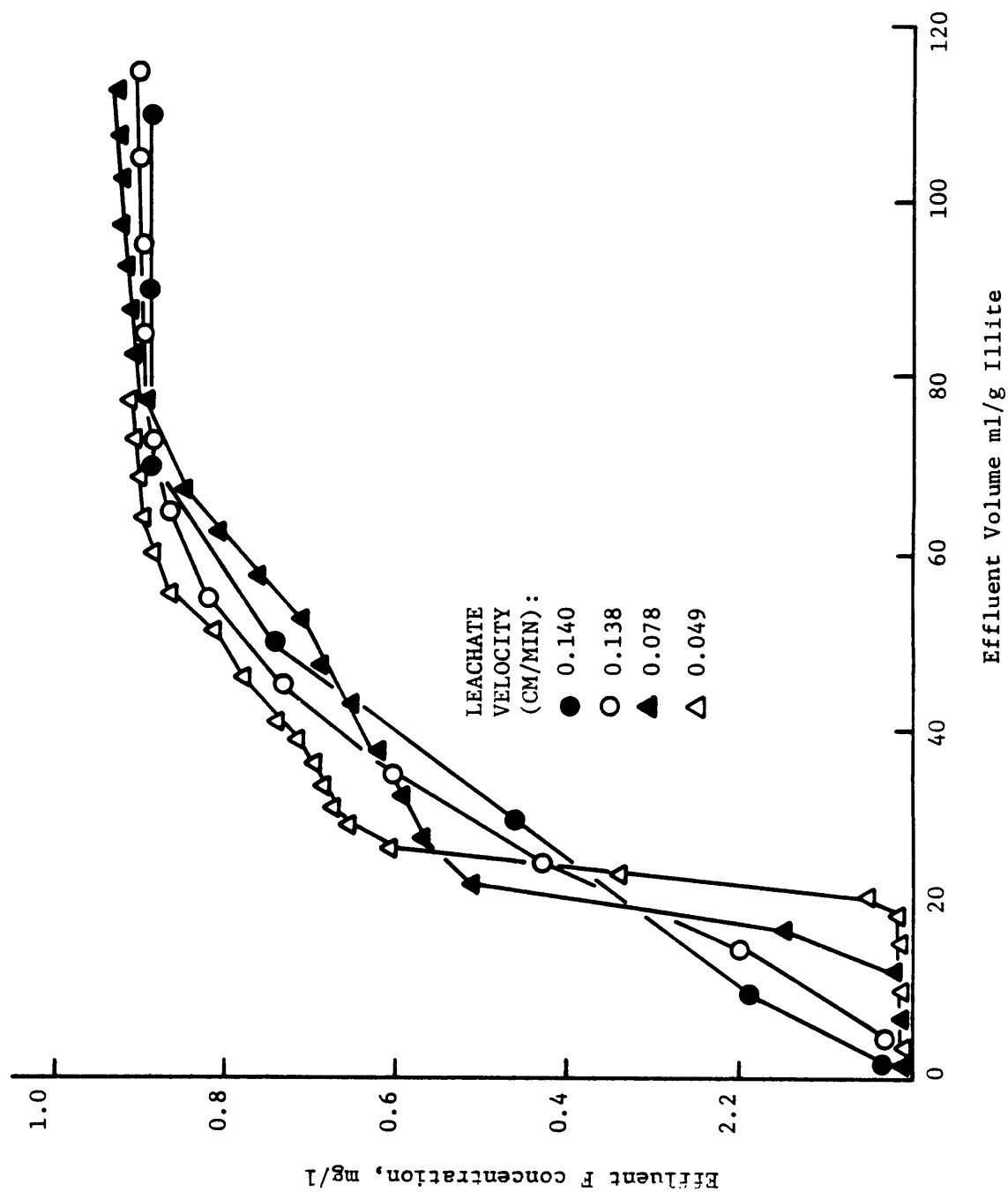


Figure 6. Effect of leachate velocity on fluoride removal in calcium fluoride sludge leachate.

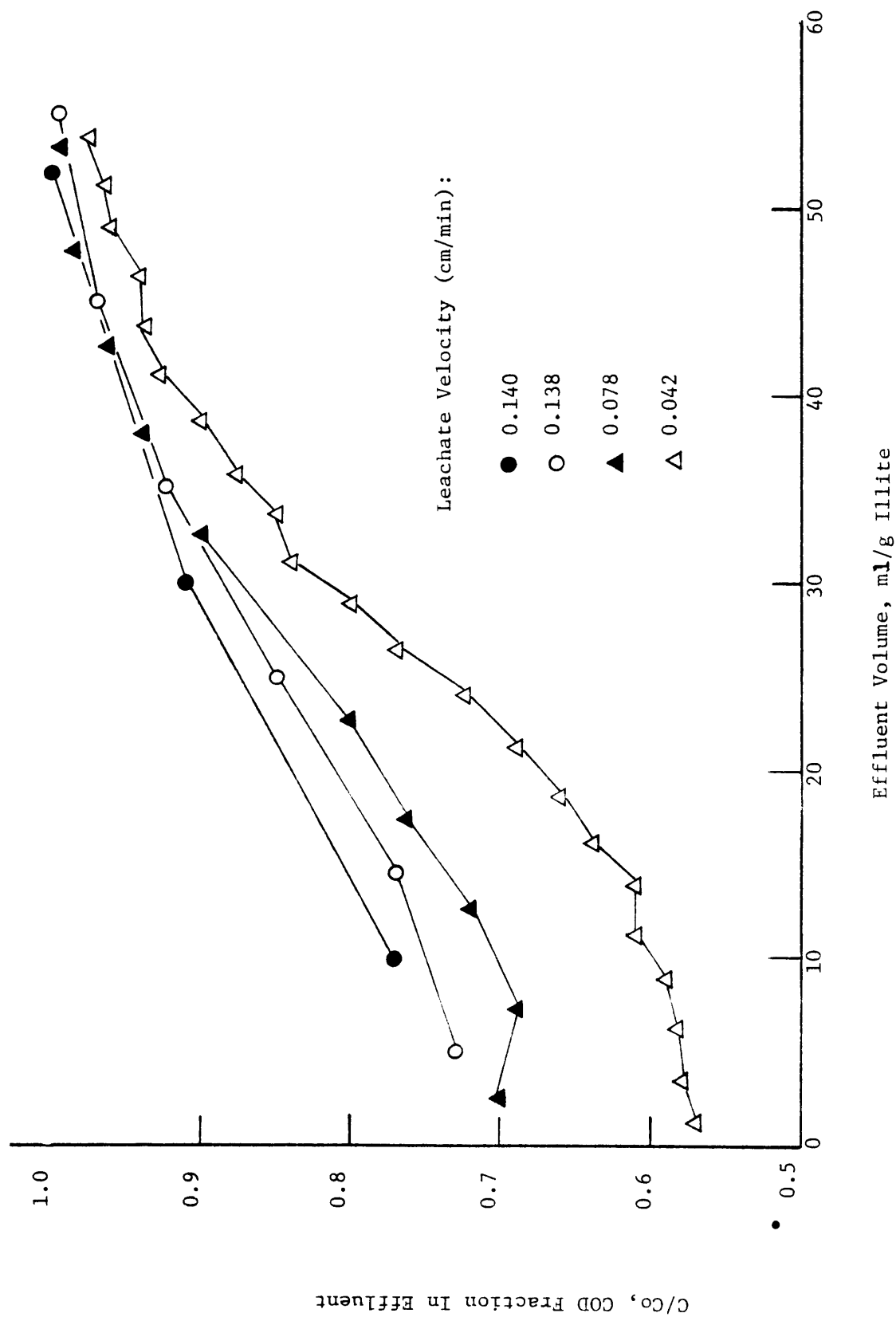


Figure 7 - Effect of leachate velocity on COD removal in calcium fluoride sludge leachate

The combinations that is effective in treating one leachate can also be used to treat the other leachates. But optimum removal of a specific constituent for a given weight of sorbent would not be achieved, because the magnitude of the sorbent capacities are influenced by the leachate pH. Thus a sorbent such as illite, which is the most effective for removing the fluoride ion in the acidic and neutral leachates, could also be used for removing the fluoride in the basic leachate. But it would be less effective than kaolinite (Table 5).

