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THE USE OF NATURAL SORBENTS FOR THE TREATMENT
OF INDUSTRIAL SLUDGE LEACHATE.

NEW JERSEY INSTITUTE OF TECHNOLOGY, D.ENG.SC.,
1979

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THE USE OF NATURAL SORBENTS FOR THE TREATMENT OF INDUSTRIAL SLUDGE LEACHATE

By

MUNG SHIUM SHEIH

A DISSERTATION
PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
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1979

ABSTRACT

A sorbent treatment process has been developed which uses natural clay soils and fly ashes as sorbents in the treatment of the hazardous contaminants of potential sludge leachate emanating from industrial landfills. Natural sorbents (i.e., vermiculite, illite, kaolinite, zeolite, acidic and basic fly ashes) were evaluated for the removal of specific cations, anions, and organics from leachates generated from three industrial sludges (i.e., calcium fluoride, metal finishing, and petroleum). The laboratory results indicate that, rather than a single sorbent, a combination of acidic and basic sorbents in a layered system is required to reduce for the measurable contaminants present in the leachate to safe levels. These combinations are: illite, vermiculite and zeolite for an acidic leachate; illite, acidic fly ash and zeolite for a neutral leachate; and illite, kaolinite, and zeolite for an alkaline leachate. The selection of these sorbent combinations is based upon a comparison of their individual sorbent capacities.

pH control of leachate is essential for effective treatment. The removal of anions is favored by acidic conditions, cations by alkaline conditions, and the organic either by acidic or alkaline conditions. A study of a pilot scale lysimeter system reveals that the effectiveness of sorbents is dependent upon two factors, namely the velocity of leachate through the sorbent and the sorbent removal capacity for specific contaminants. The sorbent costs for a combined sorbent system used to treat the industrial sludge leachates are comparable to those of refined sorbents.

APPROVAL OF DISSERTATION

THE USE OF NATURAL SORBENTS FOR THE
TREATMENT OF INDUSTRIAL SLUDGE LEACHATE

BY

MUNG SHIUM SHEIH

FOR

DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

NEW JERSEY INSTITUTE OF TECHNOLOGY

BY

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Newark, New Jersey
May, 1979

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I. INTRODUCTION

In this highly industrialized country, industrial processes, along with air and water pollution control activities, produce approximately 10 million tons of nonradioactive hazardous sludges and solid wastes annually. This quantity is expected to double in the next 10 years (22, 25). Generally, these wastes are disposed in the upper layers of the earth's crust in landfills (see Figure 1) or by ocean dumping and will continue to be the most practical solution for many years. Disposal of these wastes on land is increasing because ocean dumping is becoming legally unacceptable for this type of waste according to the Water Pollution Control Act of 1972 mandating no dumpage after 1981. The disposal of such huge volumes of solid wastes in landfills, however, is very complex due to various interacting variables. If it is not properly designed and operated, it will cause adverse environmental effects. The magnitude of the problem varies with the geography and hydrologic characteristics in the fill site area, method of fill operation, and a number of other factors including quantity of waste, leachability, permeability, and attenuative properties of the surrounding soils.

Soil is composed of air, water, microorganisms, and minerals which make up the solid matrix. As the solid waste is disposed of on the land, the soil interacts with the waste to form an integrated system. This waste may change the physical, chemical and biological processes of the in-situ soil system. These processes become more complex when infiltrated precipitation or groundwater comes in

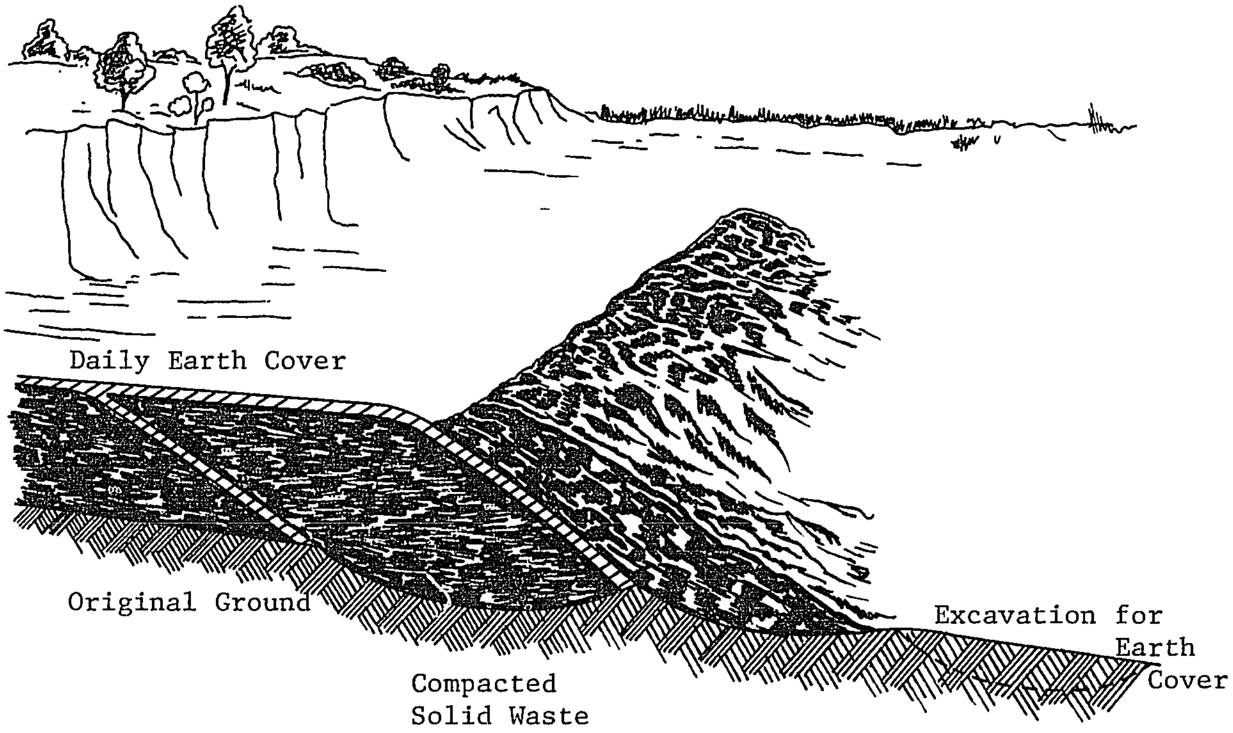

Figure 1. Conventional Sanitary Landfill

contact with solid waste which often contains hazardous substances. Thus, the potential of leaching exists. The water will dissolve organic and inorganic substances out of the solid wastes and generates a leachate which usually contains a high content of heavy metals, organic matter and inorganic anions. This leachate can move out of the fill into the surroundings and subsequently reach the ground water supplies or nearby aquifers (see Figure 2).

Various cases of such pollution have been documented (1, 3, 18, 19). For instance, a large aquifer of New Castle County in Delaware was reported to be polluted by leachate from a closed landfill. Leachate from this landfill migrated more than 800 feet in four years and polluted this aquifer (3). The concentration of organic compounds and metal ions introduced into this aquifer was so high that the water is no longer potable. To date, $800,000 has been spent in an effort to remedy this situation, but it appears that the dump must be moved to completely halt the intrusion. This will require as much as 20 million dollars. In addition, the County estimated that it would take 10 years to restore the aquifer to full use.

This example indicates the harmful effect on ground water supplies that uncontrolled dumping of hazardous wastes can cause. This leachate problem is presently minimized by one of the following treatments:

a) <u>Chemical fixation of the sludge</u>: This method applies

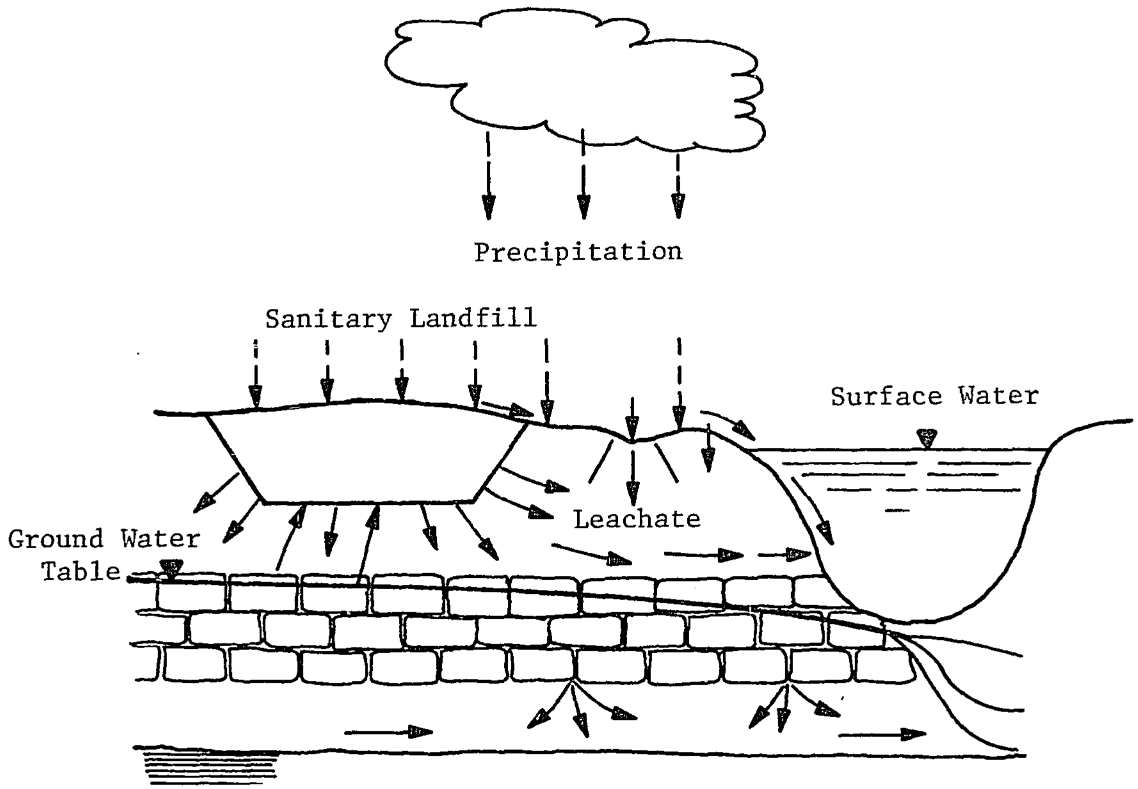

Figure 2. Leachate and Infiltration Movement

physicochemical principles to fix, or stabilize the contaminants in the sludge so that these hazardous materials will not leach into its environment. This fixation process converts the waste into an inert product in which pollutant mobility is reduced. Sludge or dry hazardous waste fixed by commercially available fixation processes have been developed and evaluated (30, 42). Results of leaching tests showed that all fixed materials were leaching pollutants to some degree but this method is expected to provide a high degree of control over the release to the environment. However, chemical fixation process is very expensive. The cost is estimated at $91 per ton of dry waste for a plant processing 20,000 tons per year (42). Thus, chemical fixation of sludge could become a viable alternative for attenuating pollutant migration from sludges only if its cost can be significantly reduced.

b) Selective location of landfill site: This method requires the landfill be located at a safe distance from surface or ground water so that the natural clay components in the soil will reduce the pollutants in the leachate. An underground mine has been used for storing hazardous industrial wastes and was found to be environmentally acceptable (41). This method is generally the most inexpensive, but acceptable disposal sites will be difficult to find in the future. Their establishment will be approved only after certain geologic and hydrologic criteria are met and their operation will be required to be environmentally acceptable.

c) Lining the landfill site: This method confines wastes in pits, ponds, lagoons and landfills by lining the disposal sites with impermeable membrane materials and collecting the leachate from these storage areas. Polyvinyl chloride, butyl rubber, and asphaltic materials, etc. have been used as liners. The leachate collected is then treated using refined sorbents, such as activated carbon and activated alumina to remove the hazardous materials. While this approach is being widely used as a means of treating hazardous wastes (22, 25), it is very expensive; i.e. the high cost of the refined sorbent necessitates additional regeneration facilities. This expense can be reduced by using inexpensive sorbents, such as clay soils in combination with waste product, to treat the leachate. The latter treatment, in essence, simulates what mother nature does but in a controlled manner.

The intent of this investigation is to identify the leachate problem associated with a selected number of industrial sludge and develop an inexpensive treatment system, using naturally occurring clays and waste products.

Because of its dynamic and heterogeneous nature, the clay soils have the property of reacting with certain anions and cations and retaining them in an exchangeable state. By these reactions, the clay soils may serve as a medium for either waste storage or for ultimate waste disposal.

With these backgrounds, many investigators have utilized soils, clays and waste products for leachate and waste water treatment. It has been found that leachates and waste streams containing organics (7, 10, 33, 34, 36) heavy metals (6, 15, 20, 21, 22) and toxic anions (9) can be treated by clay minerals, soils and waste products (17, 33, 34). Recently, several investigators have examined the effectiveness of kaolinite, illite, montmorillonite, and soil mixtures in removing pollutants such as heavy metals and organic compounds. Bittell and Miller (9) investigated the removal of lead, cadmium and calcium and found that the cations exhibited consistent preferential sorption characteristics for the three clays. Fuller et al. (17) examined eleven soil mixtures, ranging from sandy loam to clay mixtures, mixed with limestone and hydrated $FeSO_4$, as potential sanitary landfill barrier. Preliminary results indicated that both limestone and hydrated $FeSO_4$ had a significant retarding influence on the migration rate of the cations and anions. Griffin et al. (20, 21, 22), in examining the removal of heavy metals by kaolinite and montmorillonite, concluded that both cationic and anionic adsorption on these two clays were significant.

In addition, some investigators have explored the application of fly ash in treating waste waters. Deb et al. (13), Nelson and Fuarino (34) both reported the use of fly ash for treatment of COD from waste water. Ballance et al. (6) used fly ash as a coagulant aid in water treatment, reporting that fly ash has certain properties which enhances chemical coagulation and settling of turbid water.

All of the above mentioned investigators examined the effectiveness of clays and fly ash for removing specific pollutants in synthesized leachates or in laboratory-modified leachates. However, the leachate to be treated is generally a complex mixture of many compounds. First, the compounds in solutions may interfere each other; i.e. the sorption of one substance will tend to reduce the sorption of another. Hence, the quantity of sorbent available as a driving force to produce sorption of other substances is decreased and mutually depressing effects on rates of sorption may be encountered. Second, the influent concentration of substance to be absorbed is also one of the important factors to affect the capacity. Since higher concentration of that substance provide better opportunity or competition for itself to contact with sorbent, higher adsorption capacity is predicted. Also, pH could be the important factor due to the ionization of hydrogen which in turn becomes one of the cations in the solution and will compete with other cations.

In order to explain the above effects, a brief review of ion-exchange and adsorption is developed.

Two equations generally used to characterize adsorption equilibrium are the Freundlich isotherm and Langmuir equation (14). The Freundlich isotherm is expressed as:

$$\frac{X}{M} = K\ C^{1/n} \qquad (1)$$

where

X = Weight of substance adsorbed

M = Weight of Adsorbent

X/M = Adsorption Capacity of Adsorbent

C = Concentration of solute remaining in solution

K and n are constants depending on temperature, the adsorbent, and the substance to be adsorbed

The Langmuir equation is:

$$\frac{X}{M} = \frac{knC}{1+kC} \qquad (2)$$

This can be written in linear form:

$$\frac{1}{X/M} = \frac{1}{n} + \frac{1}{kn}\ \frac{1}{C} \qquad (3)$$

where

k = Constant which increases with increasing molecular size

n = Maximum adsorption

Since Langmuir equation only deals with a monomolecular adsorption layer, it is not reasonable to apply this equation directly in the most waste waters which usually contain more than one substance. By developing relationships from the Langmuir equation for a two-substance mixture, the following equations are obtained (14).

$$(X/M)_1 = \frac{K_1 n_1 C_1}{1+K_1C_1+K_2C_2} \qquad (4)$$

$$(X/M)_2 = \frac{K_2 n_2 C_2}{1+K_1C_1+K_2C_2} \qquad (5)$$

The linear form of equation (4) is

$$\frac{1}{(\frac{X}{M})_1} = \frac{1}{n_1} + \left(\frac{1+K_2C_2}{K_1n_1} \right) \frac{1}{C_1} \qquad (6)$$

More complex relationships could similarly develop for multicomponent mixtures.

Equations 3 and 6 can be plotted as a straight line in Figure 3.

In viewing the above equations, it should be noted that the adsorption capacity of a pure solute adsorbed increases as the concentration of that solute in the influent solution increases in a reciprocal linear relationship (see equation 3 in Figure 3). Furthermore, the adsorption capacity of each individual solute adsorbed in a mixture is less than that of the solute existing alone in the solution (see equation 6 in Figure 3). The latter phenomenon of reduced adsorption capacity can also be attributed to the competition of other substances.

As for the pH effect on the adsorption capacity, it can be developed from equation 6. In this equation, if C_2 represents the concentration of hydrogen ion (H^+), and C_1 represents any monovalent cations (A^+) in the solution, equation 6 can be written as

$$\frac{1}{(\frac{X}{M})} = \frac{1}{n_1} + \left(\frac{1+k_2\ H^+}{k_2n_1} \right) \frac{1}{A^+} \qquad (7)$$

In this equation, the value of $\frac{1+k_2\ H^+}{k_2}$ is the slope of this

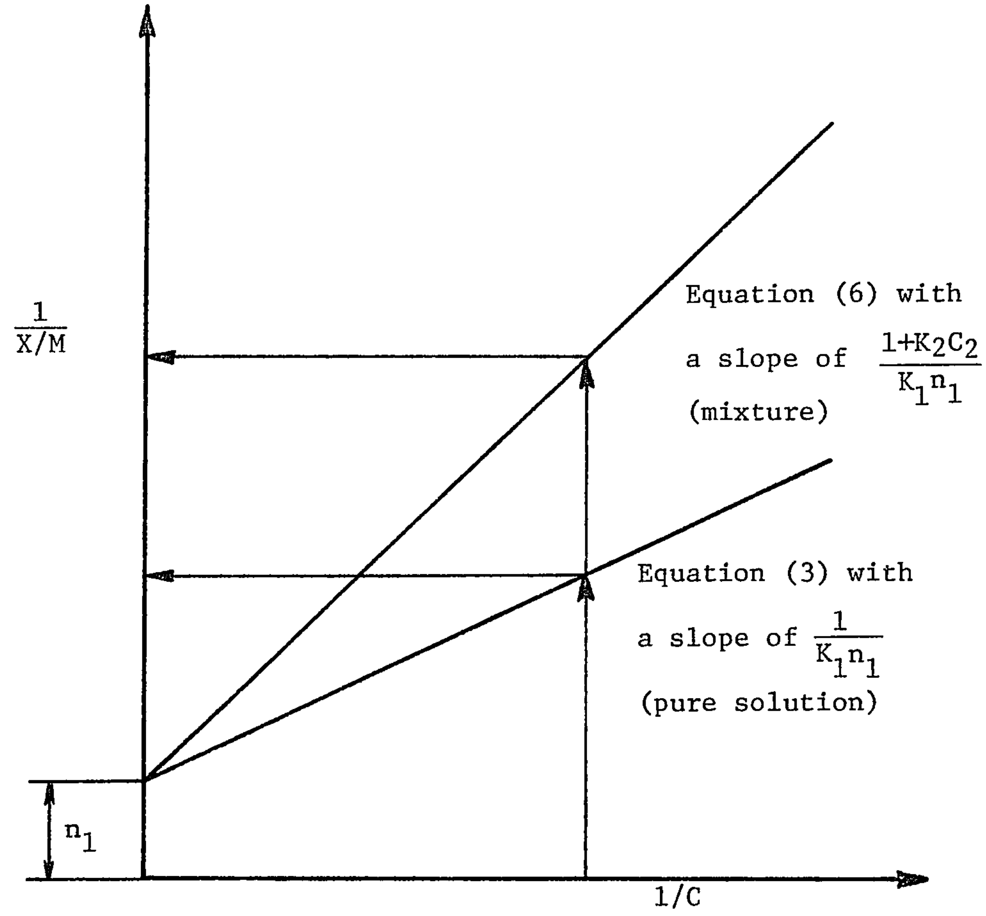

Figure 3. The effect of influent concentration and composition on the adsorptive capacity.

linear form. As pH value is raised, the concentration of hydrogen ion and the value of slope (i.e. $\frac{1+k_2\ H^+}{k_2 n_1}$) decreases. Consequently, the capacity (X/M) of the sorbent to adsorb cations other than hydrogen ion increases very considerably. On the other hand, as pH value decreases, the adsorption capacity of cations decreases.

By analogy with the adsorption of cations, equation 7 can be written as

$$\begin{gathered} \frac{1}{(X/M)} = \frac{1}{n_1} = \left(\frac{1+k_2\ OH^-}{k_2 n_1} \right) \frac{1}{A^-} \\ \text{or} \\ \frac{1}{(X/M)} = \frac{1}{n_1} + \left(\frac{1+k_2/\ H^+}{k_2 n_1} \right) A^- \end{gathered} \tag{8}$$

if C_1 and C_2 in equation 6 represent the concentration of any monovalent anions A^- and the concentration of hydroxyl ion OH^- in the solution, respectively. From equation 8, it can be noted that as pH is lowered, the value of slope (i.e. $\frac{1+k_2/\ H^+}{k_2 n_1}$) decreases, and therefore the capacity (X/M) of the sorbent to adsorb anions other than hydroxyl ions increases.

For the above reasons, the composition of a leachate can be an important parameters in defining a treatment system which uses clay sorbents to treat the leachate contaminant in landfill. It is questionable that the laboratory results based on synthesized leachates can be applied directly to a landfill operation.

Furthermore, all of the abovementioned investigators only utilized a single sorbent system for the treatment of a specified contaminant. The sludge leachate as explained above, usually contains a wide spectrum of pollutants. A sorbent, good for a specific pollutant removal, may not be necessarily good for the others.

In view of the above, an investigation was undertaken to develop an effective process which can be employed in treating hazardous leachate from industrial landfill and thereby preventing contamination of ground and surface waters. This approach is based upon the fact that many natural clays and waste products (such as fly ash) contain some exchangeable non-toxic cations and anions (ion-exchange) or available sites (adsorption) which tend to exchange or adsorb toxic constituents from liquid solution. These sorbents could be used to reduce the toxic contaminants in the leachate to safe levels if their parameters could control these removals.

In order to achieve the above stated objectives, the study programs are listed as follows:

a) Selection of sorbents and sludges: The sorbents selected for this study were acidic and basic fly ashes (waste products), vermiculite, illite, kaolinite, zeolite and cullite. The selection of these sorbents was based on three factors; namely, availability, economics and attenuative capacities. The above clay soils are the most important families in clay minerals and are readily available (10, 20, 21). Activated carbon and activated alumina, presently used commercially for the removal of cations, anions and organics in industrial waste streams and water supplies, were also included in this study for reference.