The removal capacities exhibited by the most effective natural sorbents for the removal of cations, anions, and organics are comparable to the more expensive refined sorbents, activated alumina and activated carbon, in all cases but one-- the removal of the fluoride ion in the basic leachate (Table 8). Here, the sorbent capacity exhibited by the activated alumina is some four times that exhibited by the kaolinite.

The above results are significant in that they indicate that the inexpensive natural sorbents can be utilized in the same manner and are as effective as the more expensive activated alumina and activated carbon for the treatment of leachates from industrial sludges. In addition, regeneration of the natural sorbents is not required; thus the capital investments associated with the regeneration equipment commonly used with activated alumina and activated carbon can be avoided.

Unfortunately, the natural sorbents that are effective for the removal of zinc in the neutral and basic leachates and nickel, iron, cadmium, chromium, and lead in the acidic and neutral leachates could not be identified since these ions were found to be below measurable levels in the leachates obtained from industrial sludges selected for this investigation.

Natural Sorbent Combinations for Optimum Contaminant Removals from Calcium Fluoride Sludge Leachate

Although the above results show that natural clay/fly ash combinations are feasible for treating acidic, neutral, and basic industrial sludge leachates, only the combinations that would provide optimum removals of cations, anions, and organics in calcium fluoride sludge leachate were investigated further. The most effective sorbents natural zeolite, acidic and basic fly ashes, and illite, were combined in different proportions in a layered system to define the optimum arrangement for removal of the measurable cations, anions, and organics present in this leachate.

The two sorbent combinations selected were: (1) illite, acidic and basic fly ashes, and (2) illite, acidic fly ash, and zeolite. These were placed in lysimeters in a layered system in the weight ratios of 1:1:1 or 2:2:1. The illite was the top layer, followed by acidic fly ash, or vice versa. Either the basic fly ash or the zeolite was used as the bottom layer to remove the cations such as copper and zinc that are initially leached from the illite and acidic fly ash during the period when the leachate is acidic (Table 6). Both the basic fly ash and natural zeolite show zinc and copper removals during the initial period when these ions are leaching from the illite and acidic fly ash.

TABLE 8. COMPARISON OF THE MOST EFFECTIVE NATURAL SORBENT
FOR SPECIFIC CONTAMINANTS WITH ACTIVATED ALUMINA AND
ACTIVATED CARBON IN ACIDIC, NEUTRAL, AND BASIC LEACHATES

| Ion | Acidic leachate (petroleum sludge) | | Neutral leachate (calcium fluoride) | | Basic leachate (metal finishing sludge) | |
|-------|--|-------|--|-------|--|-------|
| | Sorbent Capacity ($\mu\text{g/g}$)* | | Sorbent Capacity ($\mu\text{g/g}$)* | | Sorbent Capacity ($\mu\text{g/g}$)* | |
| Ca | Zeolite | 1,390 | Zeolite | 5,054 | Illite | 1,280 |
| | Act.alumina | 200 | Act.alumina | 6,140 | Act.alumina | 737 |
| | Act.carbon | 128 | Act.carbon | 357 | Act.carbon | 212 |
| Cu | Zeolite | 5.2 | Zeolite | 8.2 | Zeolite | 85 |
| | Act.alumina | .35 | Act.alumina | 2.9 | Act.alumina | 6.2 |
| | Act.carbon | 0 | Act.carbon | 2.0 | Act.carbon | 16.8 |
| Mg | Zeolite | 746 | Basic Fly Ash | 155 | Zeolite | 1,328 |
| | Act.alumina | 107 | Act.alumina | 514 | Act.alumina | 495 |
| | Act.carbon | 8.6 | Act.carbon | 3.0 | Act.carbon | 188 |
| Zn | Zeolite | 10.8 | - | - | - | - |
| | Act.alumina | .40 | - | - | - | - |
| | Act.carbon | 1.1 | - | - | - | - |
| Ni | - | - | - | - | Zeolite | 13.5 |
| | - | - | - | - | Act.alumina | 2.3 |
| | - | - | - | - | Act.carbon | 4.7 |
| F | Illite | 9.3 | Illite | 175 | Kaolinite | 2.6 |
| | Act.alumina | 3.4 | Act.alumina | 348 | Act.alumina | 11.4 |
| | Act.carbon | 1.2 | Act.carbon | 0 | Act.carbon | 0 |
| Total | | | | | | |
| CN | Illite | 12.1 | - | - | - | - |
| | Act.alumina | 0 | - | - | - | - |
| | Act.carbon | 2.4 | - | - | - | - |
| COD | Vermiculite | 6,654 | Acidic Fly Ash | 690 | Illite | 1,744 |
| | Act.alumina | 411 | Act.alumina | 0 | Act.alumina | 0 |
| | Act.carbon | 1,270 | Act.carbon | 956 | Act.carbon | 1,476 |

* μg of contaminant removed/g of sorbent used.

The results showed that the use of illite followed by acidic fly ash and basic fly ash in the weight ratios of 1:1:1 generally yields greater sorbent capacities than the arrangement with acidic fly ash first, than illite and basic fly ash in the weight ratio of 1:1:1 (Table 9).

TABLE 9. REMOVAL CAPACITIES¹ OF COMBINED SORBENTS IN VARIOUS LYSIMETER ARRANGEMENTS FOR NEUTRAL CALCIUM FLUORIDE SLUDGE LEACHATE

| Pollutant + | Sorbent Capacity (µg/g)* | | | |
|-----------------|--------------------------|---------|-----------------------|--------|
| | Weight ratio of 1:1:1 | | Weight ratio of 2:2:1 | |
| | I+Fa+Fb † | Fa+I+Fb | I+Fa+Fb | I+Fa+Z |
| Ca | 0 | 0 | 0 | 406 |
| Mg | 849 | 528 | 515 | 866 |
| Zn | 5.9 | 7.2 | 6.1 | 9.5 |
| F ⁻ | 110 | 105 | 128 | 148 |
| CN ⁻ | 1.3 | 1.5 | 3.9 | 1.7 |
| COD | 199 | 133 | 241 | 218 |

* Sorbent Capacities are expressed in µg of contaminant removal of sorbent used.

+ Cd, Cr, Cu, Fe, Ni, and Pb were analyzed and found to be below measurable levels.

† I = Illite, Fa = Fly Ash (Acidic), Fb = Fly Ash (Basic), Z = Zeolite.

The sorbent removal capacity exhibited by the illite, acidic fly ash, and zeolite combination (2:2:1) is the most effective for treating all the measurable contaminants (except for total cyanide) in the calcium fluoride sludge leachate. The next most effective combinations is the illite and the acidic and basic fly ashes (2:2:1).

Leaching of zinc and copper occurred only when illite and fly ash are used in combination. This leaching amounted to copper and zinc concentration of 4 mg/l and 1.7 mg/l, respectively, in the initial 1.4 l of effluent. The use of zeolite or basic fly ash as the bottom layer along with illite and acidic fly ash in a 2:2:1 combination reduced the copper and zinc in the initial 1.4 l of effluent to the influent concentration of 0.1 mg/l and 0.6mg/l, respectively.

In this latter part of the study, different calcium fluoride sludge leachate was used than in the first part because the volume of leachate required was greater than the amount that remained from the earlier tests. Analysis of this leachate (Table 10) reveals the presence of measurable concentrations of total cyanide and zinc that were not present in the earlier leachate (Table 1), even though both samples were obtained from the same source, but at different times. Discussions with plant personnel revealed that zinc and cyanide were used in several of their processes during the period that this latter sludge was collected.

TABLE 10. ANALYSIS OF THE NEUTRAL CALCIUM FLUORIDE SLUDGE LEACHATE USED TO OBTAIN SORBENT COMBINATIONS FOR OPTIMUM TREATMENT

| <u>Pollutant</u> [*] | <u>Concentration (mg/l)</u> |
|-------------------------------|-----------------------------|
| Ca | 119 |
| Mg | 89 |
| Zn | 0.60 |
| F | 15.5 |
| CN | 0.61 |
| COD (organics) | 36 |

* Cd, Cr, Cu, Fe, Ni, and Pb, contents were analyzed but found to be below measurable levels.

PILOT STUDIES

Since the combination of illite, acidic fly ash, and zeolite (2:2:1) showed the most promise for treating the neutral calcium fluoride sludge leachate in the laboratory, two large vertical lysimeters were set up outdoors with a sufficient amount of this sorbent combination to treat 530 liters of neutral calcium fluoride leachate. The leachate was collected three different times over a period of a year to study the effect of variations in leachate composition resulting from changes in plant operation. The pilot studies were designed for fluoride removal from the leachate. The combination sorbent removal capacity for fluoride (Table 9) defined the amount of sorbent required in the lysimeters. The permeability of the clay fractions was adjusted by admixing it with inert sand to obtain a leachate velocity of 0.01 cm/min through the sorbent bed and thus insure adequate removal of the fluoride ion. This leachate velocity was selected because it is only a fourth of the 0.049 cm/min shown earlier to approach the required leachate velocity needed to treat the largest volume of leachate with maximum fluoride removal. The results of this study are shown in Figures 8 through 13.

The influent calcium concentrations in the three calcium fluoride samples collected over a period of a year were 309, 115, and 228 mg/l. The illite, acidic fly ash, and zeolite combination (2:2:1) reduced these concentrations in the effluent to approximately 80 mg/l (Figure 8). During the addition of the initial leachate sample, poor removal of calcium was observed. This was probably due to channeling of the leachate through the sorbent as a consequence of adding the sorbent to the columns in the dry state rather than in slurry form. Elimination of the channeling resulted in rapid reduction of calcium concentrations to 80 mg/l.

Copper concentrations in the three leachate samples (0.12, 0.10, and 0.07 mg/l) were reduced to 0.04 mg/l (Figure 9). Also, the leaching of copper

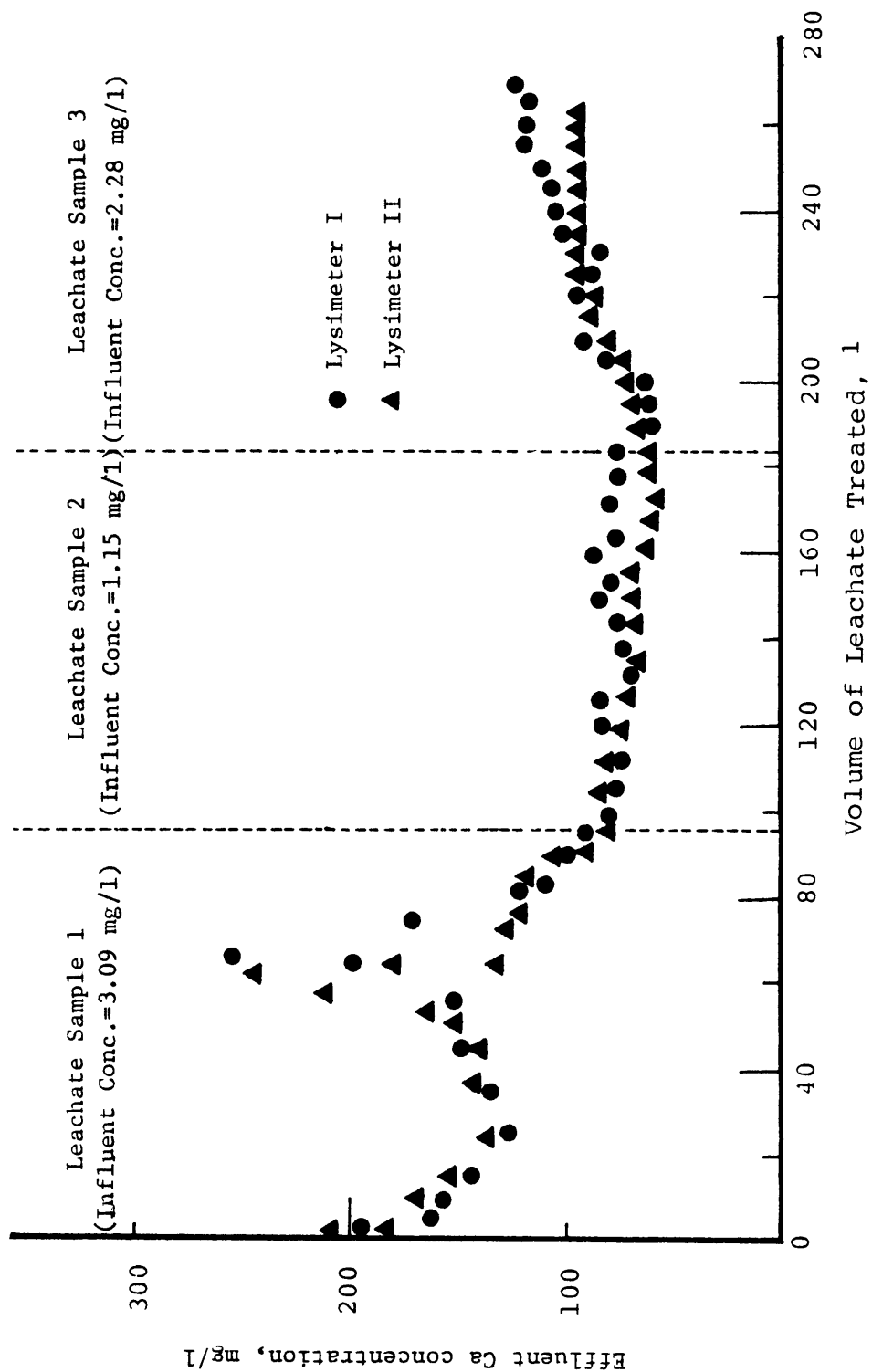


Figure 8. Effluent calcium concentration in pilot-scale lysimeter study.