The sludges used in this study were calcium fluoride sludge (generated by the electronics and aircraft industries), metal finishing sludge, and petroleum sludge. These sludge types are produced in large amounts annually and present significant disposal problems. Also, we tested them and found that their leachates contain a cross-section of heavy metals, cyanide, fluoride and organics. The calcium fluoride sludge leachate was selected for the pilot study since the levels of fluoride in this leachate were in range of 5 to 20 mg/l and there is no inexpensive process presently available for the treatment of such a leachate to acceptable discharge levels. A detailed description of the sorbent materials and sludges is presented in Chapter II.

b) Evaluation in a batch test of the most promising sorbents from selected clay soils, synthetic sorbents and products. Using leachate with the maximum concentrations of contaminants that could be obtained from the sludge, batch studies were conducted to evaluate these sorbent materials.

c) Evaluation of the removal capacities of the most promising sorbents, as indicated in the batch tests, for treating toxic pollutants in lysimeter test. This study involves the determination of pH, chemical oxygen demand (COD), total organic carbon (TOC), anionic species, and cationic species, before and after passing the leachate through sorbent materials held in a lysimeter. This study will provide information regarding the dynamic flow, continuing flow capacity and permeability characteristics of these materials.

d) Definition and identification of the most promising sorbent combinations which are most effective in removing the heavy metals, toxic anions, and organics present in leachates originating from industrial sludges. This combination study is based on individual removal capacities of pollutants for each sorbent.

e) Examination of the significant factors affecting sorbent behavior. These factors include pH and concentrations of influent leachate as well as velocity of leachate passing through the sorbent. They are included in the study because they can have a pronounced effect on the amounts of heavy metals and anions removed from solutions by clay minerals (22, 31).

f) Demonstration of the pilot scale lysimeter operation in outdoor use. This study uses the most promising waste product - clay soil combination (based on the results of the laboratory lysimeter study) to treat a large quantity of calcium fluoride sludge leachate collected over a period of one year. In this manner, the effect of compositional changes on the removal of the contaminants by the waste-clay sorbent combinations could be studied and verified.

g) Establishment of design for a sorbent treatment system to reduce the concentrations of toxic constituents from calcium fluoride sludge leachate down to acceptable discharge levels.

II. MATERIALS DESCRIPTION

SORBENTS

Eight sorbent materials representing major clay soils, waste products, and refined materials were selected for this study. These materials are illite, zeolite, vermiculite and kaolinite (clay soils); bottom ash, acidic and basic fly ashes (waste products of industry); activated alumina, activated carbon, and cullite (refined materials). Their selection was based on economics, availability, and removal potential (10, 15, 20, 21, 23, 25, 29, 34).

Illite: Illite is not a specific mineral name, but a general term for the clay mineral constituents of argillaceous sediments belonging to the mica group (23). Most of the illite clay minerals are dioctahedral, but some are trioctahedral (23, 35). In general, the term illite is used to denote the aluminum, magnesium, and iron rich mica found in the weathered clay fraction of the state of Illinois. The particle size of naturally occurring illite is very fine with well-defined edges. The illites have a moderate cation-exchange capacity (see Table 1) that is primarily due to broken bonds, or lattice substitution in poorly crystallized varieties. Illite is a common product of weathering and is particularly abundant in deep-sea clays. The sample used for this study was supplied by A. P. Green Refractory Co., Morris, Illinois. This material was originally received as rock-form, and therefore was ground to powder and passed through an 80-mesh screen before use.

Kaolinite: Kaolinite is a clay containing a relatively high ratio of aluminum to silicon; high hydrogen, but low sodium, potassium, calcium, and no magnesium and iron and an acid abrasion pH. In general, the structure of kaolinite is composed of a single silica tetrahedral sheet and single alumina octahedral sheet combined in a unit. It is a principal component of lateritic-type soils, and broken bonds around the edges of the silica-alumina units are the major cause of its exchange capacity (see Table 1). Kaolinite was selected in this study mainly because of its abundance in the clay family as well as its potential sorptive characteristics and availability. This material was obtained from Georgea Keolin Company, Elizabeth, New Jersey.

Vermiculite: Vermiculite is a hydrated magnesium silicates. It is formed as large mica-like flakes, is softer than mica and is usually red, brown or black. This clay mineral, when heated, exfoliate in an amazing fashion with an increase in volume up to 100-fold. Gruner (24) derived the average molecular composition of vermiculite as $22\ Mg\ 0 \cdot 5\ Al_2 0_3 .\ Fe_2 0_3 \cdot 22\ Si0_2 \cdot 40\ H_2 0$. The structure of vermiculite consists of trioctahedral mica sheets separated by double water layers and is unbalanced by substitution of aluminum for the tetrahedral layer. The vermiculites have a high cation-exchange capacity (150 milliequivalents per 100 g). They also adsorb certain organic molecules between the mica layers. This material was used as received and was obtained from W. R. Grace & Co., Trenton, New Jersey.

Zeolite: Zeolite is the only known example of a mineral with four silica tetrahedral arranged in the form of a ring (23, 35). Aluminum ions are also present in the tetrahedral units. Therefore, the zeolites are based on framework structures of $(Si, Al)O_2$ units (35).

The framework has a net charge deficiency which is electrically balanced by large-sized cations contained in the voids in the lattice. These ions are not held firmly, but can move freely and can be exchanged. The zeolites are commonly used as water softeners due to their large capacity for cation exchange (see Table 1). This material was selected in this study because of its potential sorption characteristics, as well as availability. The sample was supplied by the Double Eagle Petroleum and Mining Company, Casper, Wyoming.

Fly Ash: This material is defined as the fine particulate matter escaping from chimney stacks. It is a waste product of electric power generation using coal combustion. It is usually collected by electrostatic precipitators from the flue gases before they escape the stacks. The constituents of fly ash vary according to the type of coal used and the degree of combustion. In general, fly ash is a fine, sandy material, dark gray in color. The individual particle size of this material ranges from 0.5 to 100 microns. The principal chemical constituents are silica, alumina, iron, sulfur trioxide, alkali and alkaline earth metals (33). It is estimated that a total of 30 million tons of fly ash is generated annually in this

TABLE 1

ION EXCHANGE CAPACITIES OF NATURAL SORBENTS (11)

Sorbents	Cation-Exchange Capacity milliequivalent per 100 g. of sorbent	Anion-Exchange Capacity milliequivelent per 100 g. of sorbent
Kaolinite	3 - 15	6 - 20
Illite	10 - 40	4 - 17
Vermiculite	100 - 150	4
Zeolite	100 - 300	*
Fly Ash	*	*

* No data is available

country (33). Their leachate pH characteristics vary from acidic to alkaline. This material has been only used for treatment of COD from waste water (13, 34). Thus, no report of ion-exchange capacity is available for fly ash. Both the acidic and alkaline fly ashes used in this study were supplied by Public Service Electric and Gas Company, Hudson Generating Station, Jersey City, New Jersey.

Bottom Ash: Bottom ash is also a waste product of coal combustion power plants. It is collected as a residue of the furnace. Like fly ash, bottom ash is a sandy material and dark gray in color except it has an individual particle much larger than that of fly ash. The grain sizes of bottom ash range from 150 microns to 0.5 inch. They were ground to pass through a sieve size of 80 mesh before use. The sample used for this study was also furnished by Public Service Electric and Gas Company.

Activated Alumina: Activated alumina is a highly porous, granular form of aluminum oxide (Al_2O_3) having excellent adsorptive capacity for moisture and odor. The grain sizes of this material range from 0.147 mm to 0.295 mm. The sample studied was furnished by Alcoa, Bauxity, Arkansas.

Activated Carbon: Activated carbon like activated alumina is a highly porous, granular form of carbon characterized by a highly adsorptive capacity for gases, vapors, and colloidal solids. It is produced by the destructive distillation of carbonaceous materials and activated by heating to 800 - 900 C with steam or carbon dioxide. This process produces a highly porous internal structure and a very large specific area ranging from 600 to 2000 square meters per gram. The sample used for this study was obtained from Witco Chemical, Activated Carbon Division, New York, New York.

Cullite: Cullite is a commercial name of synthetic zeolite. The principal chemical constituents of cullite are oxides of sodium, aluminum, and silicon. Physically, it has a white granular form with individual particle size ranging from 16 to 40 mesh. The primary use of this material is in water softening. This material was selected in this study both because of its potential removal capacity and as a reference material. The sample used in this study is called "High Capacity Cullite," and was supplied by Culligan, Northbrook, Illinois.

SLUDGES

Calcium Fluoride: This sludge results from the lime treatment of fluoride waste water generated from etching processes used by the electronic and aircraft industries. Three samples designated as No. 1, No. 2, and No. 3, were collected over a period of one year to determine fluctuations of leachate compositions caused by changes in the production and schedules.

Metal Finishing Sludges: This sludge results from the alkaline treatment of metal-oxide waste water from a metal finishing plant.

As in the case of calcium fluoride sludge, three samples designated as No. 1, No. 2, and No. 3, were also collected over a period of one year.

Petroleum Sludge: Petroleum sludges were obtained from a storage tank bottom (No. 1) and an API Separator (No. 2) from an oil refinery.

III. EXPERIMENTAL APPARATUS AND PROCEDURES

PREPARATION OF SORBENT MATERIALS

All sorbent materials were used as received. Sorbent materials (illite, bottom ash, and vermiculite) which were not obtained as a powder, were ground using a laboratory hammer mill (Weber Bros. and White Metal Works Inc., Type 22) and passed through an eighty mesh A.S.T.M. standard sieve. All sorbents were dried to constant weight at 103°C (in accordance with "Standard Method" procedures (39)) and stored in a desiccator until used.

The leaching potential of all sorbent materials, except vermiculite was determined by shaking sorbent and deionized water in a ratio of 2.5 ml deionized water per gram of dried sorbent in a Burrell Shaker for 24 hours at ambient temperature. After this period of time, no further leaching from the sorbent occurred. For vermiculite, a ratio of 10 ml water per gram of dried sorbent was used. This was done because at the lower ratio, vermiculite absorbed all of the water, leaving no supernatant liquid for testing. The resultant mixture was then filtered using a glass fiber filter (Reeve Angel Type 934A; 1.6 microns pore size) in order to remove all undissolved and non-filtrable solids. The filtrates (leachates) were then analyzed according to procedures described later.

PREPARATION OF SLUDGE LEACHATE

The sludge leachate was prepared by mixing the original wet sludge with deionized water using a ratio of 2.5 ml of water per gram of dried sludge. (A series of moisture-content tests of wet sludge was carried out before the leachate was prepared in order to transfer the ratio of dried weight base directly into wet weight based). The sludge-water mixture was then agitated mechanically for 24 hours. Previous laboratory work by us and others (17) indicated that this period of time is sufficient to insure the maximum concentration of leachate materials in the water portion. After agitation, all suspensions were filtered through a glass fiber filter (Reeve Angle Type 934A). The resultant filtrates were analyzed and stored in screw-capped plastic containers at ambient temperature until used.

BATCH STUDIES

Each sorbent (except vermiculite) was placed in a polypropylene Erlenmeyer bottle and mixed with prepared leachate in a mix-ratio of 2.5 ml of leachate per gram of dried-weight sorbent (see Figure 4). Vermiculite, due to its deliquescent nature, was mixed with leachate in a ratio of 10 ml of leachate per gram of sorbent. These bottles were sealed and agitated in the shaker for 24 hours at ambient temperature. At the end of this time, the mixture was filtered through a glass fiber filter and the filtrate was then analyzed.

LYSIMETER STUDIES

In order to simulate the dynamic field conditions, lysimeter studies to evaluate sorbent removal capacities under flowing conditions were conducted (see Figure 5). A 500 g portion of sorbent

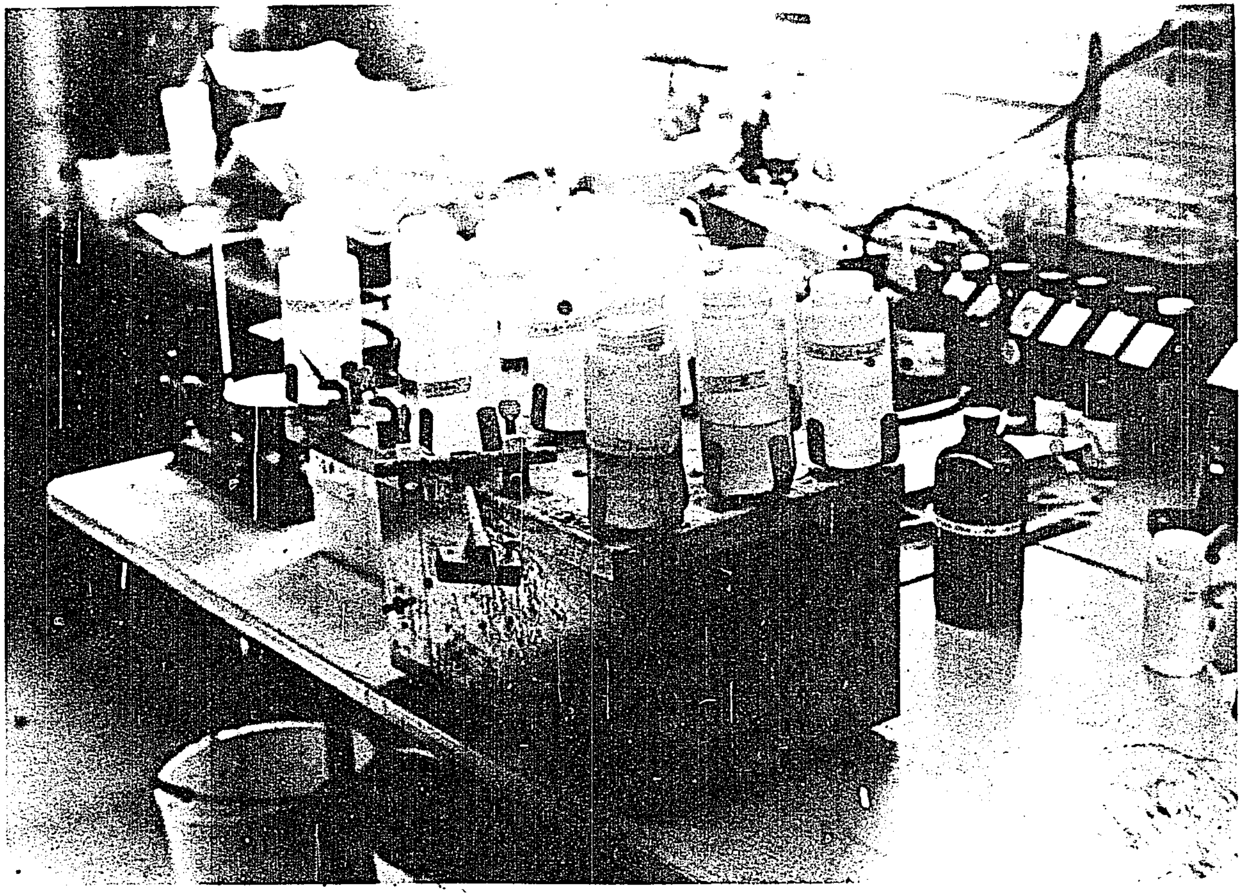

Figure 4. Batch Study

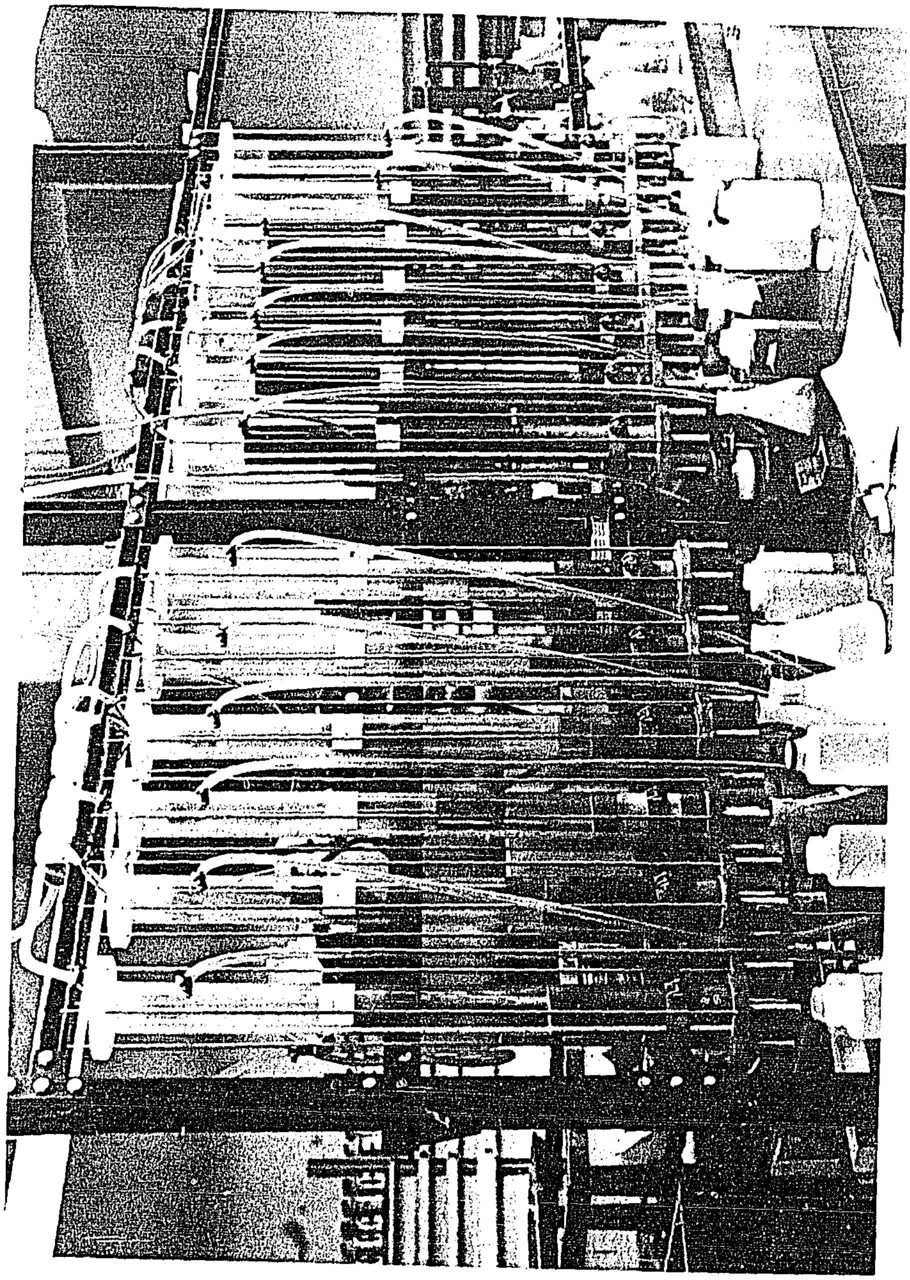

Figure 5. Laboratory Lysimeters

was used in the lysimeter for all sorbents except for activated carbon. A 250 g sample of activated carbon provided the same height in the lysimeter as the other sorbents.

Due to the low permeability of clay sorbents, a series of leachate permeability tests were conducted using varying amounts of Ottawa sand. Analyses of results indicated that a mixture of 80 percent Ottawa sand and 20 percent of clay sorbent would permit adequate flows of leachate through these clay sorbents.

Laboratory lysimeters were constructed of plexiglass tubing (6.2 cm i.d.; 0.6 cm wall thickness; 90 cm length), supported in a vertical position. The arrangement of these 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 in order to prevent clogging of the outlet and also to support the sorbent material. The column was packed with the preweighed sorbent, placing 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, which had been trapped into the top side of the column, in order to permit a constant head condition. Leachate was fed to the top of the column through a valved manifold which distributed the leachate to ten lysimeters, simultaneously, from a central reservoir. The central reservoir, a 100 liter polyethelene carbon, delivered the leachate to the manifold system by means of a gravity siphon 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 (3/8" i.d.). 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 collected at intervals and analyzed to determine the concentration of all measurable constituents remaining in the effluent after a known volume of leachate had passed through the column. This was continued until breakthrough had occurred for all measurable contaminants or excessively low permeabilities were encountered. Breakthrough is defined as that condition when the concentrations of the species of concern in the effluent sample approached or exceeded that in the influent.

PILOT STUDIES

The use of the clay-fly ash combination was evaluated on a pilot scale for the treatment of industrial sludge leachate. Two large vertical constant head lysimeters along with an agitator, filtration column and storage tanks were set up outdoors (see Figures 6 and 7).

Calcium fluoride sludge was collected from the same source over a period of one year. In this manner, the effect of compositional differences in leachate due to the different production

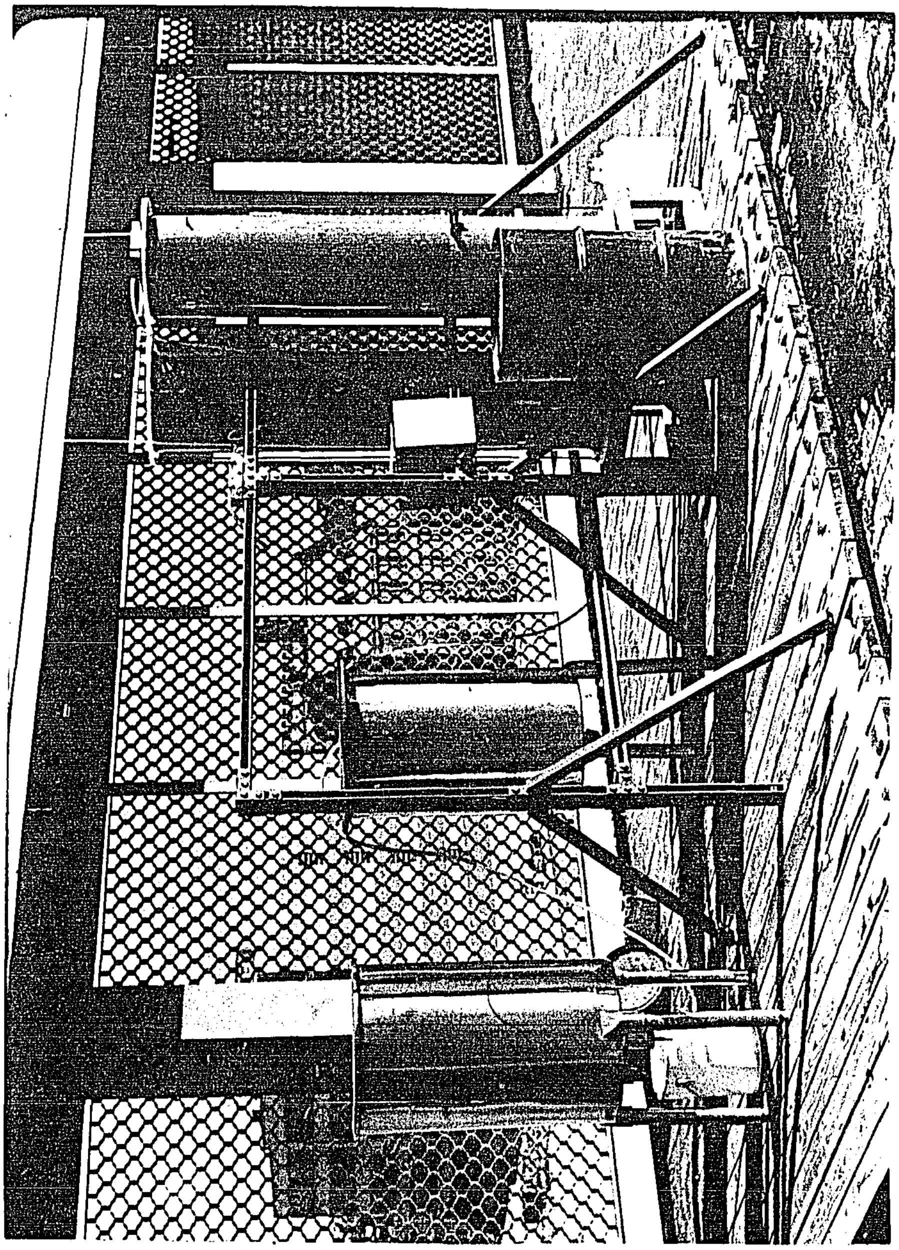

Figure 6. Pilot Lysimeters

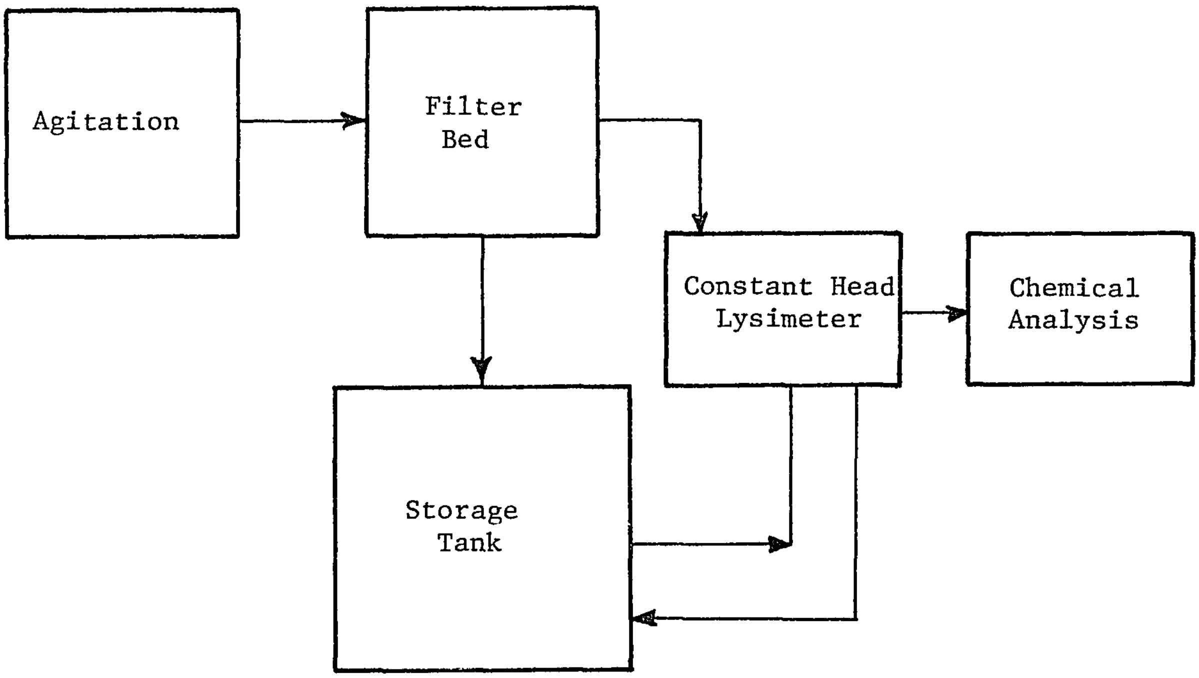

Figure 7. Schematic Diagram of Pilot Scale Study

schedules and processes could be evaluated.