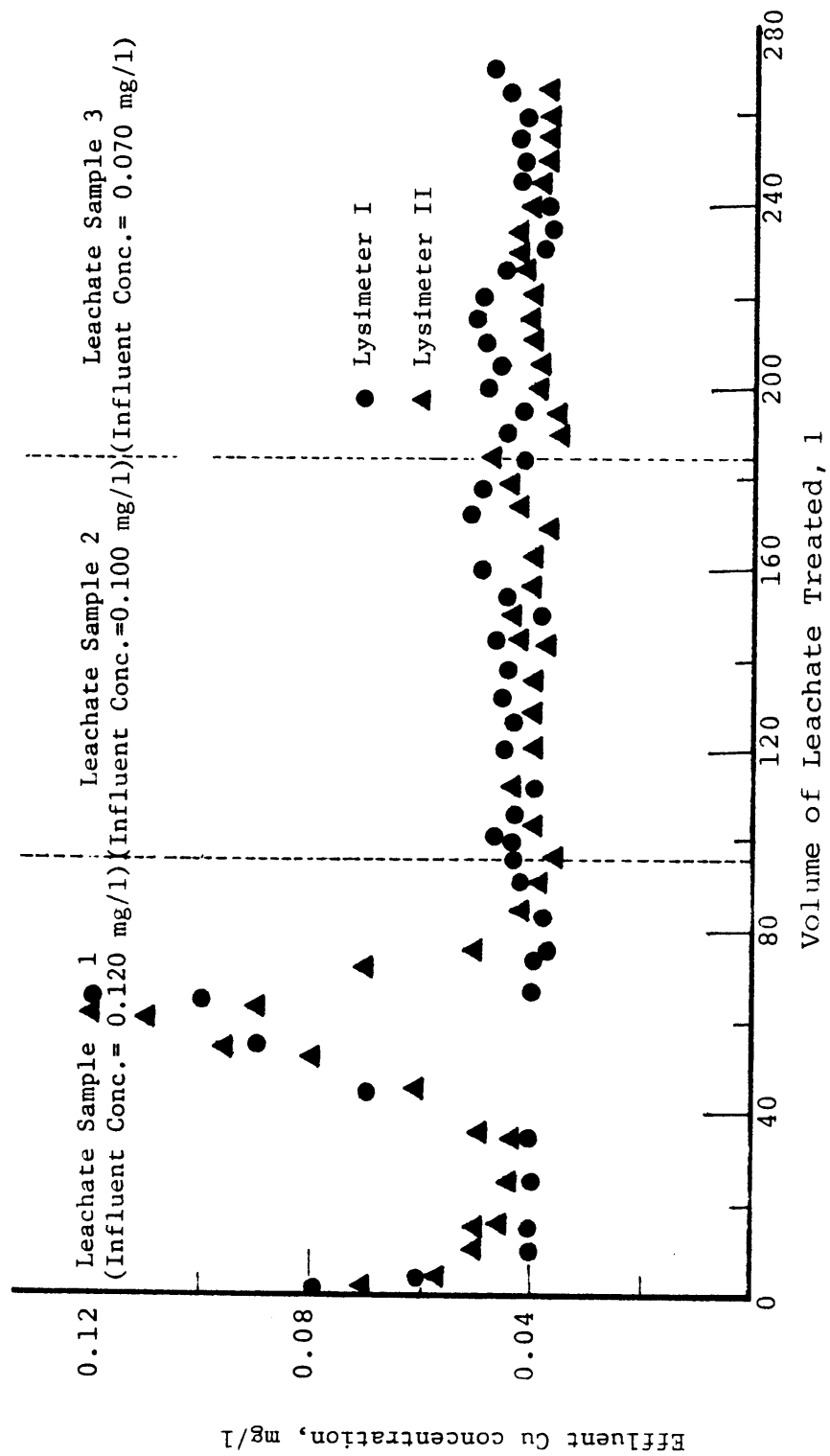


Figure 9. Effluent copper concentration in pilot-scale lysimeter study.

from the illite and acidic fly ash (discussed earlier) is effectively controlled by the natural zeolite. The copper concentration in the effluent from the leachate initially treated was 0.08 mg/l, which is well below the influent concentration of 0.12 mg/l.

The effect of channeling on copper removal can again be seen by the sudden rise in effluent copper concentration after about 40 liters of leachate was treated. However, once the channeling was minimized, by expanding the bed with reverse flow using collected effluent, the copper concentration in the effluent was again reduced to 0.04 mg/l. This channeling effect points out the need for proper dispersion of the leachate stream through the bed.

Magnesium removal by the illite, acidic fly ash, zeolite combination (2:2:1) showed a dependency on the influent concentration (Figure 10). Influent magnesium concentrations of 29.6, 75.7 and 18.5 mg/l gave effluent concentration of approximately 25, 53, and 15 mg/l, respectively. One would expect results similar to those observed for the calcium and copper removals, which appeared to be independent of the influent concentration. There is presently no explanation for these results.

The effective fluoride removal also achieved with this sorbent combination comes as no surprise, since the amount of sorbent and the leachate velocity used were designed for fluoride removal. An effluent fluoride concentration of 1 mg/l was achieved with an influent concentration that varied in the three leachate samples from 10.2 to 15.3 mg/l (Figure 11). Again, as was the case for calcium and copper, the fluoride concentration in the treated leachate was independent of the influent concentration.

This independence also appeared to hold true for the removal of the cyanide ion. Where the concentration of cyanide in the influent cyanide was significant (i.e., 0.25 and 0.37 mg/l in the first two leachates samples), the sorbents reduced these concentrations to approximately 0.06 mg/l (Figure 12). But, for the third leachate, where the influent concentration was extremely low (0.02 mg/l, no significant removal of cyanide was observed. The minimum concentration to which the cyanide can be reduced with this sorbent combination appears to be about 0.06 mg/l. However, if the illite, acidic fly ash, and basic fly ash sorbent system (2:2:1) had been used instead of the illite, acidic fly ash, and zeolite combination (2:2:1), the effluent cyanide concentration would probably have been significantly lower than 0.06 mg/l. Such a result would have been due to greater sorbent removal capacity achieved with the non-zeolite combination (3.9 mg/g) than with the natural zeolite combination (1.7 mg/g) (Table 9).

The minimum effluent concentration of the organics achieved with the illite, acidic fly ash, and zeolite combination (2:2:1) appears to be dependent on the organic influent concentration. As the concentration of organics in the influent increased from 24.2 up to 44.8 mg/l, the concentration of organics remaining in the treated leachate also increased from a low of about 2.5 to 18 mg/l (Figure 13). The reason for this behavior is not clear, but the overall results indicate that the illite, acidic fly ash, and zeolite combination is extremely effective in removing not only the cations and anions, but also the organics present in the neutral calcium fluoride sludge leachate.

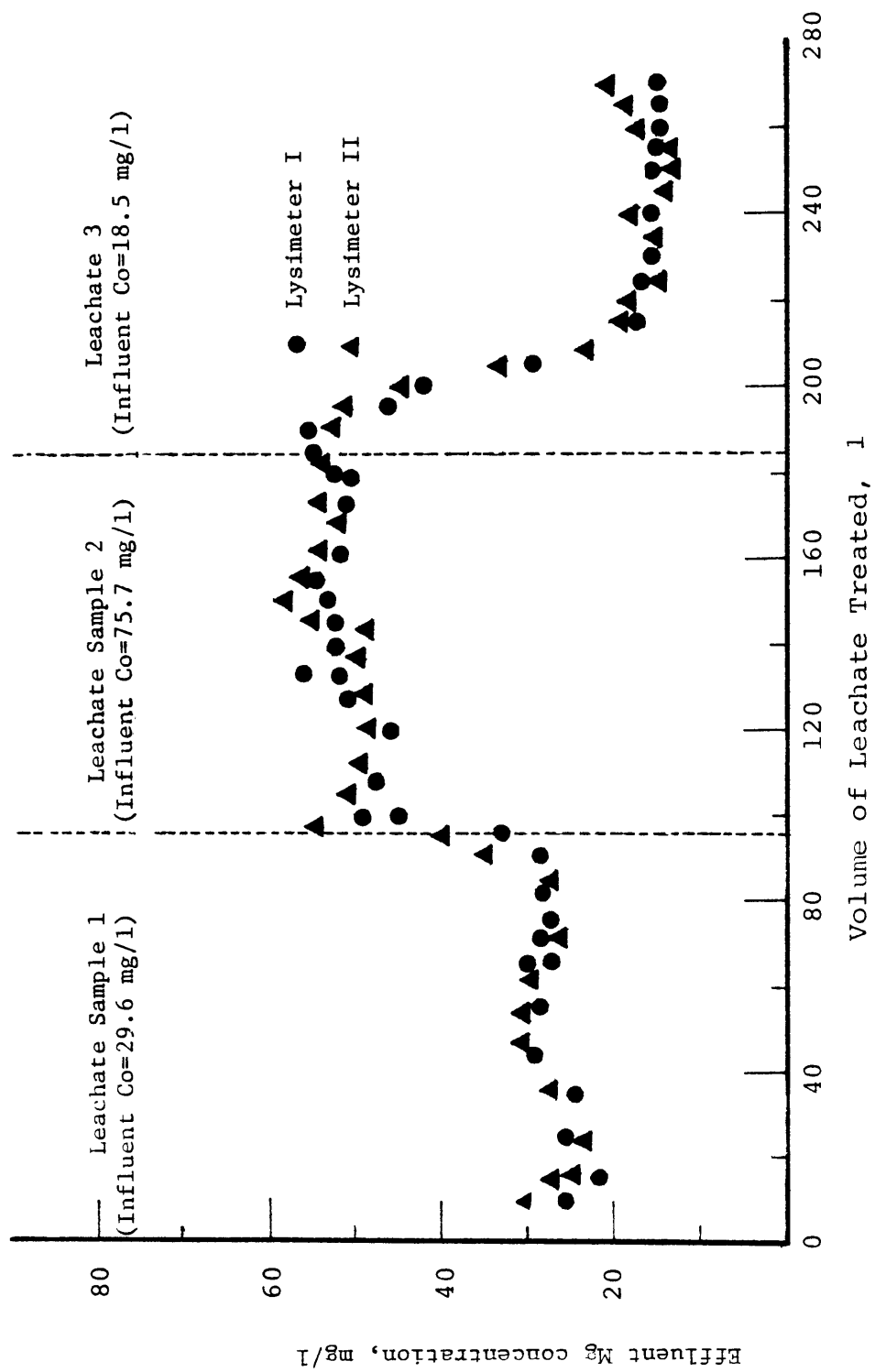


Figure 10- Effluent magnesium concentration in pilot-scale lysimeter study.