The preparation of sludge leachate for the outdoor study was carried out as follows: A sample of sludge was dried at 103°C to a constant weight in order to determine its moisture content. The original sludge was then mixed with deionized water in a ratio of 2.5 ml water per gram of sludge (dry basis) and mechanically agitated for 24 hours. The resultant mixture was then pumped through a multimedia filtration bed to remove suspended particles which could clog the sorbent bed. The filter bed was housed in a stainless steel column and consisted of five layers of filter sand and gravel. The top layer was uniform medium gravel with D_{50} = 19.1 mm and a thickness of 7.6 cm; the second layer was a fine gravel with D_{85} = 6.3 mm and D_{15} = 5.1 mm and a thickness of 10.2 cm; the fourth layer was a medium sand with D_{85} = 1.47 mm and D_{15} = 1.2 mm and a thickness of 10.2 cm; the bottom layer was a #20 - #30 Ottawa sand with D_{50} = 0.715 mm and a thickness of 22.9 cm. This arrangement provided an effluent essentially free of suspended particles.

The outdoor lysimeters were constructed of P.V.C. tubing (22" O.D. with a wall thickness of 3/16 in. and 5 ft. 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 as previously described (vide supra). The use of identical lysimeters provided a measure of the reproducibility of the sorbent system. Both lysimeters were packed with the pre-weighed sorbents sufficient to treat 140 gallons of leachate.

5 to 10 cm of Ottawa sand was placed below and above the sorbents to prevent disturbing the geometry of the sorbents during addition of leachate. Leachate was fed to the top of the column through a valved manifold which distributed leachate 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 (3/8 in. i.d.). The volume effluent 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 was continued for three different calcium fluoride sludge leachates collected from the same source at different times.

A stainless steel 50 gallon tank equipped with a drainage outlet was used as a storage tank. This storage tank was located between the filter bed and field lysimeters to serve as both a reservoir and overflow receiver.

ANALYTICAL PROCEDURES

The constituents in the sludge leachate were initially identified using emission spectroscopy. Atomic absorption was used to determine the concentration of cations, specific ion probes were used for the anions, and the concentration of organics by TOC and COD analyzers. pH and conductivity measurement were carried out to further characterize the samples. The details for the above measurement are described as follows:

Emission Spectroscopy Identification of Element:

The constituent in leachates was identified by a Jarrel Ash Spectrograph (Model 19-300/311 ARC/Spark Stand).

pH Measurement:

The pH of the samples was measured by means of an Orion Model 701 Digital pH/MV Meter using an Orion combination pH electrode, Model 91-02.

Conductivity:

Conductivity of the samples was measured by a Beckman conductivity bridge (Model RC16B2) together with a specified conductance cell having a cell constant of 1.

Determination of Metals:

The concentration of the various metals identified were determined using a Varian Techtron Atomic Absorption Spectrometer (Model 1200) according to E.P.A. procedures (16).

Chloride Ion Analysis:

Analysis of chloride ion was conducted using a chloride ion electrode (Orion Model No. 94-17) in combination with a single junction reference electrode (Orion Model No. 90-01) connected to an Orion Model 701 Digital/MV Meter. This electrode responds directly to chloride ion. The chloride ion concentration of a sample solution was determined directly by comparing the electrode potentials obtained using standards of known chloride ion content. Straight-line calibration curves were obtained over the range of 1 to 1000 ppm using reagent grade sodium chloride.

Fluoride Ion Analysis:

Analysis of fluoride ion was carried out using a fluoride ion electrode (Orion Model 94-09) in combination with a single junction reference electrode (Orion Model 90-01) connected to an Orion Model 701 Digital pH/MV Meter. The fluoride content of a sample solution was determined directly by comparing the electrode potential reading in the sample solution to electrode potentials obtained in standards of known fluoride content. Straight-line calibration curves were obtained over the range of 0.1 ppm to 1000 ppm using reagent grade sodium fluoride. A total ionic strength adjustor buffer containing cyclohexlene dinitrilo tetracetic acid (Orion Cat. No. 94-09-09A) was used in the ratio of one part reagent to one part sample for all fluoride ion measurement. This reagent will "swamp out" variations in the levels of other ions present in the solution as well as destroy polyvalent cation complexes of fluoride by preferentially complexing these cations. As a result, total fluoride was measured.

Cyanide Analysis:

A cyanide ion electrode (Orion Model 9001000) attached to a Digital pH/MV Meter (Orion Model 701) was used to perform the analysis of cyanide. All solutions were adjusted with 10M NaOH to a concentration of 0.1 M of NaOH. The free cyanide ion content of a sample solution was then determined directly by comparing the electrode potentials of the sample to that of standard solutions of known free cyanide ion concentration. Semi-logarithmic calibration curves were constructed over the range of 0.01 to 10 mg/l of cyanide.

Chemical Oxygen Demand (COD):

A Technicon Autoanalyzer II was employed to determine COD. Technicon Industrial Method No. 137-71W was used as the experimental procedure. Sample solutions were digested by a potassium dichromate-sulfuric acid digestion mixture in a temperature of 150°C. At the end of the reaction, the extent of depletion of the hexavalent chromium (due to the oxidation reaction with the samples) was measured colorimetrically and corresponded to the amount of oxygen consumed by the organic contents in the sample.

Total Organic Carbon (TOC):

A Dohrmann Envirotech DC-52D Total Carbon Analyzer was used to measure the TOC in the liquid sample. An acidified sample solution was injected into a furnace, where the water is evaporated and organic carbon catalytically burned to carbon dioxide. The carbon dioxide is then reduced to methane and the methane is burned in a flame ionization detector.

PERMEABILITY STUDIES

The permeability of leachate through the sorbent lysimeters was monitored until breakthrough occurred. In certain cases, where the flow through the lysimeters was very low, the studies were discontinued even though leachate analysis indicated that the sorptive capacity of the column was not exhausted. This was done because the resultant long detention time would not lend itself to an economically feasible system. The permeability coefficient, K, was determined by means of the following equation (28):

$$K = (Q\ L)/aht$$

where

a = cross-sectional area of lysimeter (in cm^2)

Q = total volume of flow through the lysimeter sorbent for elapsed time (in cm^3)

h = hydraulic head, (in cm) i.e., height from the bottom drain to the top of the leachate level

L = length of sorbent sample in the lysimeter (in cm)

t = total elapsed time (in seconds) for a corresponding volume of leachate collected

GRAIN SIZE DISTRIBUTION OF SORBENTS

The test procedure for determining grain size depends on the range of grain sizes of sorbent. Usually, the hydrometer test was required for those sorbents of very fine grain sizes (smaller than No. 200 mesh) while the sieve analysis was required for those sorbents of larger grain sizes (greater than No. 200 mesh). For a composition of mixed sizes, a combined test procedure was required. The test procedures of grain size distribution of sorbents are given as follows (11, 28):

Sieve Analysis:

A sieve analysis consists of passing a sample through a set of sieves and weighing the amount of material retained on each sieve. The sieves used in this analysis were 25.4 mm (1"), 19.1 mm (3/4"), 9.52 mm (3/8"), 4.76 mm (#4), 2.00 mm (#10), 0.84 mm (#20), 0.42 mm (#40), 0.25 mm (#60), 0.105 mm (#140), and 0.074 mm (#200). These sieves are all specified according to A.S.T.M. (11).

Hydrometer Analysis:

Hydrometers were used to determine the percentage of dispersed particles remaining in suspension at a given time. It was assumed that Stoke's law applies to a mass of dispersed solid particles of various diameters and shapes. The grain size equivalent to a spherical particle was computed for each hydrometer reading using Stoke's law.

The grain-size distribution curve was then obtained by plotting both the sieve and hydrometer analyses on a semi-logarithmic graph paper. The particle diameters of soil were plotted on the logarithmic abscissa and the percent finer by weight on the arithmetic ordinate.

IV. RESULTS AND DISCUSSION

Leachates from the calcium fluoride sludge, metal finishing sludge, and petroleum sludge were prepared and analyzed in accordance with "Standard Methods" (39). The chemical characteristics of these leachates are presented in Table 2. Three calcium fluoride sludges and three metal finishing sludges were collected over a one year period in order to determine the magnitude of changes in the concentration of the constituents due to changes in production seasons and manufacturing processes. Petroleum sludges were collected from two separate sources (i.e. storage tank bottom material and from an API gravity separator) to determine the effect of two different sources of petroleum sludge on the composition and concentration of the constituents in the respective leachates.

A number of pollutants were found in the leachates from the different sludges (see Table 2). The heavy metals present were copper, nickel, and zinc. The concentrations of calcium and magnesium were also determined because these metals contribute to the hardness in water. The anions present in the leachates were fluoride, cyanide and chloride. The presence of these anions in water in sufficient concentration could lead to its rejection as a drinking water source.

4-1 RESULTS OF GRAIN SIZE DISTRIBUTION AND PERMEABILITY OF SORBENTS

The results of both sieve and hydrometer analysis were plotted in the form of a grain-size distribution curve on a semi-logarithmic chart (see Figure 8) for the identification and classification of

TABLE 2

CONCENTRATIONS OF SPECIFIC CATIONS, ANIONS AND ORGANICS ENCOUNTERED IN THE CALCIUM FLUORIDE SLUDGE (NEUTRAL), METAL FINISHING SLUDGE (BASIC) AND PETROLEUM SLUDGE (ACIDIC).

Measured Pollutant	Calcium Fluoride Sludge Leachate (Neutral)	Metal Finishing Sludge Leachate (Basic)	Petroleum Sludge Leachate (Acidic)
pH	6.5-7.5	7.5-8.5	5.5-6.5
Ca	180-318	31-38	34-50
Cu	0.10-0.16	0.45-0.53	0.09-0.17
Mg	4.8-21	24-26	27-50
Ni	<0.05	0.12-0.19	0.10-0.23
Zn	<0.01	<0.01	0.13-0.17
F	6.7-11.6	1.2-1.5	0.95-1.2
Total CN	<0.02	<0.02	0.20-1.2
COD	44-49	45-50	251-340

a) All concentrations are represented as mg/l except pH.

b) Fe, Cd, Cr, and Pb were analyzed for, but found to be below measurable level.

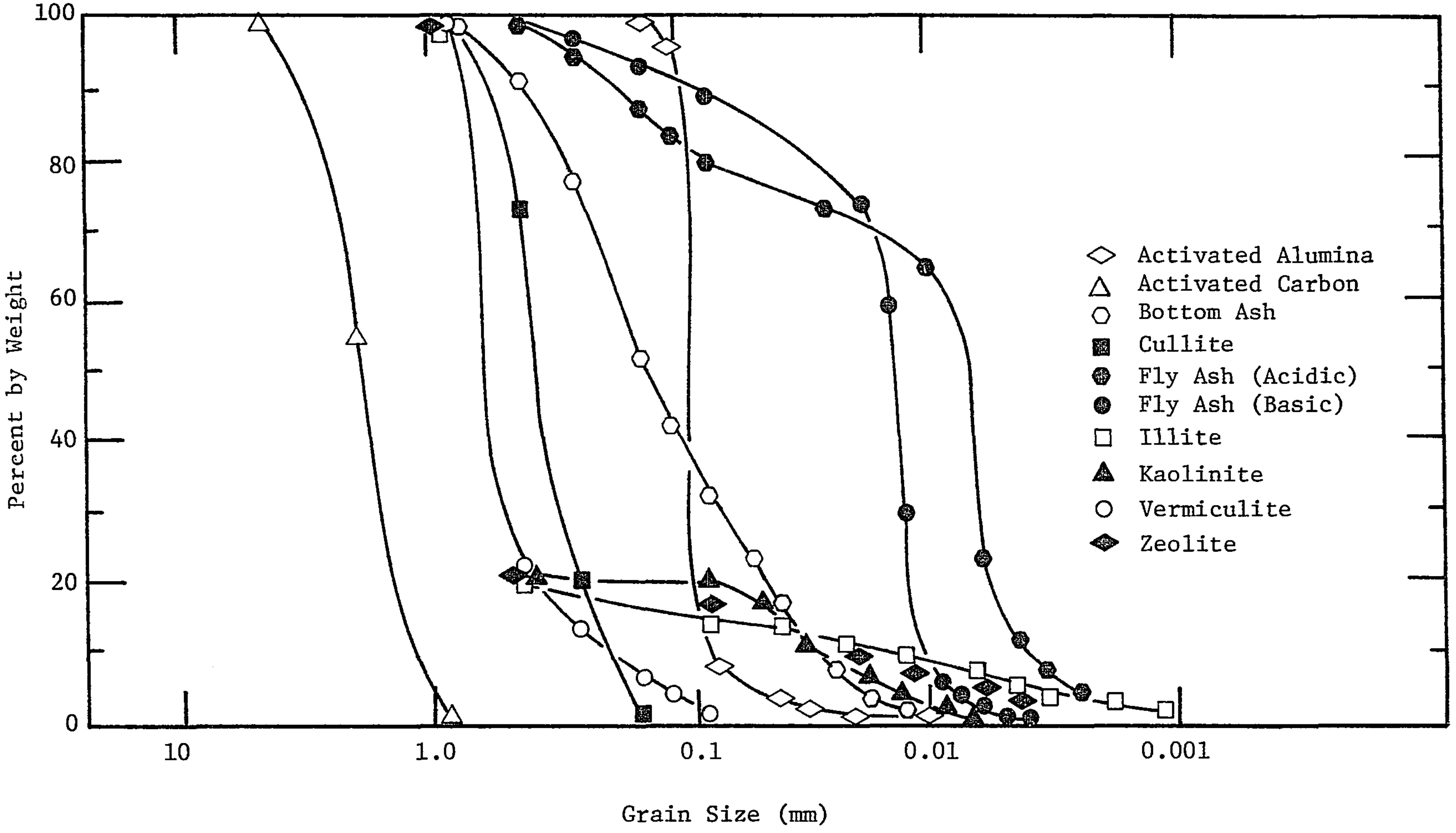

Figure 8. Grain Size Distribution of Sorbents.

sorbents (see Appendix II).

Because of the influence of the smaller grain-sizes on soil properties, "The effective diameter or D_{10}" is defined as the grain whose size is greater than that of 10 percent of the particles by weight. In order to demonstrate the characteristics of gradation, the two most commonly used indices are the uniformity coefficient and the coefficient of curvature. The uniformity coefficient is defined as the ratio of the size of the 60 percent particle diameter, by weight, to the effective diameter, i.e.,

$$Cu = (D_{60})/(D_{10})$$

The coefficient of curvature,

$$C_z = (D_{30})^2/(D_{60})(D_{10}),$$

is a value that can be used to identify samples of poorly graded materials. The reader is referred to standard texts of soil mechanics for a more detailed explanation (28, 35).

4-2 RESULTS OF STATIC STUDIES (BATCH TEST)

The static studies were carried out to define the most promising sorbents for the removal of the above mentioned pollutants in the leachates. The static capacity of eleven natural and refined sorbents for the removal of constituents in batch tests were evaluated. These sorbent capacities, in terms of microgram of element removed per gram of sorbent used, was obtained by analysis of the influent and effluent solutions. This data was calculated from the following equations.

Sorbent Capacity, (μg of pollutant removed per gram of sorbent used) = $(C_2 - C_1) \times V/W$

where

C_1 = the effluent concentration, in mg/l
C_2 = the influent concentration, in mg/l
V = the volume of leachate mixed with sorbent, in ml
W = the amount of sorbent mixed with leachate, in gram

The results of batch studies are listed in Tables 3 through 10. These tables contain (a) influent concentration of leachate, (b) leaching background of sorbent, (c) effluent concentration, and (d) removal capacity. These results indicate that there is no single sorbent material which is effective in removing all constituents in leachate. For example, illite was very effective in treating organics (COD) and anions (fluoride, chloride and cyanide) but heavy metals were not retained. On the other hand, zeolite was found to be very effective in treating most of heavy metals while organics were not retained (see Tables 3 to 10). The details of these results in three industrial sludge leachates were expanded and discussed in the following.

4-2-1 Calcium Fluoride Sludge Leachate Treatment

Three calcium fluoride sludge leachates were collected over a period of one year in this study. Analysis of the constituents in the leachate prepared from these sludges revealed that most variations in constituent concentration are within a factor of two, with the exception of cyanide (see Table 2). It also indicated that the calcium, magnesium, copper, nickel, fluoride, cyanide and organic concentrations were significant. Other heavy metals such as cadmium, iron, lead, chromium, and zinc which are generally present in industrial waste stream were found to be below safe discharge levels in influent leachates and thus were not analyzed in the treated effluent. An examination of these batch-study data suggests the following observations.

Most sorbent materials leach out a certain amount of the same constituents found in the leachate (see the sorbent background in Tables 3 to 5). This leaching background, in some cases, is more significant than that of influent leachate. For example, both acidic and basic fly ashes leached out higher concentrations of calcium (357 and 300 mg/l respectively) than was present in an influent leachate (i.e. sludge #3; Ca conc. = 318 mg/l). These two materials did however, show good removal of organics, fluoride and copper metals.

A comparison of the sorptive capacity (in terms of the micrograms of constituents removed per gram of sorbent used) between the various sorbents from these Tables indicates which sorbents are the most promising for removing a specific constituent. Among the natural sorbents, illite was found to be the most effective for fluoride, chloride, cyanide and organic removal. Among the refined sorbents, activated alumina was the best for removing fluoride, calcium and copper ions. Regarding the natural sorbents, kaolinite

TABLE 3 : STATIC STUDY RESULTS OF CALCIUM FLUORIDE SLUDGE LEACHATE #1

Measured Parameters	Initial Concentration of Leachate	Description*	Bottom Ash	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina(I)	Activated Alumina(II)	Cullite	Minimum Detectable Value
pH	6.3	(1)	7.2	8.5	7.8	8.1	3.0	5.1	9.8	9.7	9.0	-
		(2)	6.0	10.0	7.4	7.3	3.0	4.2	8.6	9.7	7.9	
Conductivity	2680	(1)	2780	2500	8150	182	4460	295	1790	4050	4010	-
		(2)	5200	2990	7000	2800	4400	1980	3590	5200	1660	
Ca (mg/l)	400	(1)	20.0	300	6.0	15	250	42.0	<0.10	<0.10	<0.10	0.10
		(2)	385	485	135	400	335	355	0.75	<0.10	<0.10	
		(3)	37.5	L**	663	0	163	113	998	1000	1000	
Cd (mg/l)	0.08	(1)	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	0.01
		(2)	<0.01	<0.01	0.03	<0.01	0.06	<0.01	<0.01	<0.01	0.02	
		(3)	0.18	0.18	0.13	0.70	0.05	0.18	0.18	0.18	0.15	
Cr (mg/l)	0.25	(1)	<0.20	0.50	0.30	<0.20	0.70	0.30	1.1	0.70	0.35	0.20
		(2)	0.25	0.80	0.30	<0.20	0.80	0.25	1.1	0.80	0.30	
		(3)	0	0	L	0.50	L	L	L	L	L	
Cu (mg/l)	0.22	(1)	0.25	0.06	0.07	<0.03	3.6	0.16	0.04	0.06	0.42	0.03
		(2)	0.10	<0.03	0.05	0.07	3.7	0.29	<0.03	<0.03	0.31	
		(3)	0.30	0.48	0.43	0.15	L	L	0.48	0.48	L	
Fe (mg/l)	0.10	(1)	<0.05	<0.05	<0.05	<0.05	2.2	<0.05	<0.05	<0.05	0.20	0.05
		(2)	0.10	<0.05	0.15	0.10	2.3	0.10	<0.05	0.10	0.30	
		(3)	0	0.13	0	0	0	0	0.13	0	L	
Mg (mg/l)	11.0	(1)	93.2	3.2	169	4.7	70.0	4.9	0.06	<0.05	0.24	0.05
		(2)	52.0	1.0	60.0	20.2	48.0	14.0	0.60	1.1	3.0	
		(3)	L	25.0	L	L	L	L	26.0	24.3	20.0	
Ni (mg/l)	0.22	(1)	<0.05	<0.05	<0.05	<0.05	0.65	<0.05	<0.05	<0.05	<0.05	0.05
		(2)	0.15	0.10	0.15	0.13	0.75	0.25	<0.05	0.08	0.21	
		(3)	0.18	0.30	0.18	0.09	L	0	0.43	0.35	0.03	
Pb (mg/l)	<0.20	(1)	<0.20	0.28	0.28	<0.20	0.33	<0.20	<0.20	<0.20	<0.20	0.20
		(2)	<0.20	0.28	0.26	<0.20	0.29	<0.20	<0.20	<0.20	<0.20	
		(3)	-	L	L	-	L	-	-	-	-	
Zn (mg/l)	0.02	(1)	<0.01	<0.01	0.03	<0.01	1.5	0.27	<0.01	<0.01	0.03	0.01
		(2)	0.10	0.02	0.04	0.03	1.7	0.06	<0.01	<0.01	0.02	
		(3)	0	0	L	0	0	L	0.03	0.03	L	
F (mg/l)	6.1	(1)	0.31	1.7	0.51	1.2	0.33	2.3	2.1	2.3	0.30	0.02
		(2)	2.5	2.2	1.7	5.9	0.64	3.1	1.6	1.9	2.0	
		(3)	9.0	9.8	11.0	0.20	13.7	7.5	11.3	10.5	10.3	
Cl^- (mg/l)	58.5	(1)	500	9.5	12.6	2.9	2.7	6.8	46.0	37.6	7.4	2.0
		(2)	470	60.0	180	56.0	40.0	50.0	89.0	91.0	61.0	
		(3)	L	L	0	2.5	46.3	21.3	L	L	0	
CN^- (mg/l)	0.60	(1)	0.07	0.04	0.04	0.03	0.03	1.2	0.22	0.20	0.03	0.03
		(2)	0.48	0.56	0.54	0.50	0.15	1.6	0.48	0.54	0.60	
		(3)	0.30	0.10	0.15	0.10	1.1	L	0.30	0.15	0	
COD(mg/l)	76.0	(1)	40.3	4.8	26.8	13.0	15.8	7.0	24.0	32.2	21.4	2.0
		(2)	79.8	36.8	76.0	53.2	48.0	140	84.8	106	87.0	
		(3)	L	93.5	L	22.8	70.0	0	L	0	L	
TOC(mg/l)	16.5	(1)	15.0	4.1	0.0	2.7	5.0	15.5	37.6	84.0	40.1	-
		(2)	16.3	8.0	16.4	10.9	8.5	26.0	16.3	60.4	17.5	
		(3)	0	21.3	0	5.6	21.3	0	L	0	L	

*(1) Background of Sorbent Material (mg/l) (2) Effluent Level After Treatment (mg/l) (3) Sorbent Capacity μg Removed per g of Sorbent Used.

**L Represents no Sorbent Capacity and a Reduction in Leaching of Contaminant When Sorbent Is Mixed with Leachate.

TABLE 4: STATIC STUDY RESULTS OF CALCIUM FLUORIDE SLUDGE LEACHATE #2

Measured Parameters	Initial Concentration of Leachate	Description*	Bottom Ash	Fly Ash (Basic)	Zeolite	Vermiculite	Illire	Kaolinite	Activated Alumina(I)	Activated Alumina(II)	Cullite	Minimum Detectable Value
pH	7.5	(1)	7.2	8.5	7.8	8.1	3.0	5.1	9.8	9.7	9.0	-
		(2)	7.2	8.9	7.6	7.3	3.2	4.3	8.7	9.4	8.0	
Conductivity	3080	(1)	2780	2500	8150	182	4460	295	1790	4050	4010	-
		(2)	5950	3410	11550	3200	4150	2680	4150	6100	5000	
Ca (mg/1)	365	(1)	20.0	300	6.0	1.5	2.50	42.0	<0.10	<0.10	<0.10	0.10
		(2)	2.61	365	88.0	318	300	231	<0.10	<0.10	0.30	
		(3)	260	L	693	47	163	335	913	913	912	
Cd (mg/1)	<0.01	(1)	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	0.01
		(2)	<0.01	<0.01	<0.01	<0.01	0.07	<0.01	<0.01	<0.01	<0.01	
		(3)	-	-	-	-	0	-	-	-	-	
Cr (mg/1)	0.30	(1)	<0.20	0.50	0.30	<0.20	0.70	0.25	1.1	0.70	0.35	0.20
		(2)	0.30	0.70	0.40	<0.20	0.70	0.30	1.1	0.70	0.40	
		(3)	0	L	L	1.0	L	L	L	L	L	
Cu (mg/1)	0.49	(1)	0.25	0.06	0.07	<0.03	3.6	0.16	0.04	0.06	0.42	0.03
		(2)	0.20	0.16	0.20	0.29	3.8	0.60	0.21	0.21	0.42	
		(3)	0.73	0.83	0.73	0.20	L	0	0.70	0.70	0.18	
Fe (mg/1)	<0.05	(1)	<0.05	<0.05	<0.05	<0.05	2.2	<0.05	<0.05	<0.05	0.20	0.05
		(2)	<0.05	<0.05	<0.05	<0.05	2.2	<0.05	<0.05	<0.05	0.20	
		(3)	-	-	-	-	0	-	-	-	0	
Mg (mg/1)	5.0	(1)	93.2	3.2	169	4.7	70.0	4.9	0.06	<0.05	0.24	0.05
		(2)	96.6	3.3	174	9.7	55.0	9.9	0.23	0.06	0.40	
		(3)	L	4.3	0	0	L	0	11.9	12.4	11.5	
Ni (mg/1)	0.10	(1)	<0.05	<0.05	<0.05	<0.05	0.65	<0.05	<0.05	<0.05	<0.05	0.05
		(2)	<0.05	<0.05	<0.05	<0.05	0.69	<0.05	<0.05	<0.05	<0.05	
		(3)	0.13	0.13	0.13	0.05	L	0.13	0.13	0.13	0.13	
Pb (mg/1)	0.38	(1)	<0.20	0.28	0.28	<0.20	0.33	<0.20	<0.20	<0.20	<0.20	0.20
		(2)	0.33	0.28	0.38	<0.20	0.38	0.33	<0.20	<0.20	<0.20	
		(3)	0.13	0.25	L	1.8	L	0.13	0.45	0.45	0.45	
Zn (mg/1)	0.02	(1)	<0.01	<0.01	0.03	<0.01	1.5	0.27	<0.01	<0.01	0.01	0.01
		(2)	0.04	<0.01	0.05	0.02	1.6	0.32	<0.01	<0.01	0.04	
		(3)	0	0.03	0	0	0	0	0.03	0.03	0	
F^- (mg/1)	5.9	(1)	0.31	1.7	0.51	1.2	0.33	2.3	2.1	1.2	0.30	0.02
		(2)	2.5	2.3	2.1	5.4	0.91	3.5	1.3	1.6	1.9	
		(3)	8.5	9.0	9.5	0.50	12.5	6.0	11.5	10.8	10.0	
Cl^-(mg/1)	78.0	(1)	500	9.5	126	2.9	2.7	6.8	46.0	28.0	7.4	2.0
		(2)	482	88.0	195	80.0	70.0	74.0	95.0	96.0	84.0	
		(3)	L	0	0	0	20.0	10.0	L	L	0	
CN^-(mg/1)	0.42	(1)	0.07	0.04	0.04	<0.03	<0.03	1.2	0.22	0.35	<0.03	0.03
		(2)	0.47	0.50	0.44	0.43	0.16	1.1	0.52	0.60	0.42	
		(3)	0	0	0	0	0.65	L	0	L	0	
COD(mg/1)	88.5	(1)	40.3	4.8	26.8	13.0	15.8	7.0	24.0	32.2	21.4	2.0
		(2)	89.3	52.1	93.8	67.0	40.0	140	98.0	120	96.0	
		(3)	L	91.0	L	21.5	121	0	L	0	L	
TOC(mg/1)	8.5	(1)	15.0	4.1	10.0	2.7	5.0	15.5	37.6	84.0	40.1	-
		(2)	8.5	4.1	8.3	8.0	5.0	18.5	8.3	57.5	10.8	
		(3)	0	11.0	0	0.5	8.8	L	L	0	L	

*(1) Background of Sorbent Material (mg/1)
(2) Effluent Level After Treatment (mg/1)
(3) Sorbent Capacity μg Removed per g of Sorbent Used
** L Represents no Sorbent Capacity and a Reduction in Leaching of Contaminant When Sorbent Is Mixed with Leachate

TABLE 5: STATIC STUDY RESULTS OF CALCIUM FLUORIDE SLUDGE LEACHATE #3

Measured Parameters	Initial Concentration of Leachate	Description*	Bottom Ash	Fly Ash (Acidic)	Fly Ash (Basic)	Vermiculite	Illite	Kaolinite	Activated Alumina(1)	Activated Carbon	Minimum Detectable Value
pH	7.2	(1)	7.2	5.1	8.5	8.1	3.0	5.1	9.8	9.4	-
		(2)	6.9	5.4	9.8	8.2	3.2	4.5	9.8	8.7	
Conductivity	1680	(1)	2780	3150	2090	115	4460	295	2790	575	-
		(2)	4160	3800	2430	1120	2360	1600	3490	1000	
Ca (mg/l)	318	(1)	20.0	357	300	15	250	42.0	<0.10	0.50	0.10
		(2)	275	344	337	266	325	250	<0.10	208	
		(3)	108	L	L	65.0	0	85.0	795	275	
Cd (mg/l)	<0.01	(1)	<0.01	<0.01	<0.01	<0.01	<0.06	<0.01	<0.01	<0.01	0.01
		(2)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
		(3)	-	-	-	-	-	-	-	-	
Cr (mg/l)	<0.20	(1)	<0.20	0.50	0.50	<0.20	0.70	0.30	1.1	<0.20	0.20
		(2)	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	1.1	<0.20	
		(3)	-	-	-	-	-	-	L	-	
Cu (mg/l)	0.10	(1)	0.25	0.29	<0.06	<0.03	3.6	0.16	0.04	<0.03	0.03
		(2)	0.10	0.34	0.06	0.09	3.6	0.27	0.04	0.09	
		(3)	L	L	0.10	0	L	0	0.15	0.25	
Fe (mg/l)	<0.05	(1)	<0.05	<0.05	<0.05	<0.05	2.20	<0.05	<0.05	<0.05	0.05
		(2)	<0.05	<0.05	<0.05	<0.05	0.60	<0.05	<0.05	<0.05	
		(3)	-	-	-	-	L	-	-	-	
Mg (mg/l)	21.3	(1)	93.2	64.4	3.2	4.7	70.0	4.9	0.06	0.10	0.05
		(2)	90.0	98.0	4.0	69.0	34.0	23.5	0.10	12.8	
		(3)	L	0	43.3	0	L	0	53.0	21.3	
Ni (mg/l)	0.15	(1)	<0.05	1.40	<0.05	<0.05	0.65	<0.05	<0.05	<0.05	0.05
		(2)	0.15	1.55	<0.05	0.50	0.49	0.13	<0.05	<0.05	
		(3)	0	0	0.25	0	L	0.25	0.25	0.25	
Pb (mg/l)	<0.20	(1)	<0.20	0.30	0.28	<0.20	0.33	<0.20	<0.20	<0.20	0.20
		(2)	<0.20	0.30	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	
		(3)	-	0	-	-	-	-	-	-	
Zn (mg/l)	0.18	(1)	<0.01	1.6	<0.01	<0.01	1.5	0.27	<0.01	<0.01	0.01
		(2)	0.14	1.8	0.28	<0.01	1.5	0.28	<0.01	<0.01	
		(3)	0.10	0	0	2.1	L	L	0.43	0.43	
F^- (mg/l)	6.7	(1)	0.31	1.7	1.7	1.2	0.33	2.3	2.3	0.64	0.02
		(2)	3.0	7.5	1.5	7.2	0.31	0.32	1.2	5.2	
		(3)	9.3	L	13.0	L	79.9	79.9	13.8	3.8	
Cl^- (mg/l)	65.0	(1)	500	10.0	9.5	2.9	2.7	6.8	46.0	5.0	2.0
		(2)	550	70.0	45.5	60.0	40.0	50.0	89.0	75.0	
		(3)	0	0	48.8	5.0	313	188	L	0	
CN^- (mg/l)	0.05	(1)	0.07	0.04	<0.03	<0.03	<0.03	1.2	0.22	<0.03	0.03
		(2)	0.06	0.04	<0.03	<0.03	<0.03	1.2	0.25	<0.03	
		(3)	L	0.03	0.05	0.02	0.25	0	0	0.05	
COD(mg/l)	44.0	(1)	40.0	<2.0	4.8	13.0	15.8	7.0	24.0	<2.0	2.0
		(2)	80.0	<2.0	14.8	39.9	22.9	40.5	49.5	2.5	
		(3)	0	105	73.0	4.1	264	43.8	L	104	
TOC(mg/l)	16.0	(1)	15.0	0.50	4.1	2.7	5.0	15.5	37.6	5.1	-
		(2)	16.0	0.70	8.0	20.5	10.3	21.3	20.0	1.3	
		(3)	0	38.3	20.0	0	71.3	L	L	36.8	

*(1) Background of Sorbent Material (mg/l)
(2) Effluent Level After Treatment (mg/l)
(3) Sorbent Capacity µg Removed per g of Sorbent Used
** L Represents no Sorbent Capacity and a Reduction in Leaching of Contaminant When Sorbent is Mixed with Leachate

could be used to remove calcium, and basic fly ash was effective at copper removal. Basic fly ash and activated alumina were the most effective in magnesium and nickel removal. Vermiculite was the most effective in removing cadmium.

In some cases, marked variations can be observed in the sorbent capacity for the removal from the three leachates of specific contaminants. For example, the sorbent capacities exhibited by the basic fly ash for the magnesium ion in three leachates are 25.0, 4.3, and 43.3 μg/g, respectively. One of the possible reasons for this variation is that the sorbent capacity was determined using a constant ratio of leachate to sorbent. The concentration of some of the contaminants in the leachate using this ratio may not have been sufficient to saturate the sorbent. As a result, the magnitude of these capacities could increase with the concentration of the contaminant in the leachate being examined.

4-2-2 Metal Finishing Sludge Leachate Treatment

As in the case of calcium fluoride sludge leachate, three metal finishing sludges were collected over a period of one year. The leachates prepared from these sludges contain different chemical components in varying concentrations. Prior emission spectrographic analysis indicated the presence of significant concentrations of calcium, copper, magnesium, nickel, fluoride, chloride, as well as organics in the metal finishing sludge leachate (see Table 2). It also showed that metals like chromium, cadmium, iron, lead, cyanide,

TABLE 6: STATIC STUDY RESULTS OF METAL FINISHING SLUDGE LEACHATE #1

Measured Parameters	Initial Concentration of Leachate	Description*	Bottom Ash	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina(I)	Activated Alumina(II)	Cullite	Minimum Detectable Value
pH	8.9	(1)	7.2	8.5	7.8	8.1	3.0	5.1	9.8	9.7	9.0	-
		(2)	8.7	9.3	8.2	8.5	3.4	7.1	9.4	9.5	9.5	
Conductivity	1200	(1)	2780	2500	8150	182	4460	295	1790	4050	4010	-
		(2)	3750	2990	8750	1185	3720	1075	2290	4000	2100	
Ca (mg/l)	6.5	(1)	20.0	300	6.0	15	250	42.0	<0.10	<0.10	<0.10	0.10
		(2)	22.0	295	10.0	7.1	25.5	<0.10	0.17	0.23	<0.10	
		(3)	L**	L	L	L	0	16.0	15.8	15.7	16.0	
Cd (mg/l)	<0.01	(1)	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	0.01
		(2)	0.02	<0.01	0.02	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	
		(3)	0	-	0	-	L	-	-	-	-	
Cr (mg/l)	<0.20	(1)	<0.20	0.50	0.30	<0.20	0.70	0.30	1.1	0.70	0.35	0.20
		(2)	<0.20	0.50	<0.20	<0.20	<0.20	<0.20	1.1	0.60	0.30	
		(3)	-	0	-	-	-	-	L	L	L	
Cu (mg/l)	0.14	(1)	0.25	0.06	0.07	<0.03	3.6	0.16	0.04	0.06	0.42	0.03
		(2)	0.22	0.14	0.09	0.05	3.6	0.19	0.05	0.07	0.53	
		(3)	L	L	0.13	0.90	0	L	0.23	0.18	0	
Fe (mg/l)	<0.05	(1)	<0.05	<0.05	<0.05	<0.05	2.2	<0.05	<0.05	<0.05	0.20	0.05
		(2)	<0.05	<0.05	<0.05	<0.05	2.1	<0.05	<0.05	<0.05	0.20	
		(3)	-	-	-	-	0	-	-	-	0	
Mg (mg/l)	18.0	(1)	93.2	3.2	169	4.7	70.0	4.9	0.06	<0.05	0.24	0.05
		(2)	42.0	17.0	53.0	20.0	48.0	2.0	0.17	0.23	0.75	
		(3)	L	2.5	L	L	L	40.0	44.6	44.4	43.1	
Ni (mg/l)	0.15	(1)	<0.05	<0.05	<0.05	<0.05	0.65	<0.05	<0.05	<0.05	<0.05	0.05
		(2)	0.15	0.08	0.16	0.08	0.68	<0.05	0.08	0.08	0.20	
		(3)	0	0.18	0	0.70	L	0.25	0.18	0.18	0	
Pb (mg/l)	<0.20	(1)	<0.20	0.28	0.28	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	0.20
		(2)	<0.20	0.28	0.29	<0.20	<0.20	<0.20	<0.20	<0.20	<0.30	
		(3)	-	0	0	-	-	-	-	-	-	
Zn (mg/l)	<0.01	(1)	<0.01	<0.01	0.03	<0.01	1.50	0.30	<0.01	<0.01	0.08	0.01
		(2)	0.02	<0.01	0.05	0.02	1.50	0.12	<0.01	<0.01	0.06	
		(3)	0	-	0	0	0	L	-	-	L	
F^- (mg/l)	1.2	(1)	0.31	1.7	0.51	1.2	0.33	2.3	2.1	1.2	0.30	0.02
		(2)	1.4	1.4	1.8	1.8	0.34	0.34	2.0	1.3	0.43	
		(3)	L	L	0	0	8.2	2.2	L	L	1.9	
Cl^- (mg/l)	125	(1)	500	9.5	126	2.9	2.7	6.8	46.0	78.0	7.4	2.0
		(2)	510	135	245	105	76.0	95.0	170	150	130	
		(3)	L	0	0	200	123	75.0	0	0	0	
CN^- (mg/l)	<0.03	(1)	0.07	0.04	0.04	<0.03	<0.03	1.2	0.22	0.35	<0.03	0.03
		(2)	0.05	0.07	0.04	<0.03	<0.03	0.05	0.11	0.17	<0.03	
		(3)	0	0	0	0	0	L	L	L	0	
COD(mg/l)	97.0	(1)	40.3	4.8	26.8	13.0	15.8	7.0	24.0	32.2	21.4	2.0
		(2)	96.5	58.0	109	77.0	50.0	122	132	146	138	
		(3)	1.3	97.5	L	200	118	0	0	0	0	
TOC(mg/l)	39.9	(1)	15.0	4.1	0	2.7	5.0	15.5	37.6	84.0	40.1	-
		(2)	39.9	23.3	37.8	20.8	3.1	42.1	61.6	112	63.7	
		(3)	0	41.5	0	191	92.0	0	0	0	0	

* (1) Background of Sorbent Material (mg/l)
(2) Effluent Level after Treatment (mg/l)
(3) Sorbent Capacity μg Removed per g of Sorbent Used
**L Represents no sorbent capacity and a reduction in leaching of contaminant when sorbent is mixed with leachate

TABLE 7: STATIC STUDY RESULTS OF METAL FINISHING SLUDGE LEACHATE #2

Measured Parameters	Initial Concentration of Leachate	Description*	Bottom Ash	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina(I)	Activated Alumina(II)	Cullite	Minimum Detectable Value
pH	8.8	(1)	7.2	8.5	7.8	8.1	3.0	5.1	9.8	9.7	9.0	-
		(2)	8.5	9.0	8.3	8.6	3.1	7.6	10.3	9.3	8.9	
Conductivity	1670	(1)	2780	2500	8150	182	4460	295	1790	3030	4010	-
		(2)	3900	3000	7500	1360	4700	1370	2390	2200	5050	
Ca (mg/l)	13.5	(1)	20.0	300	6.0	15	250	42.0	<0.10	<0.10	<0.10	0.10
		(2)	25.0	305	15.0	8.0	25.5	3.5	<0.10	<0.10	<0.10	
		(3)	L**	L	L	55.0	0	25.0	33.5	33.5	33.5	
Cd (mg/l)	<0.01	(1)	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	0.01
		(2)	<0.01	<0.01	0.02	<0.01	0.06	<0.01	<0.01	<0.01	0.02	
		(3)	-	-	0	-	0	-	-	-	-	
Cr (mg/l)	0.25	(1)	<0.20	0.50	0.30	<0.20	0.70	0.30	1.1	0.70	0.35	0.20
		(2)	<0.20	0.70	<0.20	<0.20	0.70	<0.20	1.1	0.80	0.25	
		(3)	0.13	0	>0.13	0.50	L	0.13	L	L	L	
Cu (mg/l)	0.05	(1)	0.25	0.06	0.07	<0.03	3.6	0.16	0.04	<0.03	0.42	0.03
		(2)	0.28	0.09	0.07	<0.03	3.5	0.10	0.04	<0.03	0.43	
		(3)	0	0	0	0.20	0	L	0.03	0.05	0	
Fe (mg/l)	<0.05	(1)	<0.05	<0.05	<0.05	<0.05	2.2	0.10	<0.05	<0.05	0.20	0.05
		(2)	<0.05	<0.05	<0.05	<0.05	2.1	0.10	<0.05	<0.05	0.20	
		(3)	-	-	-	-	0	0	-	-	0	
Mg (mg/l)	20.0	(1)	93.2	3.2	169	4.7	70.0	4.9	0.06	<0.05	0.24	0.05
		(2)	46.0	4.0	54.0	15.0	51.0	1.9	0.10	<0.05	0.75	
		(3)	L	40.0	L	50.0	L	45.3	49.8	49.9	48.1	
Ni (mg/l)	0.12	(1)	<0.05	<0.05	<0.05	<0.05	0.65	<0.05	<0.05	<0.05	<0.05	0.05
		(2)	0.15	0.10	0.16	0.08	0.68	0.13	0.06	<0.05	0.17	
		(3)	0	0.05	0	0.40	L	0	0.15	0.18	0	
Pb (mg/l)	<0.20	(1)	<0.20	0.28	0.28	<0.20	0.33	<0.20	<0.20	<0.20	<0.20	0.20
		(2)	<0.20	0.28	0.28	<0.20	0.32	<0.20	<0.20	<0.20	<0.20	
		(3)	-	0	0	-	-	-	-	-	-	
Zn (mg/l)	<0.01	(1)	<0.01	<0.01	0.03	<0.01	1.5	0.30	<0.01	<0.01	0.08	0.01
		(2)	<0.01	<0.01	0.03	<0.01	1.6	0.10	<0.01	<0.01	0.06	
		(3)	-	-	0	-	0	L	-	-	0	
F^- (mg/l)	1.4	(1)	0.31	1.7	0.51	1.2	0.33	2.3	2.1	1.2	0.30	0.02
		(2)	1.6	1.6	1.9	2.0	0.35	1.2	1.7	1.4	0.38	
		(3)	L	L	0	L	2.6	0.50	L	L	2.6	
Cl^- (mg/l)	360	(1)	500	9.5	126	2.9	2.7	6.8	46.0	28.0	7.4	2.0
		(2)	700	375	425	260	230	360	400	390	370	
		(3)	L	0	L	340	325	0	0	0	0	
CN^- (mg/l)	<0.03	(1)	0.07	0.04	0.04	<0.03	<0.03	<0.03	0.22	0.20	<0.03	0.03
		(2)	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.18	0.15	<0.03	
		(3)	-	-	-	-	-	-	0	0	-	
COD(mg/l)	402	(1)	40.3	4.8	26.8	13.0	15.8	7.0	24.0	22.1	21.4	2.0
		(2)	324	350	127	189	114	214	400	410	342	
		(3)	195	130	688	2130	720	470	L	0	150	
TOC(mg/l)	157	(1)	15.0	4.1	10.0	2.7	5.0	15.5	37.6	76.0	40.1	-
		(2)	137	149	53.2	151	18.9	59.9	195	219	179	
		(3)	50.0	20.0	260	60.0	345	243	0	0	0	