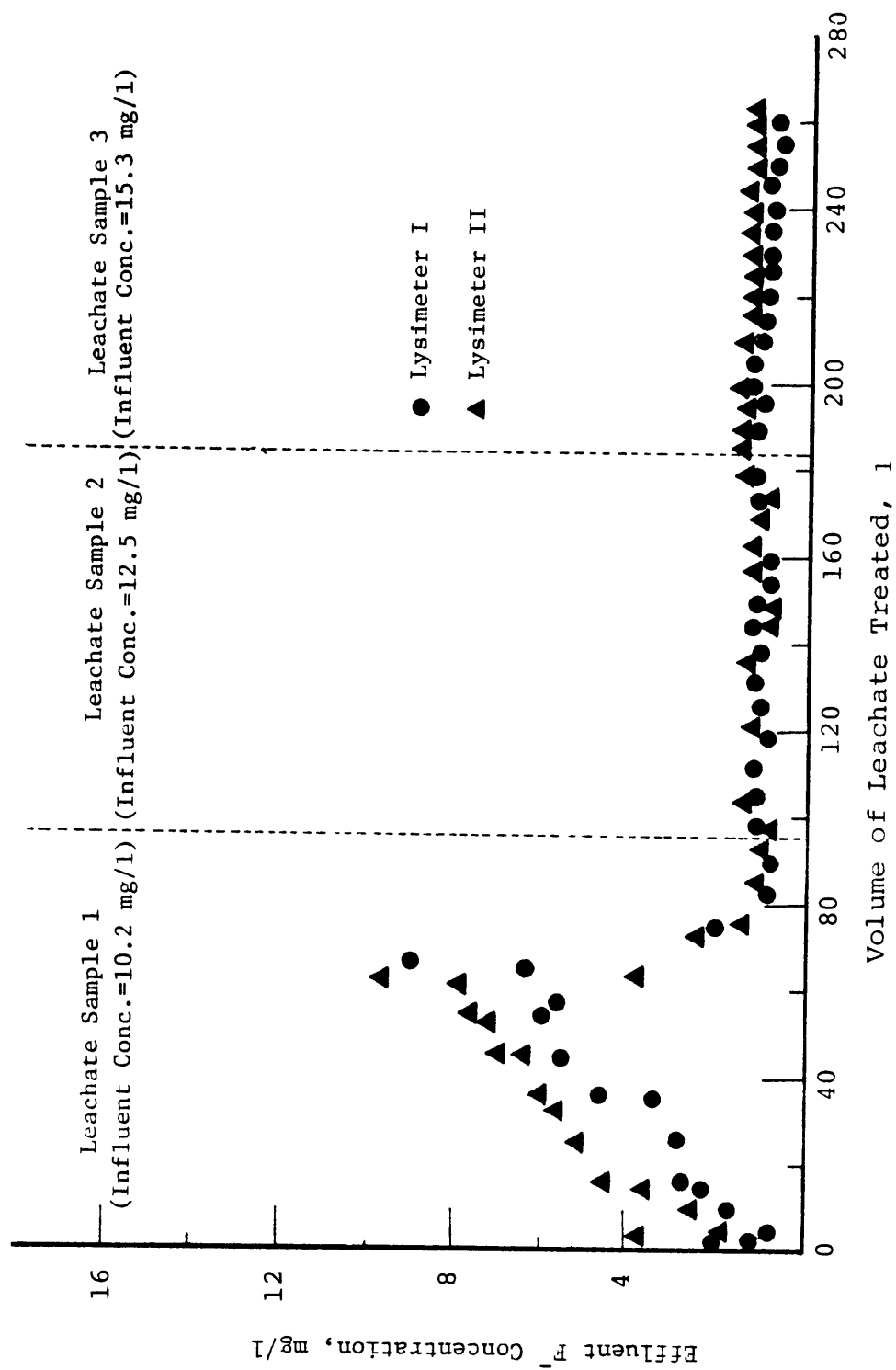


Figure 11 Effluent fluoride concentration in pilot scale lysimeter study

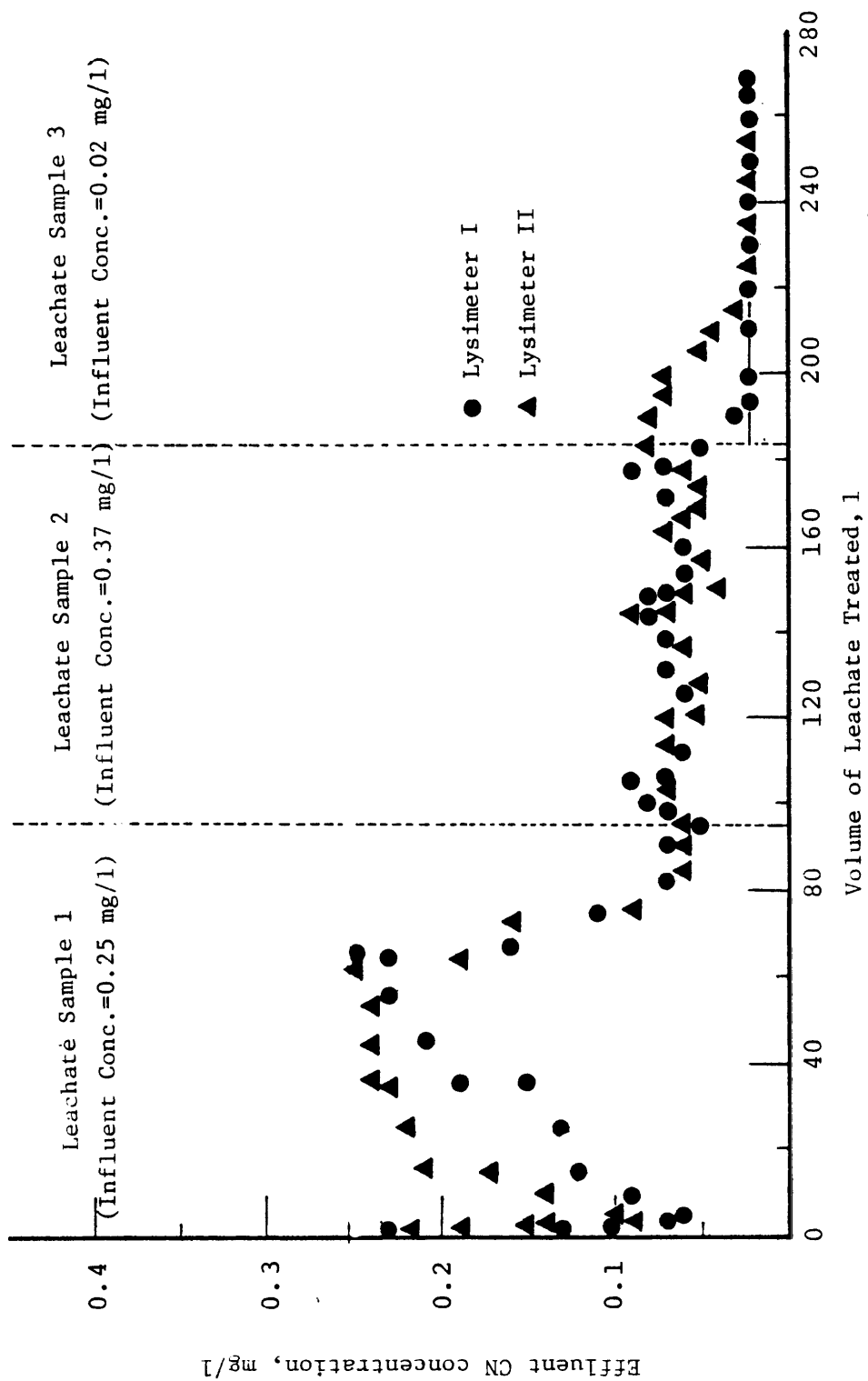


Figure 12. Effluent cyanide concentration in pilot-scale lysimeter study.