* (1) Background of Sorbent Material (mg/l)
(2) Effluent Level After Treatment (mg/l)
(3) Sorbent Capacity µg Removed per g of Sorbent Used

**L. Represents no Sorbent Capacity and a Reduction in Leaching of Contaminant When Sorbent is Mixed with Leachate

TABLE 8 : STATIC STUDY RESULTS OF METAL FINISHING SLUDGE LEACHATE #3

Measured Parameters	Initial Concentration of Leachate	Description*	Bottom Ash	Fly Ash (Acidic)	Fly Ash (Basic)	Vermiculite	Illite	Kaolinite	Activated Alumina(I)	Activated Carbon	Minimum Detectable Value
pH	8.2	(1)	7.2	5.1	8.5	8.1	3.0	5.1	9.8	9.4	-
		(2)	7.5	6.6	8.9	8.4	3.8	8.0	9.8	9.0	
Conductivity	1140	(1)	2780	3150	2090	115	4460	295	2790	575	-
		(2)	3800	4580	2600	1075	1680	900	3080	1125	
Ca (mg/l)	38.1	(1)	20.0	357	300	15	250	42.0	<0.10	0.50	0.10
		(2)	30.5	446	472	16.3	258	7.5	<0.10	6.5	
		(3)	19.0	0	0	273	0	383	95.3	79.0	
Cd (mg/l)	<0.01	(1)	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	0.01
		(2)	<0.01	<0.01	<0.01	<0.01	0.07	<0.01	<0.01	<0.01	
		(3)	-	-	-	-	0	0	-	-	
Cr (mg/l)	<0.20	(1)	<0.20	0.50	0.50	<0.20	0.70	0.30	1.1	<0.20	0.20
		(2)	<0.20	0.50	<0.20	<0.20	0.30	0.30	1.1	<0.20	
		(3)	-		-	-	0	L	0	-	
Cu (mg/l)	0.53	(1)	0.25	0.29	0.06	<0.03	3.6	0.16	0.04	<0.03	0.03
		(2)	0.39	0.13	0.16	0.16	3.6	0.28	0.14	<0.03	
		(3)	0.35	1.0	0.93	4.6	L**	3.1	0.98	1.3	
Fe (mg/l)	<0.05	(1)	<0.05	<0.05	<0.05	<0.05	0.60	<0.05	<0.05	<0.05	0.05
		(2)	<0.05	<0.05	<0.05	<0.05	0.65	<0.05	<0.05	<0.05	
		(3)	-	-	-	-	0	-	-	-	
Mg (mg/l)	25.5	(1)	93.2	64.4	3.2	4.7	70.0	4.9	0.10	0.10	0.05
		(2)	95.8	15.3	2.2	18.4	25.0	16.0	0.10	2.1	
		(3)	L	25.5	58.3	88.8	6.3	30.6	63.5	58.5	
Ni (mg/l)	0.19	(1)	0.20	1.4	<0.05	<0.05	0.45	0.06	0.06	<0.05	0.05
		(2)	0.25	1.4	0.10	0.08	0.15	0.08	0.06	0.10	
		(3)	L	0	0.23	1.4	0.50	1.4	0.33	0.23	
Pb (mg/l)	<0.20	(1)	<0.20	0.30	0.28	<0.20	<0.20	<0.20	<0.20	<0.20	0.20
		(2)	<0.20	0.30	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	
		(3)	-	0	-	-	-	-	-	-	
Zn (mg/l)	0.06	(1)	<0.01	1.6	<0.01	<0.01	1.5	0.30	<0.01	<0.01	0.01
		(2)	0.10	1.4	<0.01	<0.01	1.5	<0.01	<0.01	<0.01	
		(3)	L	L	0.13	0.63	L	0.63	>0.13	0.13	
F^- (mg/l)	1.5	(1)	0.31	1.7	1.1	4.7	0.33	2.3	2.1	0.04	0.02
		(2)	0.90	1.6	1.1	2.2	0.49	0.70	1.0	1.6	
		(3)	1.4	L	0.88	L	12.6	2.0	1.2	0	
Cl^- (mg/l)	95.0	(1)	500	10.0	9.5	2.9	2.7	6.8	46.0	5.0	2.0
		(2)	575	75.0	57.5	70.0	65.5	60.0	79.9	75.9	
		(3)	0	50.0	93.8	313	369	438	37.8	47.8	
CN^- (mg/l)	<0.03	(1)	0.07	0.04	<0.03	<0.03	<0.03	1.2	0.22	<0.03	0.03
		(2)	0.05	0.04	<0.03	<0.03	<0.03	1.2	0.30	<0.03	
		(3)	0	0	-	-	-	0	0	-	
COD(mg/l)	49.8	(1)	40.3	<2.0	4.8	13.0	16.8	7.0	24.0	<2.0	2.0
		(2)	70.9	19.8	26.4	25.8	29.2	30.3	63.2	3.9	
		(3)	0	75.0	58.5	300	258	244	L	115.0	
TOC(mg/l)	19.7	(1)	15.0	0.50	4.1	2.7	5.0	15.5	37.6	5.1	-
		(2)	19.5	6.6	12.0	10.5	8.3	8.3	39.3	4.4	
		(3)	0	32.8	19.3	115	143	143	0	38.3	

* (1) Background of Sorbent Material (mg/l)
(2) Effluent Level After Treatment (mg/l)
(3) Sorbent Capacity μg Removed per g of Sorbent Used
**L Represents no Sorbent Capacity and a Reduction in Leaching of Contaminant when Sorbent is mixed with Leachate

and zinc were present in the influent leachate, but their concentrations were found below safe discharge levels and thus were not analyzed in the treated effluent.

The sorbent capacities with respect to each of the measurable constituents in the three metal finishing sludge leachates are presented in Tables 6 through 8. A comparison of the sorbent capacities from these tables show that among the natural sorbents, illite was found to be the most promising for organics and fluoride ion removal. Kaolinite was found to have the largest sorptive capacity for calcium; vermiculite for magnesium, nickel and copper. Only vermiculite and illite showed some capacity for chloride removal.

4-1-3 Petroleum Sludge Leachate Treatment

The two petroleum sludges used for this study were collected from a tank bottom and a gravity separator. Significant differences in the concentration of constituents between these two sludge leachates were observed (see Table 2). Both leachates contained significant concentrations of calcium, copper, iron, magnesium, nickel, zinc, fluoride, cyanide, and organics. However, the tank bottom sludge showed a much higher concentration level of constituents than that present in the separator sludge leachate.

The sorbent capacities, with respect to each of the significant constituents in the two petroleum sludge leachate, are listed in Tables 9 and 10.

TABLE 9 : STATIC STUDY RESULTS OF TANK BOTTOM PETROLEUM SLUDGE LEACHATE

Measured Parameters	Initial Concentration of Leachate	Description*	Bottom Ash	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon	Minimum Detectable Value
pH	7.4	(1)	7.2	8.5	7.8	8.1	3.0	5.1	9.8	9.7	9.0	9.4	-
		(2)	8.3	9.1	8.1	8.4	3.2	7.4	9.4	9.1	9.2	9.6	
Conductivity	15000	(1)	2780	2500	8150	182	4460	295	1790	4060	4010	575	-
		(2)	14800	14200	19000	8400	14200	13600	13200	12700	16000	13300	
Ca (mg/l)	327	(1)	20.0	300	6.0	15	250	42.0	<0.10	<0.10	<0.10	0.45	0.10
		(2)	342	327	327	330	161	31.5	2.4	2.7	21.0	36.0	
		(3)	0	L**	0	0	415	300	812	811	765	728	
Cd (mg/l)	0.05	(1)	<0.01	<0.01	<0.01	<0.01	0.60	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
		(2)	0.06	0.06	0.07	0.06	0.75	0.05	0.03	0.04	0.05	0.05	
		(3)	0	0	0	0	0	0	0.05	0.03	0	0	
Cr (mg/l)	0.22	(1)	<0.20	0.50	0.30	<0.20	0.70	0.30	1.1	0.70	0.35	<0.20	0.20
		(2)	0.22	0.75	0.32	0.22	0.75	0.22	1.1	0.67	0.22	0.22	
		(3)	0	0	L	0	L	L	L	L	L	0	
Cu (mg/l)	0.09	(1)	0.25	0.06	0.07	<0.03	3.6	0.16	0.04	<0.03	0.42	<0.03	0.03
		(2)	0.19	0.17	0.14	0.14	3.6	<0.03	<0.03	<0.03	0.25	0.06	
		(3)	L	0	0	0	L	0.15	0.15	0.15	L	0.08	
Fe (mg/l)	0.20	(1)	<0.05	<0.05	<0.05	<0.05	2.2	0.10	<0.05	<0.05	0.20	<0.05	0.05
		(2)	0.14	<0.05	0.24	0.10	2.5	0.28	<0.05	<0.05	0.41	<0.05	
		(3)	0.15	0.38	0	1.0	0	0	0.38	0.38	0	0.38	
Mg (mg/l)	400	(1)	93.2	3.2	169	4.7	70.0	4.9	0.06	<0.05	0.24	0.09	0.05
		(2)	438	397	356	390	372	385	1.6	2.1	39.0	213	
		(3)	L	7.5	110	100	70.0	37.5	996	995	503	468	
Ni (mg/l)	0.23	(1)	<0.05	<0.05	<0.05	<0.05	0.65	<0.05	<0.05	<0.05	<0.05	<0.05	0.05
		(2)	0.24	0.19	0.24	0.21	0.29	0.25	0.13	0.14	0.22	0.17	
		(3)	0	0.10	0	0.20	0	0	0.25	0.23	0.03	0.15	
Pb (mg/l)	0.48	(1)	<0.20	0.28	0.28	<0.20	0.33	<0.20	<0.20	<0.20	<0.20	<0.20	0.20
		(2)	0.61	0.48	0.78	0.50	0.59	0.43	0.34	0.43	0.43	0.20	
		(3)	0	L	0	L	L	0.13	0.35	0.13	0.13	0.70	
Zn (mg/l)	0.06	(1)	<0.01	<0.01	0.03	<0.01	1.5	0.30	<0.01	<0.01	<0.08	<0.01	0.01
		(2)	0.03	0.03	0.04	0.03	1.5	0.20	0.02	0.04	0.04	0.02	
		(3)	0.08	0.08	0.05	0.30	0	L	0.10	0.05	0.05	0.10	
F (mg/l)	1.5	(1)	0.31	1.7	0.51	1.2	0.33	2.3	2.1	1.2	0.30	0.04	0.02
		(2)	0.89	1.3	1.0	1.4	0.22	0.17	0.44	0.73	0.86	0.17	
		(3)	1.5	0.50	1.3	1.0	3.2	3.3	2.7	1.9	1.6	3.3	
Cl^- (mg/l)	10990	(1)	500	9.5	126	2.9	2.7	6.8	46.0	28.0	7.4	5.0	2.0
		(2)	6740	6200	6740	6030	3080	4080	6380	6340	5500	2800	
		(3)	10630	11980	10630	49600	19780	17280	11530	11630	13730	20480	
CN^- (mg/l)	7.9	(1)	0.07	0.04	0.04	<0.03	<0.03	1.2	0.22	0.35	<0.03	<0.03	0.03
		(2)	2.9	4.9	3.0	3.4	1.4	5.3	5.3	6.0	7.2	0.30	
		(3)	12.5	7.5	12.3	45.0	16.3	6.5	6.5	4.8	1.8	19.0	
COD	1299	(1)	40.3	4.8	21.8	13.0	15.8	7.0	24.0	32.2	21.4	<0.2	2.0
		(2)	1048	1048	1018	1014	648	1113	1069	1120	1131	105	
		(3)	628	628	703	2850	1628	465	575	448	420	2985	
TOC	448	(1)	15.0	4.1	10.0	2.7	5.0	16.5	37.6	84.0	40.1	5.1	-
		(2)	365	358	378	367	201	363	347	376	405	26.0	
		(3)	208	225	175	810	618	213	253	180	108	1055	

* (1) Background of Sorbent Material (mg/l)
(2) Effluent Level after Treatment (mg/l)
(3) Sorbent Capacity μg Removed per g of Sorbent Used

**L Represents no Sorbent Capacity and a Reduction in Leaching of Contaminant when Sorbent is mixed with Leachate

TABLE 10: STATIC STUDY RESULTS FOR API SEPARATOR PETROLEUM SLUDGE LEACHATE

Measured Parameters	Initial Concentration of Leachate	Description*	Bottom Ash	Fly Ash (Acidic)	Fly Ash (Basic)	Vermiculite	Illite	Kaolinite	Activated Alumina(I)	Activated Carbon	Minimum Detectable Value
pH	5.9	(1)	7.2	5.1	8.5	8.1	3.0	5.1	9.8	9.4	-
		(2)	7.3	5.0	8.0	7.6	3.5	4.3	9.4	8.1	
Conductivity	550	(1)	2780	3150	2090	115	4460	295	2790	575	-
		(2)	230	3900	2500	670	1500	700	2600	770	
Ca (mg/l)	50.0	(1)	20.0	257	300	15	250	42.0	<0.10	0.45	0.10
		(2)	102	340	284	55.0	50.0	42.0	<0.10	10.5	
		(3)	0	0	L**	0	0	100	125	92.8	
Cd (mg/l)	<0.01	(1)	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	0.01
		(2)	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	
		(3)	-	-	-	-	0	-	-	-	
Cr (mg/l)	<0.20	(1)	<0.20	0.50	0.50	<0.20	0.70	0.30	1.1	<0.20	0.20
		(2)	<0.20	<0.20	<0.20	<0.20	<0.20	0.30	1.1	0.20	
		(3)	-	-	-	-	-	-	L	-	
Cu (mg/l)	0.17	(1)	0.25	0.29	0.06	<0.03	3.6	0.16	0.04	<0.03	0.03
		(2)	<0.03	0.28	0.06	<0.03	1.27	0.23	0.06	0.08	
		(3)	>0.35	L	0.28	1.8	0	L	0.28	0.23	
Fe (mg/l)	<0.05	(1)	<0.05	<0.05	<0.05	<0.05	0.60	<0.05	<0.05	<0.05	0.05
		(2)	<0.05	<0.05	<0.05	<0.05	0.60	<0.05	<0.05	<0.05	
		(3)	-	-	-	-	0	-	-	-	
Mg (mg/l)	27.5	(1)	93.2	64.4	3.2	4.7	70.0	4.9	0.10	0.10	0.05
		(2)	71.4	74.8	4.0	36.0	24.0	26.0	0.30	10.0	
		(3)	L	L	58.8	0	25.6	18.8	68.0	43.8	
Ni (mg/l)	0.10	(1)	0.20	1.4	<0.05	<0.05	0.45	0.06	0.06	<0.05	0.05
		(2)	0.20	1.5	<0.05	0.15	0.40	0.08	<0.05	<0.05	
		(3)	L	0	0.13	0	L	0.25	0.13	0.13	
Pb (mg/l)	0.36	(1)	<0.20	0.30	0.28	<0.20	<0.20	<0.20	<0.20	<0.20	0.20
		(2)	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	
		(3)	0.40	0.40	0.40	2.0	2.0	2.0	0.40	0.40	
Zn (mg/l)	0.13	(1)	<0.01	1.6	<0.01	<0.01	1.5	0.30	<0.01	<0.01	0.01
		(2)	<0.01	0.37	<0.01	<0.01	1.5	0.11	<0.01	<0.01	
		(3)	0.30	L	0.30	1.5	L	0.25	0.30	0.30	
F^- (mg/l)	1.2	(1)	0.31	1.7	1.1	4.7	0.33	2.3	2.1	0.04	0.02
		(2)	0.84	1.2	1.1	5.0	0.39	2.9	2.1	1.0	
		(3)	0.90	L	0.25	L	10.1	L	L	0.50	
Cl^- (mg/l)	415	(1)	500	10.0	7.5	2.9	2.7	6.8	46.0	5.0	2.0
		(2)	647	399	335	390	275	387	400	300	
		(3)	L	40.0	75.0	313	1750	350	15.0	288	
CN^- (mg/l)	0.20	(1)	0.07	0.04	<0.03	<0.03	<0.03	1.2	0.22	<0.03	0.03
		(2)	0.07	<0.03	0.06	0.06	<0.03	1.2	0.31	<0.03	
		(3)	0.33	0.43	0.35	1.8	2.1	0	0	0.43	
COD(mg/l)	340	(1)	40.3	<2.0	4.6	13.0	16.8	7.0	24.0	<2.0	2.0
		(2)	105	10.0	55.1	108	57.9	84.0	217	39.0	
		(3)	588	824	712	2900	3526	3200	308	753	
TOC(mg/l)	130	(1)	15.0	0.50	4.1	2.7	5.0	15.5	37.6	5.1	-
		(2)	40.3	2.9	21.0	40.1	24.0	30.8	80.1	14.5	
		(3)	224	318	273	1124	1325	1240	125	289	

* (1) Background of Sorbent Material (mg/l)
(2) Effluent Level after Treatment (mg/l)
(3) Sorbent Capacity μg Removed per g of Sorbent Used

**L. Represents no Sorbent Capacity and a Reduction in Leaching of Contaminant when Sorbent is mixed with Leachate

Among the natural sorbents, illite is effective in treating magnesium, fluoride, chloride, cyanide and organics. Vermiculite is more effective than illite in removing the cyanide in the tank bottom sludge leachate. The reverse is true for the separator sludge leachate where the cyanide ion concentration is much lower. A similar observation was made for illite and kaolinite. Illite is better than kaolinite for treating calcium in the tank bottom sludge leachate where a higher concentration of calcium is encountered (see Tables 9 and 10), but kaolinite appears more effective for treating the calcium ion in the separator-sludge leachate where a lower concentration is encountered. Vermiculite appears to be the most promising sorbent for treating copper in the separator sludge leachate, iron in the tank bottom sludge leachate, and zinc in both leachates. Basic fly ash exhibited a capacity for nickel in both leachates (see Tables 10 and 11).

In summary, the best two sorbents for treating the leachates are listed in Table 11. Inspection of this Table, it is observed that a sorbent material which is good for the attenuation of a specific pollutant in one leachate is also good for the attenuation of that pollutant in other leachates. For example, kaolinite favors the removal for calcium, fly ash (basic) for magnesium and iron, illite for fluoride, chloride, cyanide and organics, and vermiculite for lead, chromium and zinc in all the leachates tested. Some exceptions, however, are noted. For example, zeolite is found to show good removal of calcium, and fly ash (basic) shows good removal for chromium and nickel in calcium fluoride sludge leachate (neutral), but neither sorbent exhibits the same behavior when contacted with the other two leachates. These differences could be due to the interacted effects of pH, influent concentration, common ion effects, and total dissolved salts as discussed earlier from Equations 1 through 8 in Chapter 1.

All of the tested clay soils, except illite, were found useful for reducing cation concentrations in the leachates. Illite is the only clay sorbent to show anion removals in all the leachates treated. The reason for this difference of sorption could be due to the pH effect. Illite was shown to be very acidic (pH = 3-4) when compared with other clay sorbents tested in this study. As described in Equation 7 and 8, the capacity of sorbent to adsorb cations increases as the value of pH increases, and the capacity to adsorb anions increases as pH decreases.

4-3 RESULTS OF LYSIMETER STUDIES USING A SINGLE SORBENT

Based upon the results obtained in the batch study, the sorbents of acidic fly ash, basic fly ash, zeolite, vermiculite, illite, kaolinite, activated alumina and activated carbon were selected to treat the sludge leachates in lysimeter under gravitational flow. Leachates from petroleum sludge, metal finishing sludge and calcium fluoride sludge were prepared, analyzed (see Table 2), and passed through individual lysimeters that contained one of the above sorbents. The volume of effluent from each of these lysimeters was

TABLE 11: SUMMARY SELECTIONS OF NATURAL SORBENTS TO TREAT LEACHATES (Batch Condition)

	Calcium Fluoride Sludge (Neutral)	Metal Finishing Sludge (Basic)	Petroleum Sludge (Acidic)
Ca	(1) Zeolite (2) Kaolinite	(1) Kaolinite (2) Vermiculite	(1) Kaolinite
Cd	(1) Vermiculite (2) Kaolinite	*	*
Cr	(1) Vermiculite	(1) Vermiculite (2) Kaolinite	*
Cu	(1) Fly Ash (2) Zeolite (Basic)	(1) Vermiculite (2) Kaolinite	*
Fe	(1) Fly Ash (Basic)	*	(1) Fly Ash (Basic)
Mg	(1) Fly Ash (Basic)	(1) Vermiculite (2) Fly Ash (Basic)	(1) Zeolite (2) Fly Ash (Basic)
Ni	(1) Fly Ash (2) Kaolinite (Basic)	(1) Vermiculite (2) Kaolinite	(1) Zeolite
Pb	(1) Vermiculite (2) Fly Ash (Basic)	*	(1) Vermiculite (2) Kaolinite
Zn	(1) Vermiculite	(1) Vermiculite (2) Kaolinite	(1) Vermiculite (2) Fly Ash (Basic)
F	(1) Illite (2) Kaolinite	(1) Illite (2) Kaolinite	(1) Illite (2) Kaolinite
Cl	(1) Illite (2) Kaolinite	(1) Vermiculite (2) Illite	(1) Vermiculite (2) Illite
CN	(1) Illite	*	(1) Vermiculite (2) Illite
Organic	(1) Illite (2) Fly Ash (A)	(1) Vermiculite (2) Illite	(1) Vermiculite (2) Illite

Remarks: Represents no sorbent available for treatment.

measured and samples of these effluents were analyzed for pH, and the concentration of calcium, copper, magnesium, zinc, nickel, fluoride, total cyanide and organics. These parameters were measured in order to evaluate the removal capacities of selected sorbents for specific toxic pollutants under gravitational flow conditions. After the sorbent became saturated, repeated washings of the spent sorbents were carried out until no measurable contaminants appeared in the washed effluent. In this manner, a net removal capacity of sorbent was determined to define the amount of sorbent required to treat specific volume of leachate.

Due to low permeability of natural clay, the vermiculite, illite and kaolinite were mixed with 80 percent of inert Ottowa sand in the lysimeter studies. This ratio of mixture was established from the results of a series of permeability tests using different ratios of sand to sorbents to provide flows of leachate through the sorbent bed that would lead to saturation of the sorbents within a reasonable time.

The permeability of leachate through the sorbent in all the lysimeters was determined to characterize the conditions of flow (such as clogging, channeling, etc.) during the testing period. These results are summarized in Appendix II. Permeability curves are also presented in Appendix IV.

The Ottowa sand used to mix with clay soils was tested in a batch reaction (i.e. mixed with deionized water). This sand was found to be an inert material which showed no measurable leaching and no removal capacity for the constituents present in the leachate. Therefore, Ottowa sand could be admixed with clay soils to improve the permeability without significantly altering the leaching backgrounds and removal capacity exhibited by these clay sorbents.

The capacities of selected sorbents for removing those constituents present in the leachate in measurable concentration was determined by measuring the amount of these constituents in the leachate before and after it had percolated through the sorbent bed. This was carried out until breakthrough was achieved or the flow of leachate through sorbent became excessively low. Breakthrough is defined as the point where the concentration of a specific contaminant in the effluent reaches that encountered in the influent leachate. This is indicative of sorbent saturation. The concentration of the constituents remaining in the effluent was plotted vs. that volume of leachate that had passed through the column. The area above the curve was integrated to provide the total amount of contaminant removed by the sorbent. The amount of constituent that is desorbed by washing was determined by passing water through the saturated sorbent until leaching was no longer significant. The net sorbent capacity for the removal of trace elements was calculated from the amount of contaminants attenuated, subtracting that of contaminant released in the desorptive phase. These sorbent capacities are presented in Tables 12, 13, and 14, and their breakthrough curves for all of the measurable pollutants in the three leachates are presented in Appendix III (Figures 28 to 48).

The results show that in general the pH of sorbent background influences the pH of the effluent leachate initially. Considerable variations were observed in the pH of the effluents collected initially (see Figures 9, 10, and 11). However, as the leachate was passed through the sorbents in lysimeters, the pH of the effluent eventually became the same as that of the influent. For example, the effluent from the illite lysimeter was initially acidic (pH 3 to 4), but then approached the pH of the influent leachate (the influent pH's are 7.2, 8.3 and 5.8 in calcium fluoride, metal finishing and petroleum sludge leachates respectively) as elution progressed (see Figures 9, 10, and 11). Thus, the pH of leachate flowing through the sorbent bed in the column is affected initially by sorbent, and finally by the leachate.

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. A comparison of the three most promising sorbents (selected from Tables 12, 13, and 14), based upon their removal capacities for a specific constituent in the three leachates, shows an increase in the removals of calcium, copper and magnesium ions as the pH of the leachate is raised (see Table 15). For example, zeolite, acidic fly ash and kaolinite sorbent removal capacities for copper were 5.2, 2.4 and 0, respectively, in the presence of acidic leachate (see brackets in Table 15), but became 8.2, 2.1 and 6.7 μg/g, respectively, in the presence of neutral leachate.

TABLE 12

SORBENT REMOVAL CAPACITIES FOR TREATING ACIDIC PETROLEUM SLUDGE LEACHATE

Measured Parameters	Description	Fly Ash (Acidic)	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina	Activated Carbon
Ca	Net Capacity	0	0	1390	686	721	10.5	200	128
Cu	Net Capacity	2.4	1.9	5.2	1.1	0	0	0.35	0
Mg	Net Capacity	0	102	746	67	110	595	107	8.6
Zn	Net Capacity	1.6	1.7	10.8	4.5	0	0	0.40	1.1
F^-	Net Capacity	8.7	6.2	4.1	0	9.3	3.5	3.4	1.2
CN^-	Net Capacity	2.7	2.5	4.7	7.6	12.1	3.1	0	2.4
COD	Net Capacity	3818	3998	468	6654	4807	541	411	3000
TOC	Net Capacity	1468	737	170	2545	2175	191	176	1270

Remarks: Cl^-, Cd, Cr, Fe, Ni, and Pb were measured and found in low concentrations.

Sorbent capacities are expressed in μg of ion removed per g of sorbent used.

TABLE 13

SORBENT REMOVAL CAPACITIES
FOR TREATING NEUTRAL CALCIUM FLUORIDE SLUDGE LEACHATE

Measured Parameters	Description	Fly Ash (Acidic)	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina	Activated Carbon
Ca	Net Capacity	261	0	5054	0	0	857	6.140	357
Cu	Net Capacity	2.1	0.36	8.2	0	0	6.7	2.9	2.0
Mg	Net Capacity	230	155	0	0	0	0	214	3.0
F^-	Net Capacity	102	51.8	27.7	0	175	132	348	0
COD	Net Capacity	690	203	171	0	108	185	0	956
TOC	Net Capacity	153	44.7	93	0	26.1	71	0	325

Sorbent capacities are expressed in µg of ion removal per g of Sorbent used.

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

TABLE 14

SORBENT REMOVAL CAPACITIES FOR TREATING BASIC METAL FINISHING SLUDGE LEACHATE

Measured Parameters	Description	Fly Ash (Acidic)	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina	Activated Carbon
Ca	Net Capacity	87.3	97.8	1240	819	1280	735	737	212
Cu	Net Capacity	13.0	6.1	85.4	15.2	43.1	23.7	6.2	16.8
Mg	Net Capacity	296	176	1328	344	1122	494	495	188
Ni	Net Capacity	3.8	1.7	13.5	2.3	5.1	4.6	2.3	4.7
F^-	Net Capacity	0	0	2.1	0	2.2	2.6	11.4	0
COD	Net Capacity	1080	259	0	618	1744	0	0	1476
TOC	Net Capacity	430	115	0	244	729	0	0	589

Sorbent capacities are expressed in µg of ion removal per g of sorbent used.

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

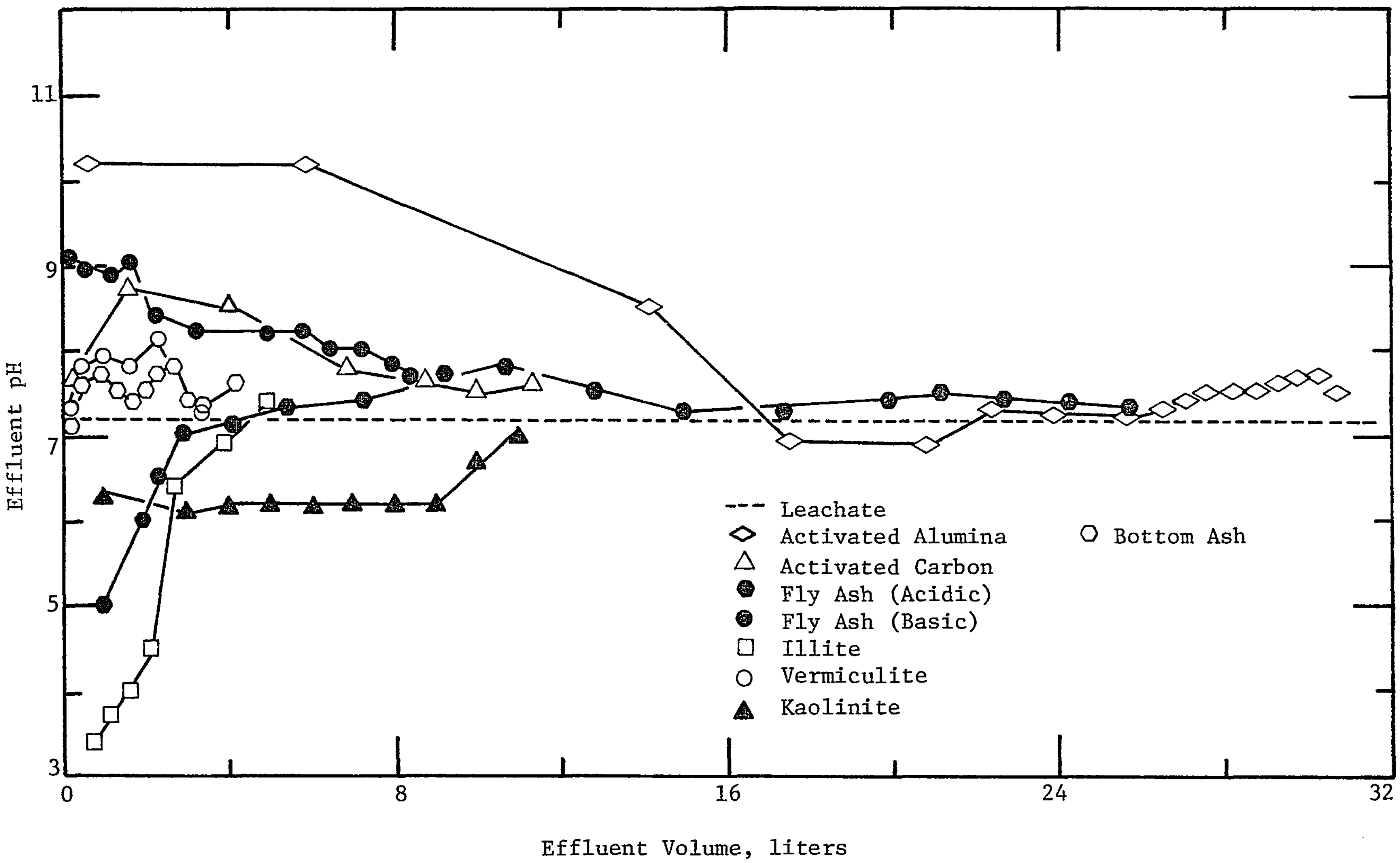

Figure 9. Lysimeter Studies of pH in Calcium Fluoride Sludge Leachate.

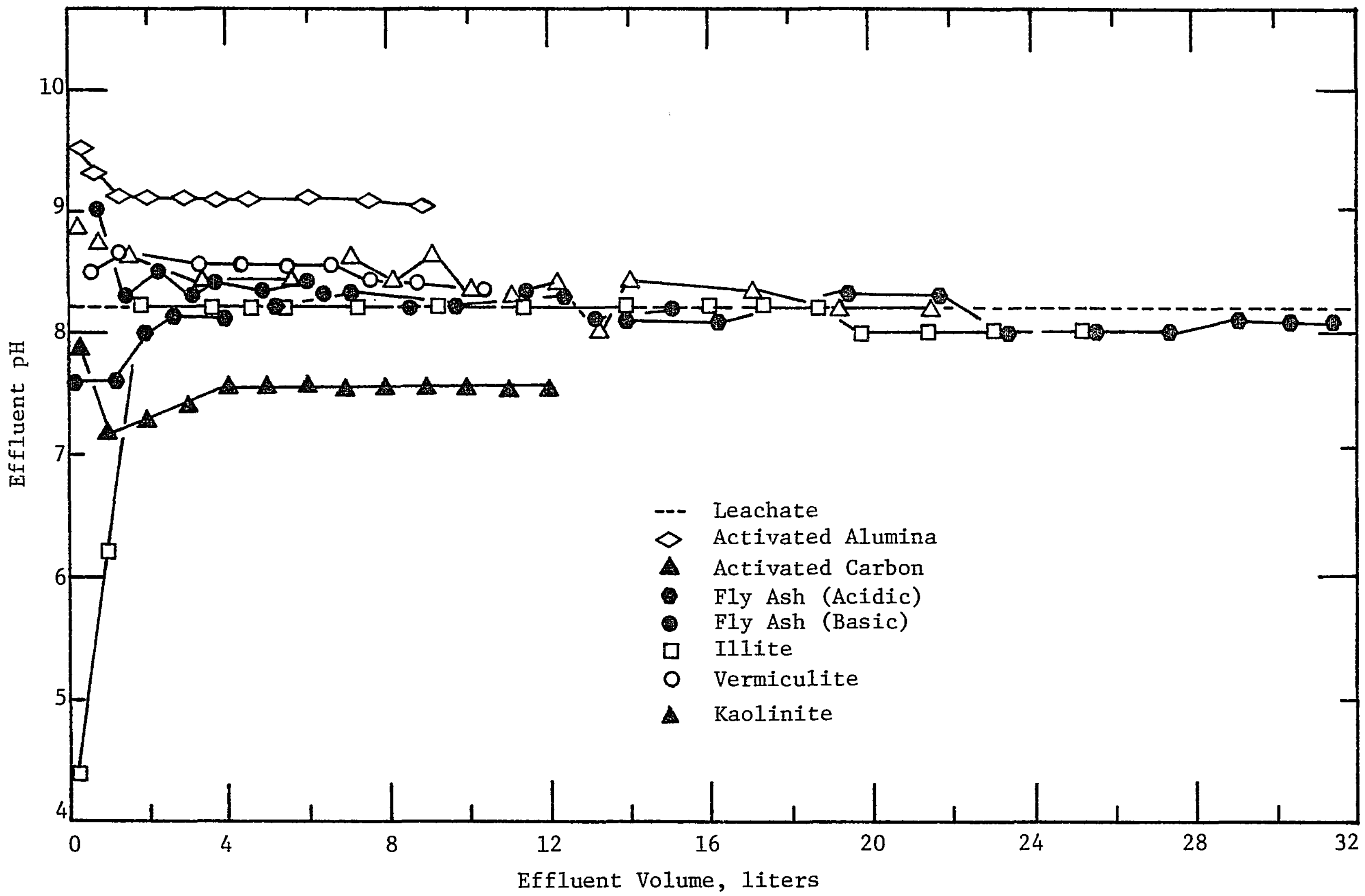

Figure 10. Lysimeter Studies of pH in Metal Finishing Sludge Leachate.

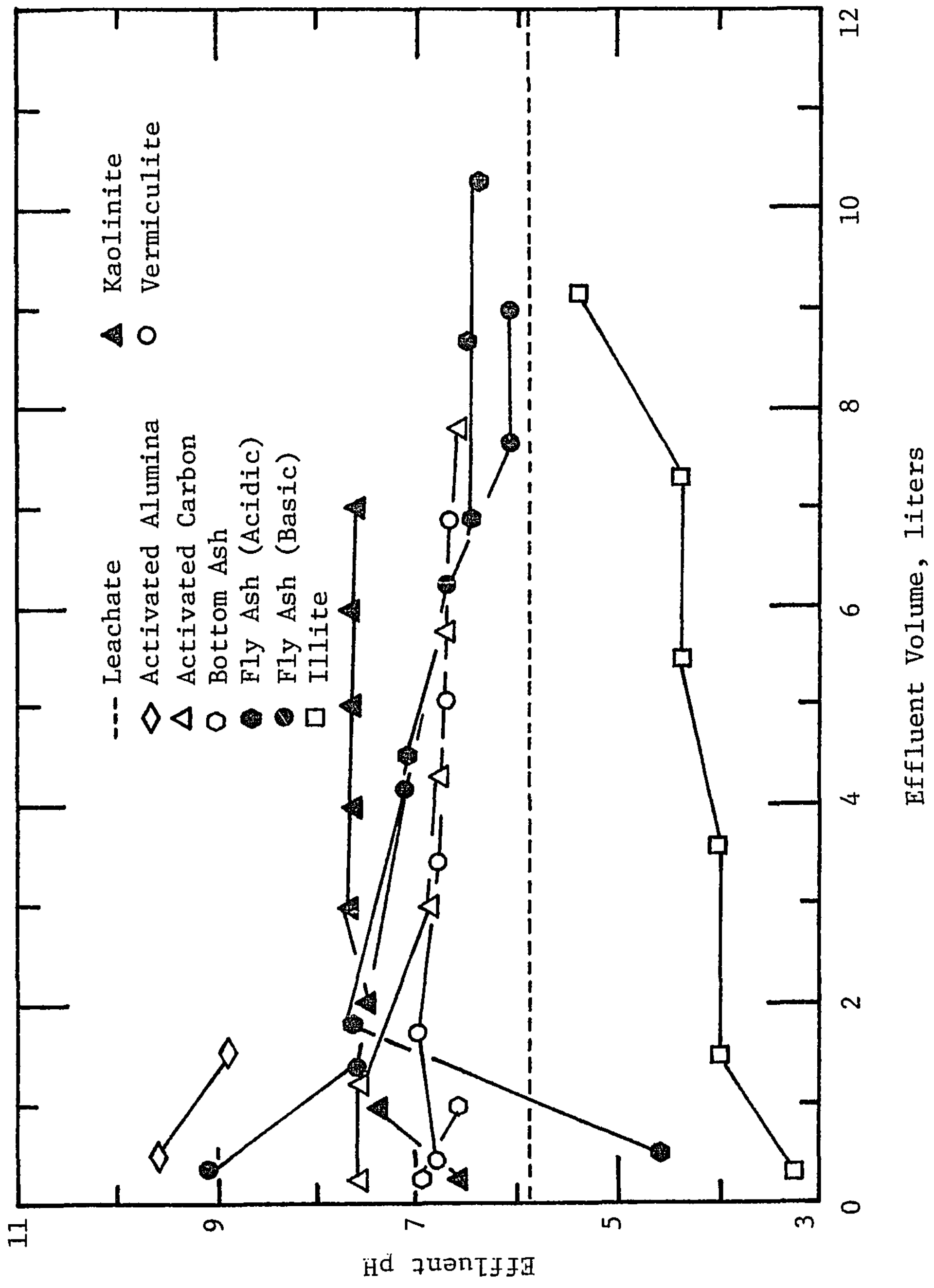

Figure 11. Lysimeter Studies of pH in Petroleum Sludge Leachate.

Griffin, et al. (22) has also reported similar results. In his study, which was limited to only kaolinite and montmorillonite, removals of copper, cadmium and zinc increased as the pH of the leachate changed from acidic to alkaline. Maximum removals were obtained at a pH of about 8. The reason for this significant pH effect on the capacity of sorbent to remove cationic pollutants may be ascribed to the competition of the cationic hydrogen. According to Equation 7, higher concentration of hydrogen ion generated at lower pH will compete with other cations, and some of the hydrogen ion will be adsorbed by the sorbent. As a result, the original capacity of sorbent to attenuate specific cation will be reduced correspondingly.

The influence of pH of the leachate on the different sorbent removal capacities for the zinc, nickel, iron, cadmium, chromium and lead could not be established in this study. Unfortunately, the 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 (see Table 2).

The sorbent capacities for the removal of the fluoride were also dependent on the pH of the leachate. However, the influence of leachate pH on the removal of this anion was opposite to that encountered with cations. Here, sorbent capacities increased as the pH of the leachate decreases from alkaline to acidic conditions.

For example, the sorbent capacities for illite, acidic fly ash and kaolinite were 2.2, 2.6 and 0 μg/g, respectively, for the removal of fluoride in the basic leachate and increased to 9.3, 8.7 and 3.5,μg/g respectively, for the acidic leachate (see Table 15). Griffin, et al. (22) showed this to be the case for the anions $HaSO_4^-$ using kaolinite and montmorillonite. Maximum removal of this anion was achieved under acidic conditions, around a pH of 6. The reason for this pH effect on the capacity of sorbent to remove anionic pollutants may be due to the competition of anionic hydroxyl. This is similar to the hydrogen ion effect on the cation removal. According to Equation 8, higher concentration of hydroxyl ion generated at higher pH will compete with other anions, and some of the hydroxyl ion will be adsorbed by the sorbent. Therefore, the original capacity of sorbent to remove specific anion could be reduced significantly.

The removals of organics also appear to be pH dependent. The sorbent removal capacities for the COD in both acidic and basic leachates are significantly higher than that achieved with the neutral leachate. However, a trend in the change of sorbent capacity with pH was difficult to identify in our study because the concentration of organics in the acidic leachate was significantly different from that measured in the basic leachate (see Table 2). Maximum sorption of pyridine by sodium kaolinite and sodium montmorillonite were reported to occur at the pH range of 4.0 - 5.5 (5).

The pH of the leachate in the lysimeter also influenced the leaching of ions from specific sorbents. When the leachate in the

TABLE 15

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

Ion	Neutral Leachate (Calcium Fluoride)		Basic Leachate (Metal Finishing Sludge)		Acidic Leachate(*) (Petroleum Sludge)	
Ca	Zeolite	(5054)	Illite	(1280)	Zeolite	(1390)
	Kaolinite	(857)	Zeolite	(1240)	Illite	(721)
	Illite	(0)	Kaolinite	(733)	Kaolinite	(10.5)
Cu	Zeolite	(8.2)	Zeolite	(85)	Zeolite	(5.2)
	Kaolinite	(6.7)	Kaolinite	(24)	Acidic F.A.	(2.4)
	Acidic F.A.	(2.1)	Acidic F.A.	(13)	Kaolinite	(0)
Mg	Basic F.A.	(155)	Zeolite	(1328)	Zeolite	(746)
	Zeolite	(0)	Illite	(1122)	Illite	(110)
	Illite	(0)	Basic F.A.	(176)	Basic F.A.	(1.7)
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	(175)	Kaolinite	(2.6)	Illite	(9.3)
	Kaolinite	(132)	Illite	(2.2)	Acidic F.A.	(8.7)
	Acidic F.A.	(102)	Acidic F.A.	(0)	Kaolinite	(3.5)
Total CN$^-$					Illite	(12.1)
					Vermiculite	(7.6)
					Acidic F.A.	(2.7)
COD	Acidic F.A.	(690)	Illite	(1744)	Vermiculite	(6654)
	Illite	(108)	Acidic F.A.	(1080)	Illite	(4807)
	Vermiculite	(0)	Vermiculite	(244)	Acidic F.A.	(3818)

(*) Bracket represents sorbent capacity (µg of contaminant removed per g of sorbent used.

lysimeter was initially acidic, as indicated by its effluent pH, the concentration of some specific ions in the effluent was found to exceed the concentration of this ion in the influent. However, as the pH of the effluent approached the value of 6 and above, the leaching of the specific ion ceased and, in fact, the sorbent actually began to remove this ion. For example, when the pH of the effluent approached 6 (see Figures 9, 10 and 11) the illite and acidic fly ash either ceased to leach copper and/or began to remove the copper (see Figures 12, 13, and 14). The removal of copper was indicated when its concentration in the effluent fell below that present in the influent. This same behavior was observed for zinc (see Figure 15). Similar results with fly ash was recently reported by Theis and Wirth (43). In this study, the average release of the trace heavy metals carried out under batch conditions was shown to be minimal at a pH of 6 and above.

The concentration of the contaminants in the leachate also appeared to influence the sorbent removal capacity. As the concentration increased, the sorbent removal capacity also increased. The copper concentration ranged from 0.43 - 0.53 mg/l in the basic leachate as compared to only 0.09 - 0.17 and 0.10 - 0.16 mg/l in the acidic and neutral leachates, respectively (see Table 2). This influence of concentration on the sorbent removal capacities was also seen in the treatment of other cations and the fluoride anion. The highest concentrations of calcium and fluoride were encountered in the neutral leachate (see Table 2). The zeolite sorbent capacity for calcium in the neutral leachate was 5054 µg/g as opposed to only 1240 µg/g in the basic leachate, even though alkaline conditions favor the removal of cations. Similarly, the illite sorbent capacity for fluoride was 175 µg/g in the neutral leachate, as opposed to 9.3 µg/g and 2.2 µg/g in the acidic and basic leachates, respectively.

The influence on the sorbent removal capacities of the concentration of a specific constituent in the leachate was 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 in the influent leachate, the greater the driving force to remove that ion will be. As a result, greater amounts of the ion will be removed from the leachate in the presence of a given amount of sorbent.

Generally, the results of gravitational bed flow operations indicate higher removal capacities than observed for batch type operations (see Tables 3 to 10 and 15). For example, illite has a removal capacity of fluoride, 17.5, 9.3 and 2.6 µg/g in calcium fluoride, metal finishing and petroleum sludge leachate lysimeters respectively (see Table 15), but only has 16.0, 2.6, and 3.2 µg/g in calcium fluoride, metal finishing and petroleum sludge batch reactors respectively.