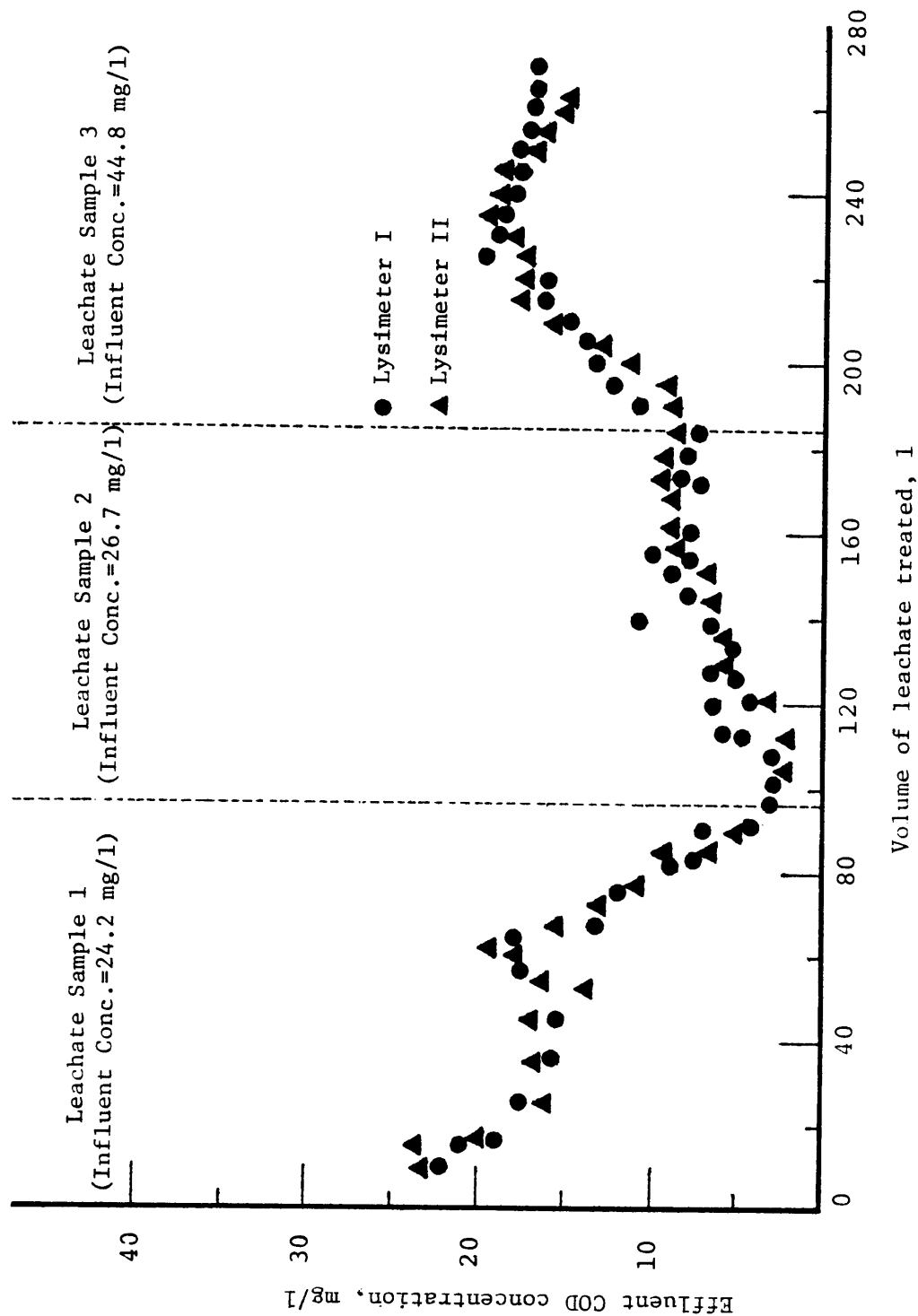


Figure 13. Effluent Organics (COD) concentration in pilot-scale lysimeter study

SECTION 6

PROPOSED DESIGNS FOR A CALCIUM FLUORIDE SLUDGE LEACHATE TREATMENT SYSTEM

In view of the results of the pilot study, several designs are considered for a treatment system for leachate that will originate from a landfill (62.5 x 62.5 x 3.7 m.) which will contain an estimated 10 years production (2.49×10^4 metric tons) of calcium fluoride sludge. The 3.7 m. depth is presently being used in the storage pit at the plant where the sludge is generated.

The designs are based upon the use of the illite, acidic fly ash, zeolite combinations and the illite, acidic fly ash, basic fly ash combinations in the weight ratio of 2:2:1. The pilot study results indicated that the combination sorbent capacity of $148 \mu\text{g F}^-/\text{g}$ of sorbent used (Table 9) and a leachate velocity of 0.01 cm/min through the illite, acidic fly ash, and zeolite combination (2:2:1) were effective in treating all the measurable constituents (Ca, Mg, Cu, F, CN, and organics) in 530 liters of leachate with no breakthrough.

SYSTEM 1

One approach (System 1, Figure 16) involves lining the sludge pit with an impermeable liner to prevent groundwater intrusion. A 1-ft. filter bed is placed at the base of the landfill to remove the suspended solids. The leachate is collected at the bottom of this filter bed and pumped on to an adjacent bed of illite, acidic fly ash, and zeolite (2:2:1), the dimensions of which are 8.5 x 8.5 x 2.7 m. The bed contains sufficient sorbent to treat a year's production of leachate at a rate of 7.5 l/min without ponding and still maintaining a maximum leachate velocity through the bed of 0.01 cm/min (see calculation in Appendix). The 7.5-l/min flow rate was determined by assuming that the annual average rainfall is 102 cm, and that all the rain that falls on the landfill becomes leachate.

SYSTEM 2

The second approach (System 2, Figure 17) is to line the sides of the sludge pit with an impermeable liner to prevent the escape of leachate from the landfill and to place at the bottom of the landfill a 2-ft. layer of the illite, acidic fly ash, and zeolite (2:2:1). This sorbent layer is covered with a 1-ft. layer of filter media to prevent clogging of the sorbent bed by the suspended solids in the leachate (Figure 17). The 62.5x62.5x0.6 m layer of sorbent combination would be adequate to treat 10 years production of leachate containing an average 10 mg/l of fluoride at a flow rate of 7.5 l/min (see calculation in Appendix). This approach would be limited, however,

to areas where the groundwater table is well below the landfill so that groundwater intrusion through the sorbent bed into the landfill would not increase the rate of leachate production beyond 7.5 l/min.

The sorbent cost for using the illite, acidic fly ash, and zeolite combination (2:2:1) is estimated to be \$1.37/ton of calcium fluoride sludge disposed of in landfill. Prices of \$10/ton for illite and \$50/ton for zeolite were used to estimate the sorbent cost. No cost was associated with obtaining the acidic fly ash, since it is a waste product and the utility is presently paying to have it hauled away.

Although the illite, acidic fly ash and basic fly ash sorbent combination (2:2:1) was not evaluated on the pilot scale because of the time constraints of the grant, the laboratory studies (Table 9) show this combination to be effective for treating the measurable constituents (except for calcium) in the calcium fluoride sludge leachate. The illite, acidic fly ash, and basic fly ash combination offers a far less expensive approach than the illite, acidic fly ash, and zeolite combination. If the calcium ion concentration encountered in this leachate (Table 1) presents no significant problems, the sorbent cost for disposing of 1 ton of calcium fluoride sludge decreases from \$1.37 to \$0.45. All bed or layer dimensions remain the same (see calculation in Appendix).

Presently, one disadvantage does exist to using basic fly ash rather than zeolite. The supply of basic fly ash from the utility that has been supplying it is somewhat limited, since the power station generates more acidic than basic fly ash.