The reason for this difference of removal capacity between batch reaction and gravitation-bed-flow-reaction is that a sorbent tends to remove a given amount of a specified pollutant provided

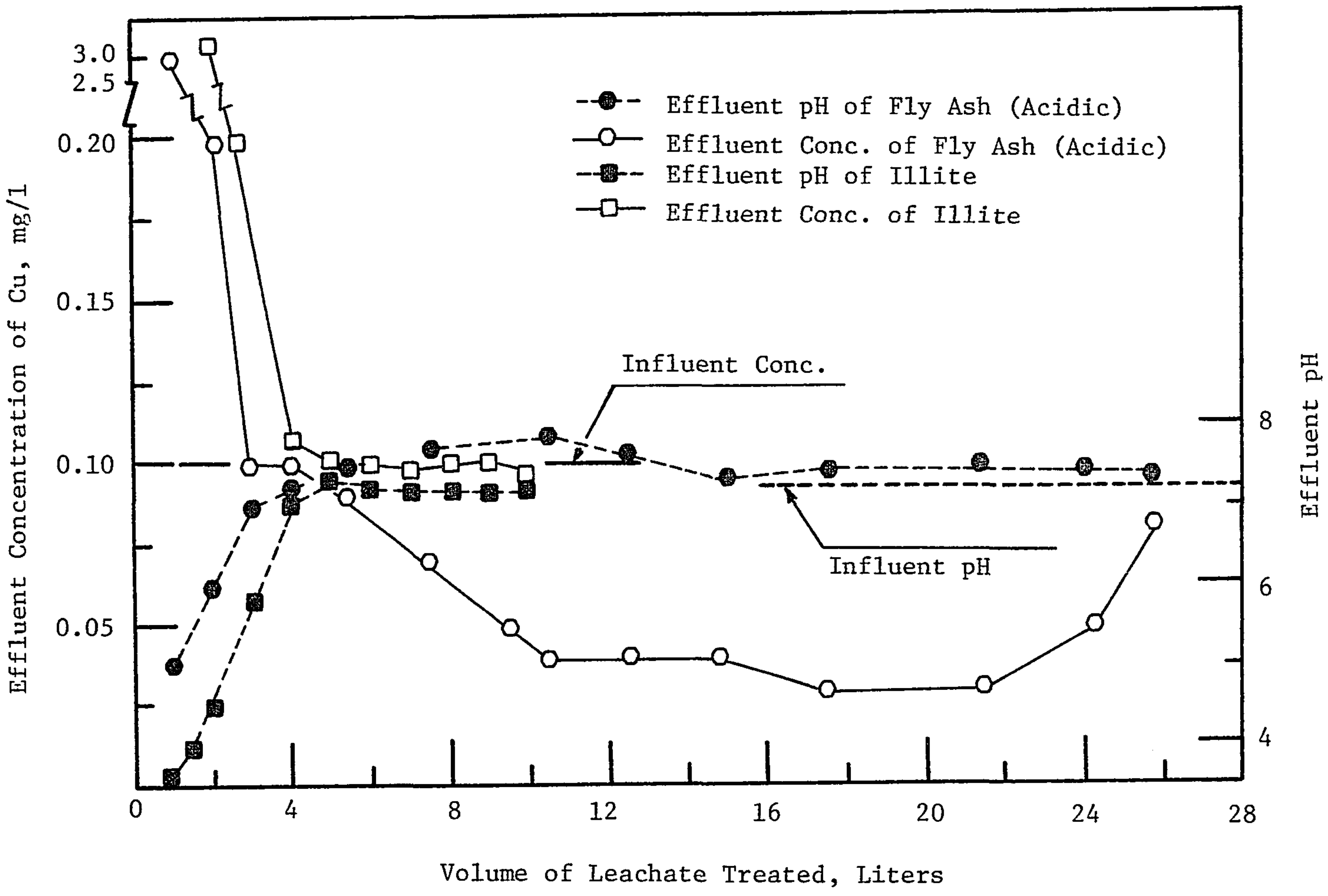

Figure 12. Effluent Cu Concentration and pH Profile in Lysimeter (Neutral Calcium Fluoride Sludge Leachate)

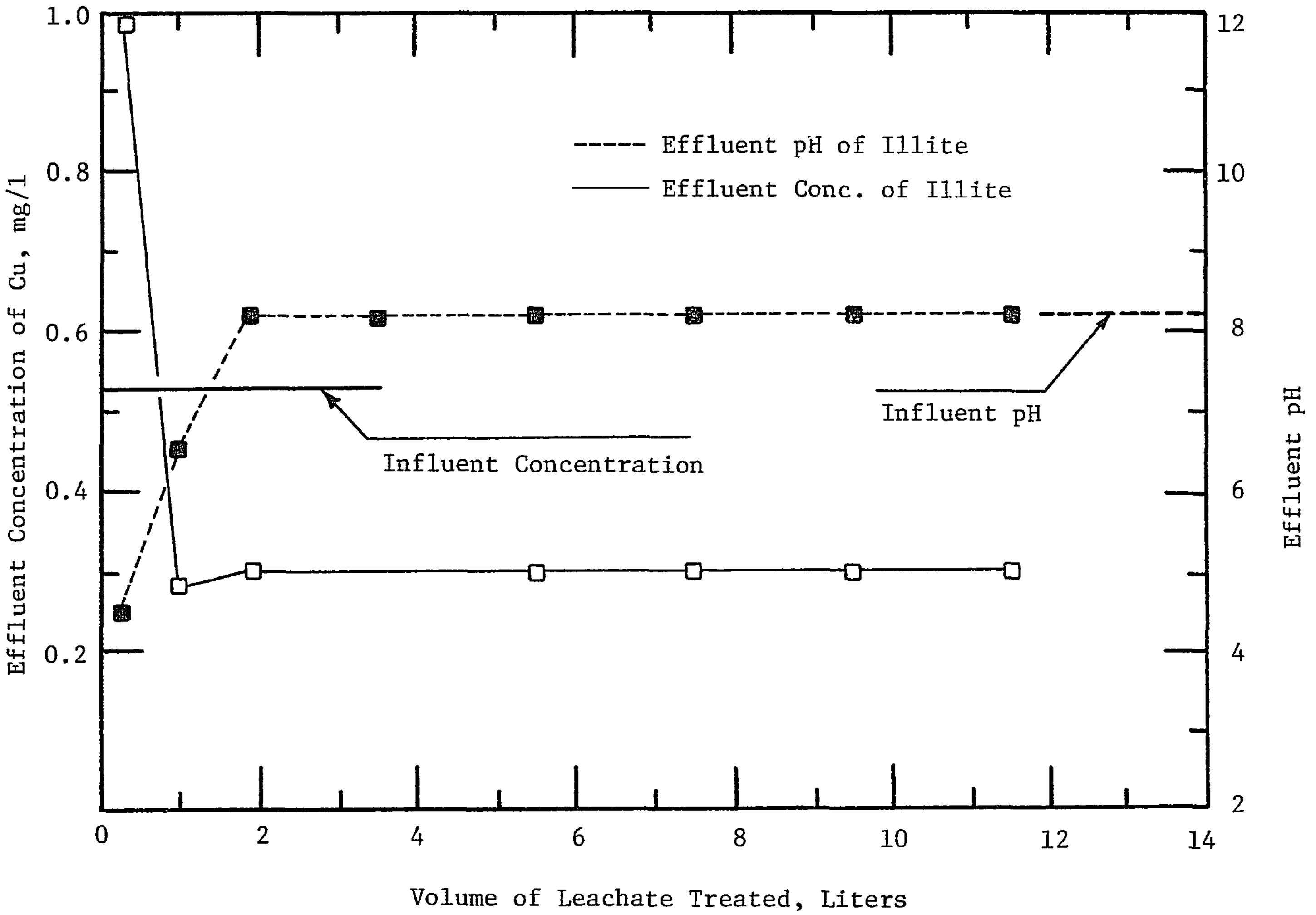

Figure 13. Effluent Cu Concentration and pH Profile of Illite in Lysimeter
(Alkaline Metal Finishing Sludge Leachate)

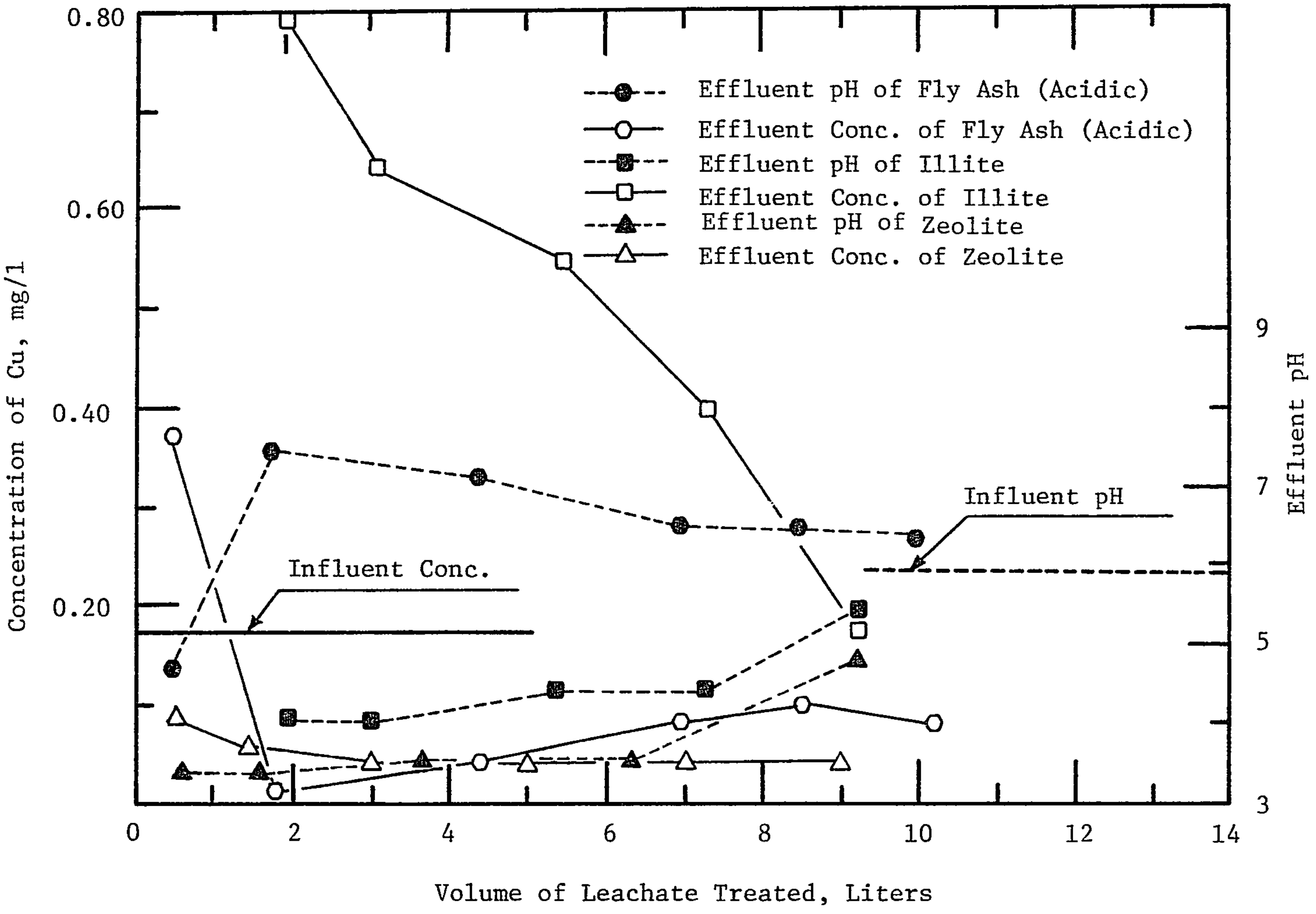

Figure 14. Effluent Cu Concentration and pH in Lysimeter (Acidic Petroleum Sludge Leachate)

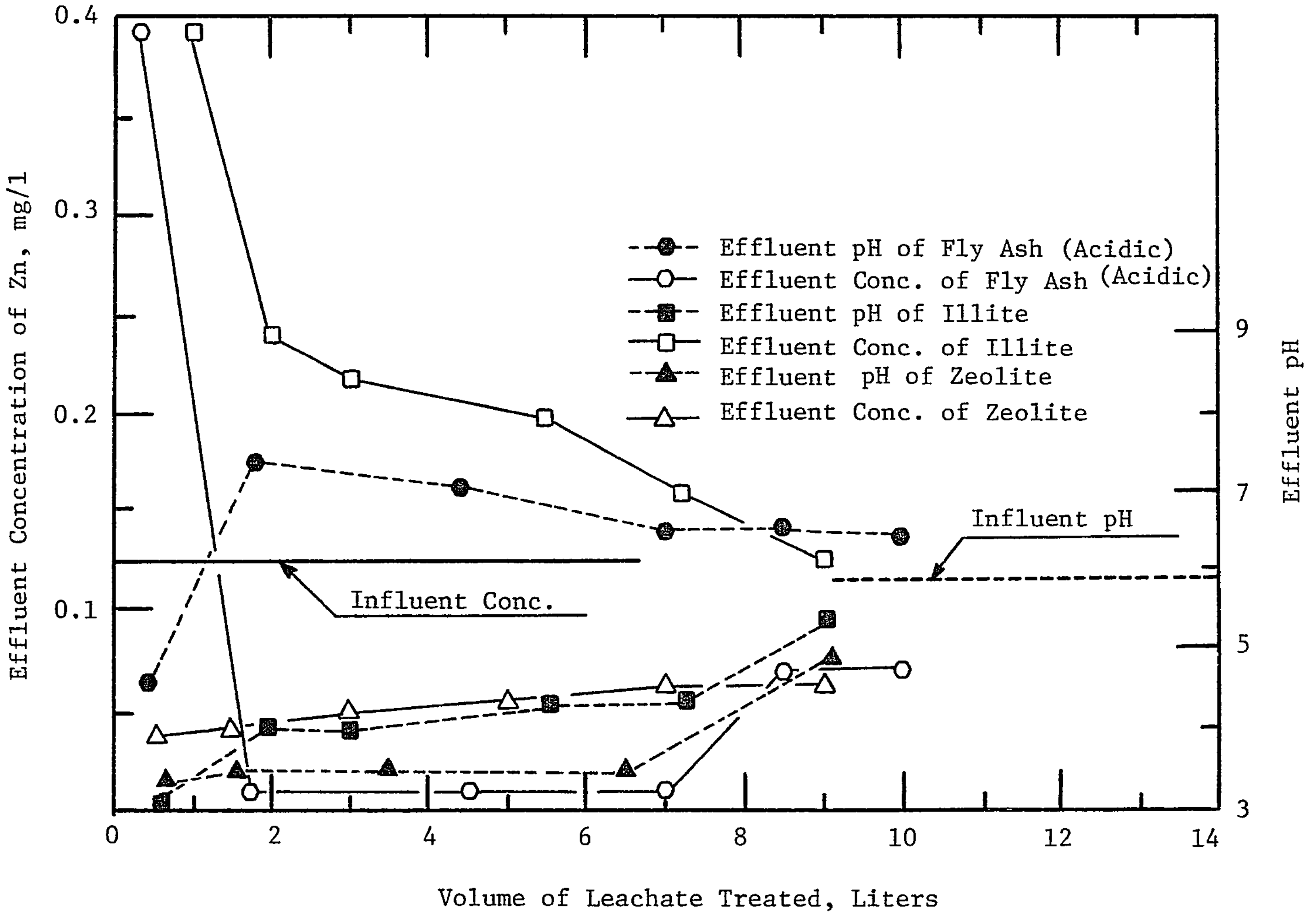

Figure 15. Effluent Zn Concentration and pH Profile in Lysimeter (Acidic Petroleum Sludge Leachate)

that there is sufficient of that pollutant to saturate the sorbent. However, in lysimeter bed reaction, the leachate were passed through sorbent until breakthrough occurred. As a result, sufficient amount of specified constituents were removed by sorbent. Consequently, the maximum removal of pollutants by specified sorbents could be attained in gravitational-bed flow but not in batch reaction under the condition used in this investigation.

4-4 RESULTS OF THE VELOCITY EFFECT (LYSIMETER STUDY)

The velocity of the leachate through the sorbent bed in lysimeters also was found to influence the removal of the cations, anions and organics in the leachates. It did not affect the total amount of contaminant that could be removed by a sorbent (sorbent removal capacity), but it did define the volume of leachate that could be treated with maximum removal of the contaminant. These phenomenon is observed when neutral calcium fluoride sludge leachate was passed through four lysimeters that contained different amounts of illite.

The fluoride and COD concentrations in the effluent were monitored until breakthrough was achieved. These results are shown in Figures 16 and 17, where the fraction of fluoride and COD remaining in the lysimeter effluent is plotted against the volume of leachate treated per gram of illite used. Here it is seen that, as the velocity of the leachate decreases, the volume of effluent that contains minimal amounts of fluoride and COD increases.

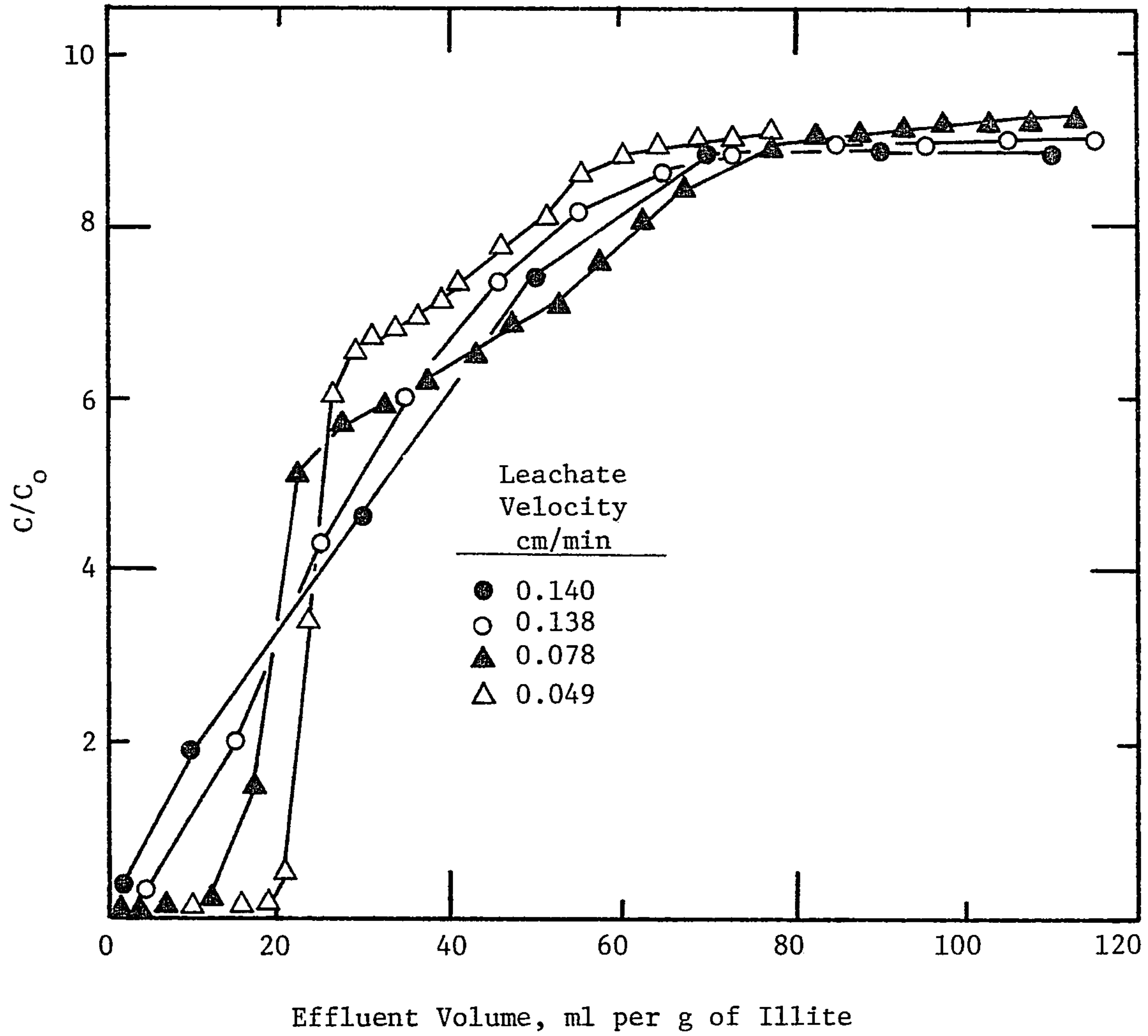

Figure 16. Effect of Leachate Velocity on the Removal of Fluoride in Calcium Fluoride Sludge Leachate

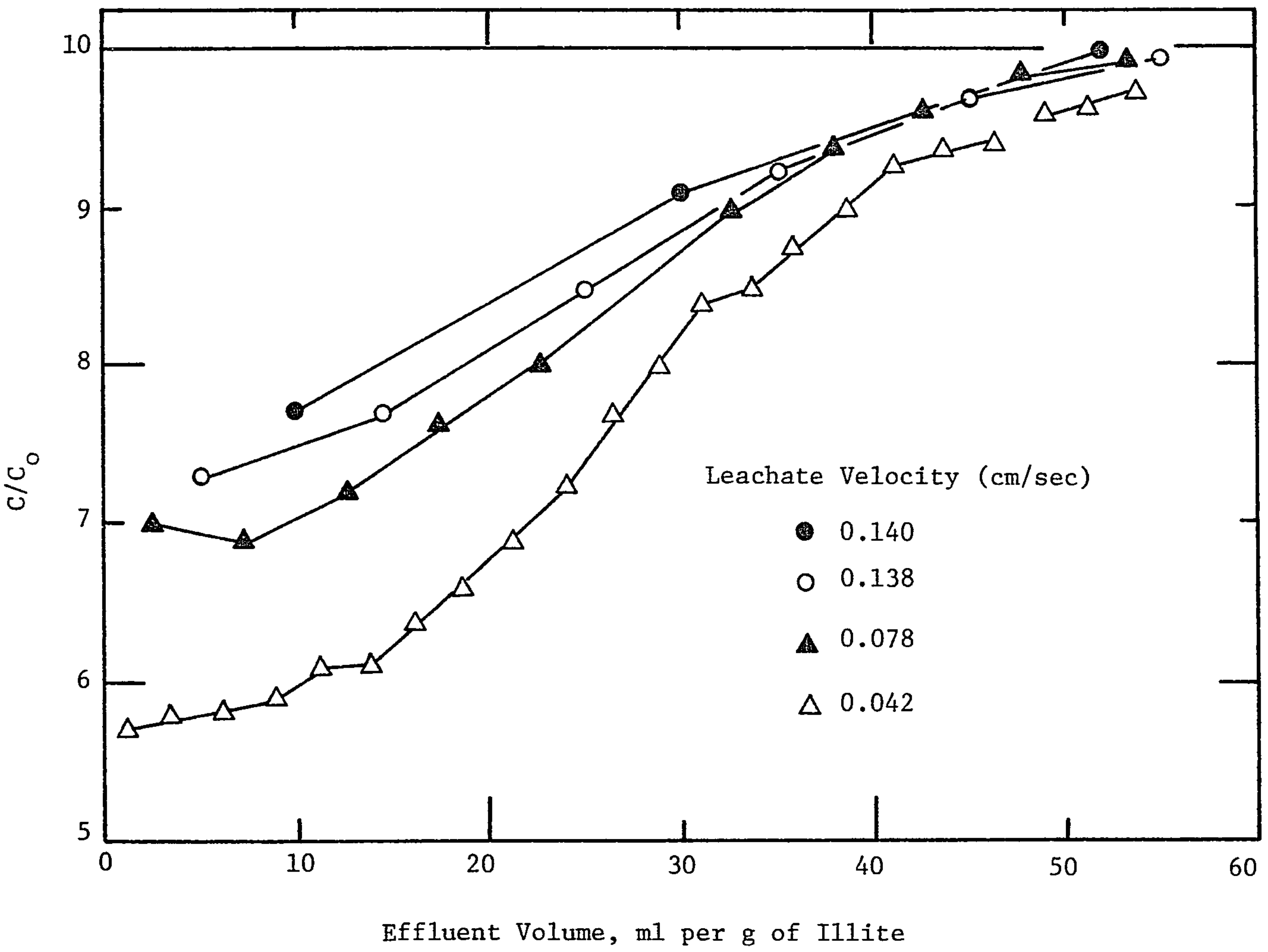

Figure 17. Effect of Leachate Velocity on the Removal of COD in Calcium Fluoride Sludge Leachate.