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APPENDIX

TREATMENT SYSTEM DESIGN CALCULATIONS

1. Amount of Calcium Fluoride Sludge Production (10 Years)

Annual sludge production estimated by sludge producer:

$$2,740 \text{ tons} = 2.74 \times 10^{10} \text{ g}$$

$$10 \text{ years production} = 2.74 \times 10^{11} \text{ g}$$

2. Volume of Sludge Pit

Assume the compacted sludge density = 1.76 g/cm^3

$$\begin{aligned} \text{Therefore, the sludge pit volume for 10 years} &= 2.74 \times 10^{10} \text{ g} / 1.7 \text{ g per cm}^3 \\ &= 1.55 \times 10^{10} \text{ cm}^3 \end{aligned}$$

3. Calculation of Surface Area of Sludge Pit

Depth of sludge in existing storage pit = 3.66 m

$$\begin{aligned} \text{Mean surface area required} &= 1.56 \times 10^4 \text{ m}^3 / 3.66 \\ &= 4.26 \times 10^3 \text{ m}^2 \end{aligned}$$

Assume the pit has a wall slope for 1 vertical on 1 horizontal with a square configuration for both of top and bottom surface.

Let top surface dimension = $a \text{ (m)} \times a \text{ (m)}$

and bottom dimension = $b \text{ (m)} \times b \text{ (m)}$

$$\text{then } (a^2 + b^2)/2 = 4.26 \times 10^3 \text{ m}^2$$

$$a = b + 12 \times 2$$

The top and bottom areas will be:

$$a \times a = 62.5 \text{ m} \times 62.5 \text{ m} = 3.91 \times 10^3 \text{ m}^2$$

$$b \times b = 54.9 \text{ m} \times 54.9 \text{ m} = 3.01 \times 10^3 \text{ m}^2$$

4. Volume of Sludge Leachate Generated by Rainfall

Assuming the annual rainfall is 1.02 cm per year, the annual leachate generated is:

$$1.02^m \times 3.91 \times 10^3 = 3.99 \times 10^3 \text{ m}^3$$

Assuming that all the rain that falls on the sludge becomes leachate, the amount of sludge leachate generated in 10 years:

$$= 3.99 \times 10^4 \text{ m}^3$$

5. Total Sorbents Required for Each Year

Average leachate concentration of fluoride is 10 mg/l (based on laboratory and pilot studies) using the illite, acidic fly ash, and natural zeolite:

System 1: Using the illite, acidic fly ash, and zeolite combination (2:2:1), the sorbent removal capacity for fluoride is 0.148 mg/g; therefore, amount of sorbent required annually:

$$= 3.99 \times 10^9 \times 10^{-3} \text{ l} \div 0.148 = 2.70 \times 10^8$$

System 2: Using the illite, acidic fly ash, and basic fly ash combination (2:2:1), the sorbent removal capacity for fluoride is 0.128 mg/l; therefore, amount of sorbent required annually:

$$= 3.99 \times 10^9 \times 10^{-3} \text{ l} \div 0.128 = 3.12 \times 10^8$$

6. Average Flowrate of Leachate to be Treated

$$Q = 3.96 \times 10^6 / (365 \times 24 \times 60) = 7.35 \text{ l/min.}$$

7. Required Sorbent Bed Area to Avoid Ponding

$$K = Ql/Ah \quad (\text{assume } l = h)$$

The permeability of clay will be adjusted by mixing with inert material (i.e., sand) to provide a coefficient of permeability.

$$K = 1.8 \times 10^{-4} \text{ cm/sec (i.e., exhibited by the fly ash)}$$

$$A = Q/K = 7.53 \text{ cm}^3/\text{sec} (1.84 \times 10^{-4} \text{ cm/sec} \times 60 \text{ sec/min})$$

$$= 6.97 \times 10^5 \text{ cm}^2 = 8.35 \text{ m} \times 8.35 \text{ m}$$

8. Volume of Sorbent Bed

System 1: Using the illite, acidic fly ash, and zeolite combination (the illite requires 40 percent sand, and zeolite requires 80 percent to achieve the above coefficient of permeability):

$$\text{Amount of sorbents} = 2.68 \times 10^8 \text{ g}$$

$$\text{Sand for illite} = 4.29 \times 10^9 \text{ g}$$

$$\text{Sand for zeolite} = 4.29 \times 10^9 \text{ g}$$

$$\text{Total amount of materials} = 3.54 \times 10^8 \text{ g}$$

$$\text{Packing density} = 1.76 \text{ g/cm}^3$$

$$\text{Total volume} = 201 \text{ m}^3$$

$$= 8.55 \text{ m} \times 8.55 \text{ m} \times 2.75 \text{ m}$$

System 2: Using the illite, acidic fly ash, and basic fly ash combination:

$$\text{Amount of sorbents} = 3.09 \times 10^8 \text{ g}$$

$$\text{Sand for illite} = 4.94 \times 10^7 \text{ g}$$

$$\text{Total amount of materials} = 3.58 \times 10^8 \text{ g}$$

$$\text{Total volume} = 2.03 \times 10^8 \text{ cm}^3$$

$$= 8.55 \text{ m} \times 8.55 \text{ m} \times 2.78 \text{ m}$$

9. Cost of Sorbents

System 1: Using the illite, acidic fly ash, and zeolite combination,

$$\text{Illite cost} = \$10/\text{ton}$$

$$\text{Natural zeolite cost} = \$50/\text{ton}$$

$$\text{Fly ash cost} = \$0$$

$$\text{Total sorbent cost} = 2.68 \times 10^8 \times 0.4 \times 10^{-6} \times 10$$

$$+ 2.68 \times 10^8 \times 0.2 \times 10^{-6} \times 50 = \$3,752$$

or $\$3,752/2,740$ ton of sludge produced annually

$$\text{Sorbent cost per ton of sludge} = \$1.37$$

Sample 2: Using the illite, acidic fly ash, and basic fly ash combination,

Illite cost = \$10/ton

Fly ash cost = \$0

Total sorbent cost = $3.09 \times 10^8 \times 0.4 \times 10^{-6} \times 10 = \$1,240$

or $\$1,240/2,740 \text{ ton} = \$0.45/\text{ton}$ of sludge produced annually

Sorbent cost per ton of sludge = \$0.45

10. Design of Liner Bed

System 1: Using the illite, acidic fly ash, and zeolite combination, total sorbent,

Volume = $201 \text{ m}^3/\text{year}$

Depth of sorbent bed = $\frac{201 \times 10}{54.9 \times 54.9} = 0.67 \text{ m}$

System 2: Using the illite, acidic fly ash, and basic fly ash combination,

Total sorbent volume = $203 \text{ m}^3/\text{year}$

Depth of sorbent bed = $\frac{203 \times 10}{54.9 \times 54.9} = 0.67 \text{ m}$

11. Sorbent Cost

System 1: The illite, acidic fly ash, and zeolite combination weight and cost of sorbents required for 10 years are:

Fly Ash (acidic) = $1,072 \text{ tons} \times \$0/\text{ton} = 0$

Illite = $1,072 \text{ tons} \times \$10/\text{ton} = \$10,720$

Zeolite = $\underline{536 \text{ tons} \times \$50/\text{ton} = \$26,800}$

Total 2,680 \$37,520

Tons of sludge produced in 10 years = 27,400

Sorbent cost/ton of sludge = $\frac{\$37,520}{27,400 \text{ tons}} = \1.37

System 2: The illite, acidic fly ash, and basic fly ash combination weight and cost of sorbents required for 10 years are:

$$\text{Fly Ash (basic)} = 620 \text{ tons} \times 0 \text{ ton} = 0$$

$$\text{Fly Ash (acidic)} = 1,240 \text{ tons} \times 0/\text{ton} = 0$$

$$\text{Illite} = \underline{1,240} \text{ tons} \times \$10/\text{ton} = \underline{\$12,400}$$

$$\text{Total} = 2,100 \text{ tons} = \$12,400$$

$$\text{Tons of sludge produced in 10 years} = 27,400$$

$$\frac{\text{Sorbent cost}}{\text{Tons of sludge produced}} = \frac{\$12,400}{27,400} = \$0.45$$

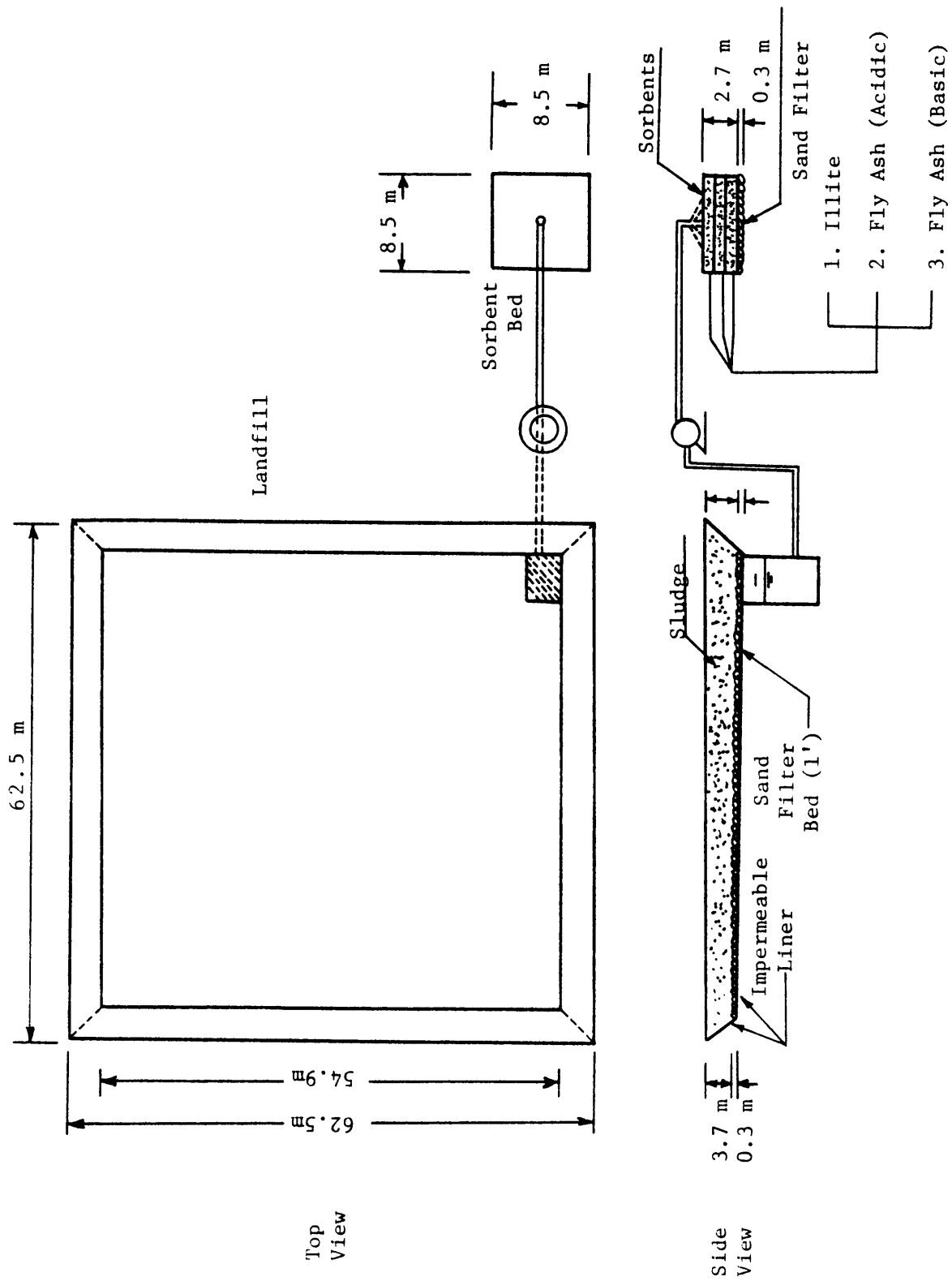
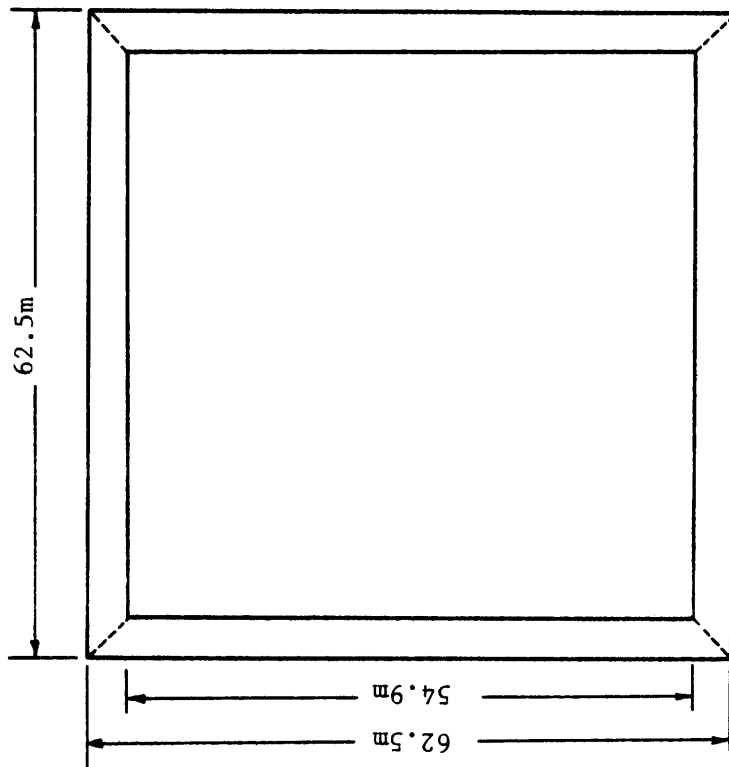


Figure 14. System 1 design for leachate treatment system.



Plan
View

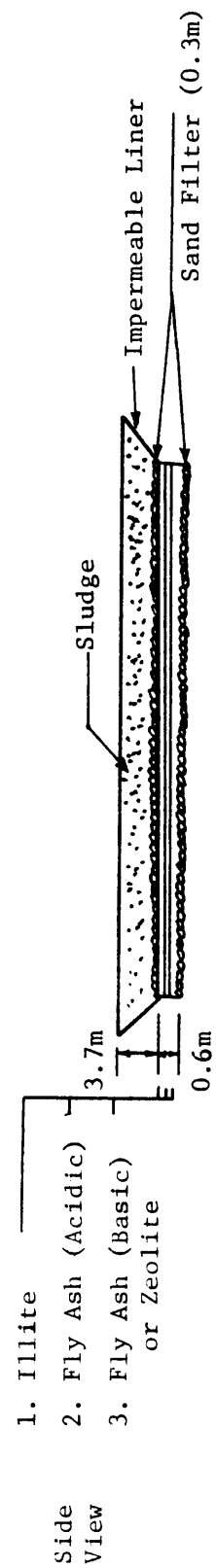


Figure 15. System 2 design for leachate treatment system.

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| 16. ABSTRACT <p>A laboratory and outdoor pilot-scale investigation was conducted on the use of selected sorbents for removing leachate contaminants from three industrial sludges.</p> <p>The laboratory results indicated that, rather than a single sorbent, a combination of acidic and basic sorbents is required in a layered system for removal of all the measurable contaminants from the leachates. These combinations are illite, vermiculite, and a natural zeolite for the acidic leachate; illite, acidic fly ash for the neutral leachate; and illite, kaolinite, and a natural zeolite for the alkaline leachate. The sorbent capacities exhibited by the natural sorbents are comparable to those exhibited by refined sorbents.</p> <p>The outdoor pilot study, which was limited to the treatment of the calcium fluoride sludge leachate, using lysimeters, some 80 times larger than the laboratory lysimeters, revealed that the sorbent effectiveness depends on the velocity of the leachate through the sorbents and the sorbent removal capacity for specific contaminants. Except for magnesium, effective reductions of the measurable leachate constituents were achieved with the use of illite, acidic fly ash, and a zeolite in the weight ratio of 2:2:1.</p> <p>Sorbent costs have been estimated for various combinations required for treating leachate from calcium fluoride sludge over a ten-year period of landfill operation. For the illite/acidic fly ash/zeolite combination and the illite/acidic fly ash/basic fly ash combination, costs are \$1.37 and \$0.45 per ton of sludge, respectively.</p> | | | | | |
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