The sorbent removal capacities, however, are independent of the velocity of the leachate through the sorbent bed. For example, different velocities were found to have no significant effect on the sorbent removal capacity exhibited by the illite for fluoride and COD removals (see Table 16).

TABLE 16

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 µg/g	Sorbent Capacity for COD µg/g
0.140	190	185
0.138	186	192
0.079	179	198
0.042	175	216

An examination of the curves in Figure 16 reveals that the optimum velocity for treating the largest volume of leachate. With a minimum level of fluoride in the effluent should be less than 0.042 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 C/C_o to breakthrough.

4-5 SELECTION OF SORBENT COMBINATIONS

Since there is no single sorbent found to be able to remove all the measurable contaminants present in the leachates (see Table 15), a study of using combinations of various specific sorbents to treat the leachates was undertaken.

The combination of "illite, acidic and basic fly ashes, and zeolite" appears to be the most effective for treating the neutral leachate, and "illite, kaolinite, and zeolite" for the basic leachate, and "illite, vermiculite, and zeolite" for the acidic leachate (see Table 15).

The above combinations, which are effective in treating one leachate, can also be used to treat the other leachates. However, optimum removal of a specific constituent for a given weight of sorbent cannot be achieved because the sorbent capacities are influenced by the pH of the leachate. Thus, a sorbent such as illite, which is the most effective in removing fluoride in the acidic and neutral leachates, could also be used for removing fluoride in the basic leachate. However, it would be less effective than kaolinite which exhibits favorable fluoride ion removals under alkaline conditions (see Table 15).

The removal capacities exhibited by the most effective natural sorbents for the removal of the cations, anions and organics are comparable to those achieved by the more expensive refined sorbents (i.e. activated alumina and activated carbon) in all cases with the exception of the removal of the fluoride ion from a basic leachate (see Table 17). Here, the sorbent capacity exhibited by the activated alumina was some four times that exhibited by the kaolinite.

The above results are significant in that they indicate that 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 these inexpensive sorbents is not required. Thus the capital investment associated with the regeneration equipment can be saved.

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

4-6 RESULTS OF SORBENT COMBINATION STUDY

Although the above results show that the natural clay-fly ash combinations are feasible for treating acidic, neutral and basic industrial sludge leachates, only the combination that provided optimum removals of the cations, anions and organics in calcium fluoride sludge leachate was further investigated. The most effective sorbents (zeolite, acidic and basic fly ashes and illite) were combined in different proportions in a layered system and their

TABLE 17

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

Ion	Neutral Leachate (Calcium Fluoride)		Basic Leachate (Metal Finishing Sludge)		Acidic Leachate$^{(*)}$ (Petroleum Sludge)	
Ca	Zeolite	(5054)	Illite	(1280)	Zeolite	(1390)
	Act. Alumina	(6140)	Act. Alumina	(737)	Act. Alumina	(200)
	Act. Carbon	(357)	Act. Carbon	(212)	Act. Carbon	(128)
Cu	Zeolite	(8.2)	Zeolite	(85)	Zeolite	(5.2)
	Act. Alumina	(2.9)	Act. Alumina	(6.2)	Act. Alumina	(.35)
	Act. Carbon	(2.0)	Act. Carbon	(16.8)	Act. Carbon	(0)
Mg	Basic Fly Ash	(155)	Zeolite	(1328)	Zeolite	(746)
	Act. Alumina	(514)	Act. Alumina	(495)	Act. Alumina	(107)
	Act. Carbon	(3.0)	Act. Carbon	(188)	Act. Carbon	(8.6)
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	(175)	Kaolinite	(2.6)	Illite	(9.3)
	Act. Alumina	(348)	Act. Alumina	(11.4)	Act. Alumina	(3.4)
	Act. Carbon	(0)	Act. Carbon	(0)	Act. Carbon	(1.2)
Total CN$^-$					Illite	(12.1)
					Act. Alumina	(0)
					Act. Carbon	(2.4)
COD	Acidic F.A.	(690)	Illite	(1744)	Vermiculite	(6654)
	Act. Alumina	(0)	Act. Alumina	(0)	Act.Alumina	(411)
	Act. Carbon	(956)	Act. Carbon	(1476)	Act.Carbon	(1270)

* Brackets represent sorbent capacity (μg of contaminant removed per gram of sorbent used.

behavior studied in order to define the optimum arrangement for removal of the measurable cations, anions and organics present in this leachate.

Prior to the selection of this layered system to conduct the following sorbent combination study, a complete mix-bed of sorbent combination had been carried out to compare the removal capacities with the layered system. It was found that the layered system has a consistently 40 percent higher removal capacity than those of complete-mix-bed system. This difference of removal capacity is probably due to better pH control in the lysimeter bed for removal of toxic cations and anions. Since we have shown earlier that slightly acidic conditions favor anion removal and slightly alkaline conditions favor cation removal, the anions would be removed more effectively first in the upper layers, followed by the cation removals in the lower layers provided that the acidic sorbents are placed in the upper layers and basic sorbents are placed in the bottom layers.

The two sorbent combinations selected were: (a) illite, acidic and basic fly ashes and (b) illite, acidic fly ash and zeolite. These were placed in lysimeters in a layered system using a weight ratio of 1:1:1 or 2:2:1, with the illite being the top layer followed by acidic fly ash or visa versa and either basic fly ash or zeolite forming the bottom layer. The basic fly ash or zeolite was placed at the bottom 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 (see Figures 18 and 19). Both the basic fly ash and zeolite showed zinc and copper removal during the initial period when these ions are leached from the illite and acidic fly ash.

The results obtained from the use of illite and acidic fly ash in the top layer indicates that the sorbent combination of illite, followed by acidic fly ash and basic fly ash (in the weight ratios of 1:1:1) generally shows greater sorbent capacities than the sorbent combination of the acidic fly ash, illite and basic fly ash (in the weight ratio of 1:1:1; see Table 18).

TABLE 18

REMOVAL CAPACITIES[1] OF COMBINED SORBENTS IN LYSIMETER FOR NEUTRAL CALCIUM FLUORIDE SLUDGE LEACHATE

Measured Parameters[2]	Description	I+Fa+Fb 1:1:1	Fa+I+Fb 1:1:1	I+Fa+Fb 2:2:1	I+Fa+Z 2:2:1
Ca	Sorbent Capacity	0	0	0	0
Mg	Sorbent Capacity	849	528	515	866
Zn	Sorbent Capacity	5.9	7.2	6.1	9.5
F^-	Sorbent Capacity	110	105	128	148
CN^-	Sorbent Capacity	1.3	1.5	3.9	1.7
COD	Sorbent Capacity	199	133	241	218

Remarks: (1) Sorbent Capacities are expressed in μg of contaminant removal per gram of sorbent used. I = Illite, Fa = Fly Ash (Acidic), Fb = Fly Ash (Basic), Z = Zeolite.

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

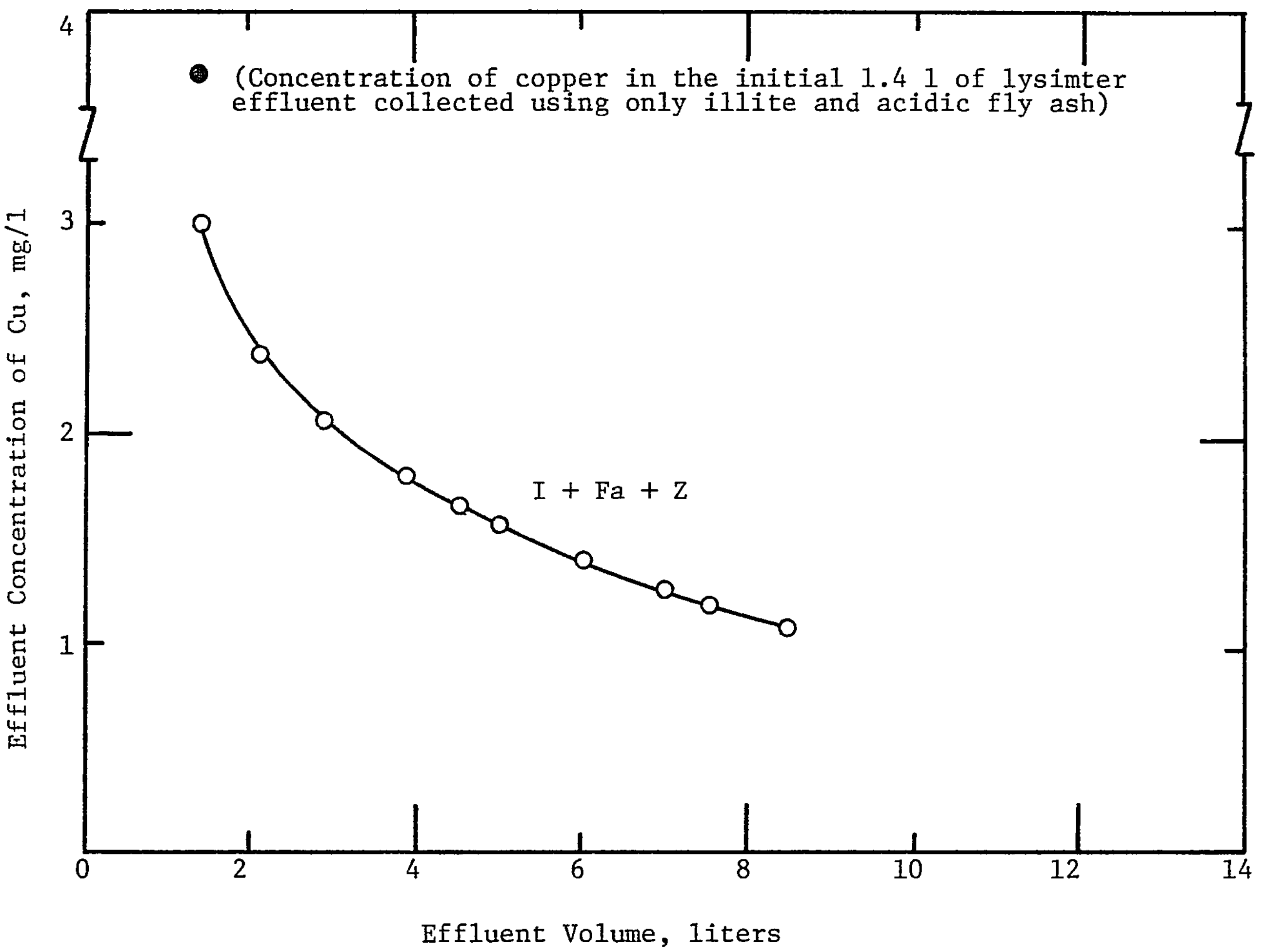

Figure 18. Control of Copper Leaching from Illite and Acidic Fly Ash Using Zeolite.

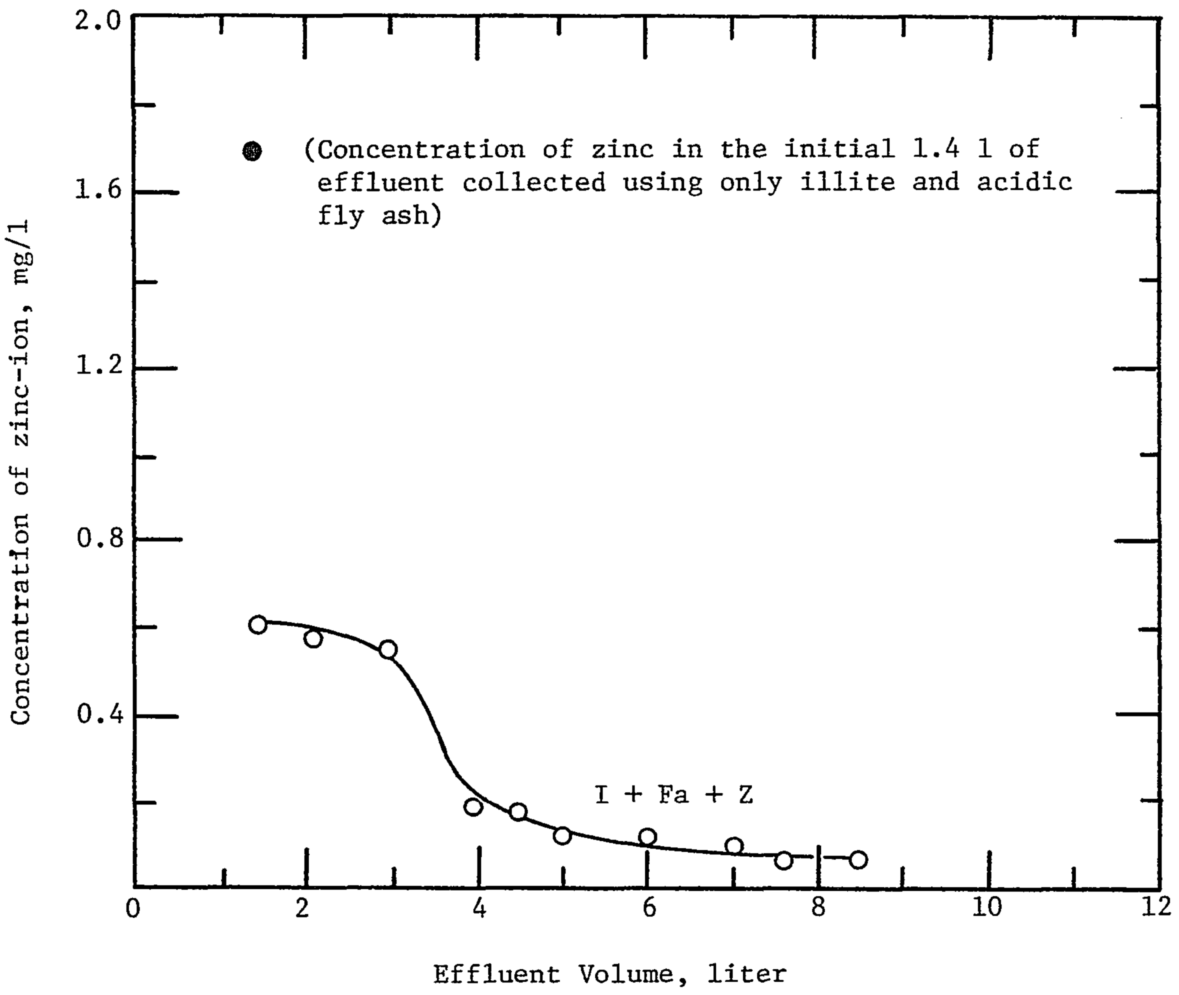

Figure 19. Control of zinc leaching from illite and acidic fly ash using zeolite

With the exception of total cyanide, the sorbent removal capacity exhibited by the illite, acidic fly ash and zeolite (2:2:1) was the most effective for treating all the measurable contaminants in the calcium fluoride sludge leachate. The next best removal capacity was shown by the illite, acidic and basic fly ashes (2:2:1) combination. In addition, the use of zeolite or basic fly ash as bottom layer in the 2:2:1 sorbent combination minimizes the initial leaching of copper and zinc. This initial leaching amounted to 4 ppm copper and 1.7 ppm zinc in the first 1.4 liters of effluent collected. This occurs only when the illite and acidic fly ash combination was used in the lysimeter. When zeolite is used as the bottom layer, the copper and zinc concentrations were reduced from 4 ppm and 1.7 ppm to 0.3 ppm and 0.6 ppm, respectively, in the initial 1.4 liter of effluent collected from the lysimeters (in the weight ratio of 2:2:1 of illite, acidic fly ash and zeolite, see Figures 18 and 19). Basic fly ash, when used in combination with the illite and acidic fly ash, reduces the copper and zinc concentrations from 4 ppm and 1.7 ppm to 1 ppm and 0.6 ppm, respectively.

4-7 RESULTS OF PILOT STUDY

Since the combination of illite, acidic fly ash and zeolite (2:2:1) showed the most promise for treating the nautral calcium fluoride sludge leachate in the laboratory, two large vertical lysimeters were set up outdoors with sufficient sorbent to treat 140 gallons of neutral calcium fluoride sludge leachate. The principal objective of the pilot study program was to obtain a long-term evaluation of the behaviors of packed-bed sorbents with a calcium fluoride sludge leachate. The pilot study used a mixed-media filtration for the removal of suspended solids. This pretreatment system showed very good efficiency for removing the suspended solids (99 percent) from leachate and is comparable to a laboratory vacuum filtration (100 percent) using a membrane filter paper. The sludge used in this phase of study was collected at three different times over a period of one year. This was done in order to study the effect of variations in the composition in the leachate on the removal process due to changes in plant production and scheduling. The pilot-scale lysimeter studies were designed for fluoride removal. The combination sorbent removal capacity for fluoride (see Table 18) is defined as the amount of sorbent required in the lysimeters. The permeability of the clay fractions were adjusted by admixing with inert sand to obtain a leachate velocity of 0.01 cm/min through the sorbent bed. This leachate velocity was selected because it is 4 times smaller than the 0.042 cm/min which was shown earlier to approach the required maximum leachate velocity needed to treat the largest volume of leachate with maximum removal of fluoride ion and should therefore insure adequate fluoride removal. The results of this study are shown in Figures 20 through 25.

The concentration of calcium in the leachates of three different collecting times that was passed sequentially through these lysimeters were 309, 115, and 228 mg/1 (see Figure 20). The illite,

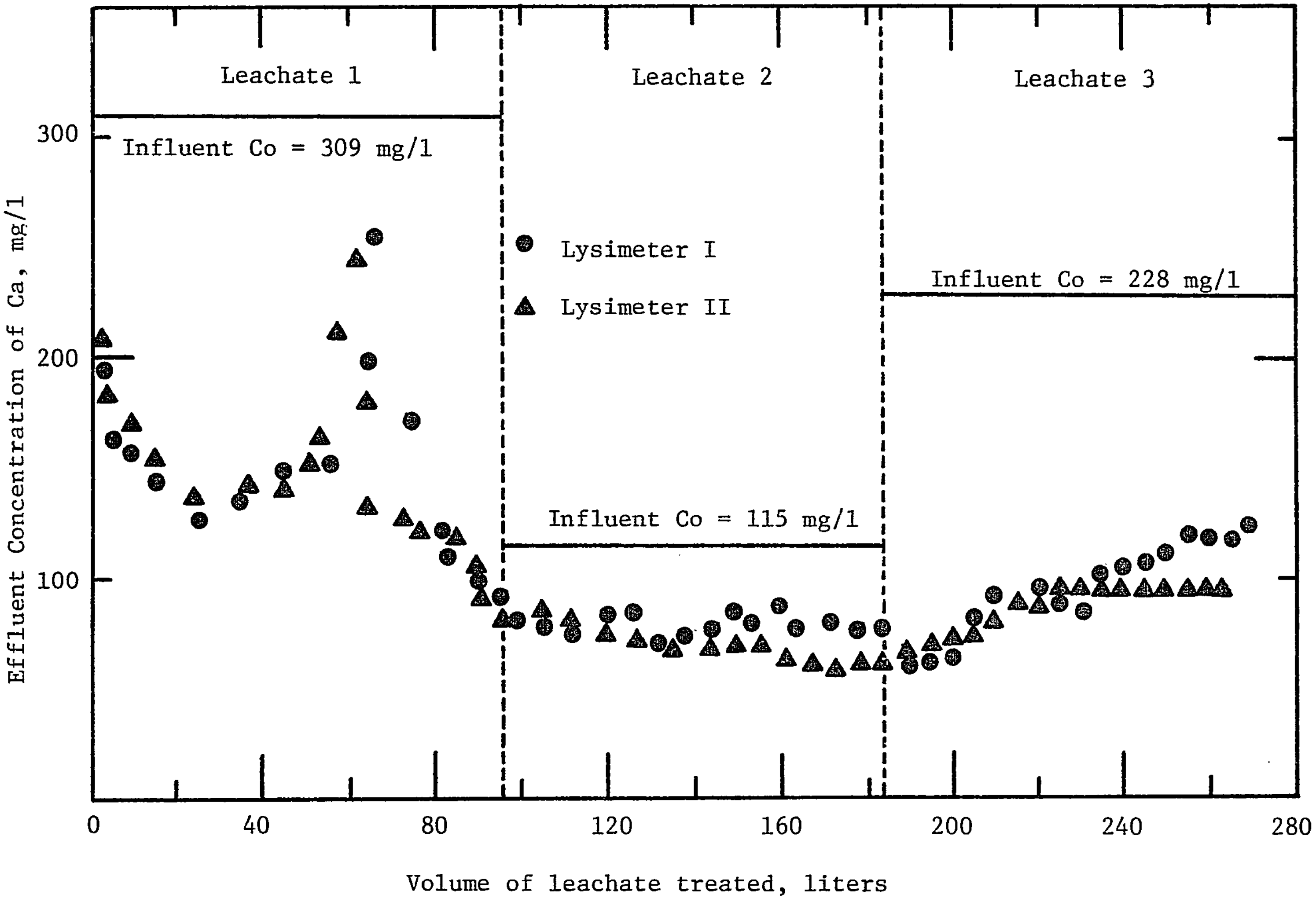

Figure 20. Calcium effluent concentration in Pilot Scale Lysimeter Study

acidic fly ash, zeolite combination (2:2:1) reduced the effluent concentrations to approximately 80 mg/l. During the initial addition of the leachate, poor removal of calcium was observed. This was due to channelling 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. However, elimination of the channelling resulted in calcium concentrations being repidly reduced to 80 mg/l. For the case of copper treatment, the copper concentrations in the three leachates, 0.12, 0.10, and 0.07 mg/l were reduced to 0.04 mg/l (see Figure 21). Also, the leaching of copper from the illite and acidic fly ash was effectively controlled by the zeolite. The copper concentration in the effluent initially was 0.08 mg/l, which is well below the influent concentration of 0.12 mg/l.

The effect of channelling on the copper removal could again be seen by the sudden rise in the effluent concentration after about 40 liters of leachate was treated. However, once the channelling was minimized, the copper concentration in the effluent was again reduced to 0.04 mg/l. This channelling effect on the removals emphasizes the need for proper dispersion of the leachate stream through the bed.

The removal of the magnesium by illite, acidic fly ash, zeolite combination (2:2:1) showed a dependency upon the influent concentration (see Figure 22). Influent magnesium concentration of 29.6 mg/l, 75.2 mg/l, and 18.5 mg/l gave effluent concentration of

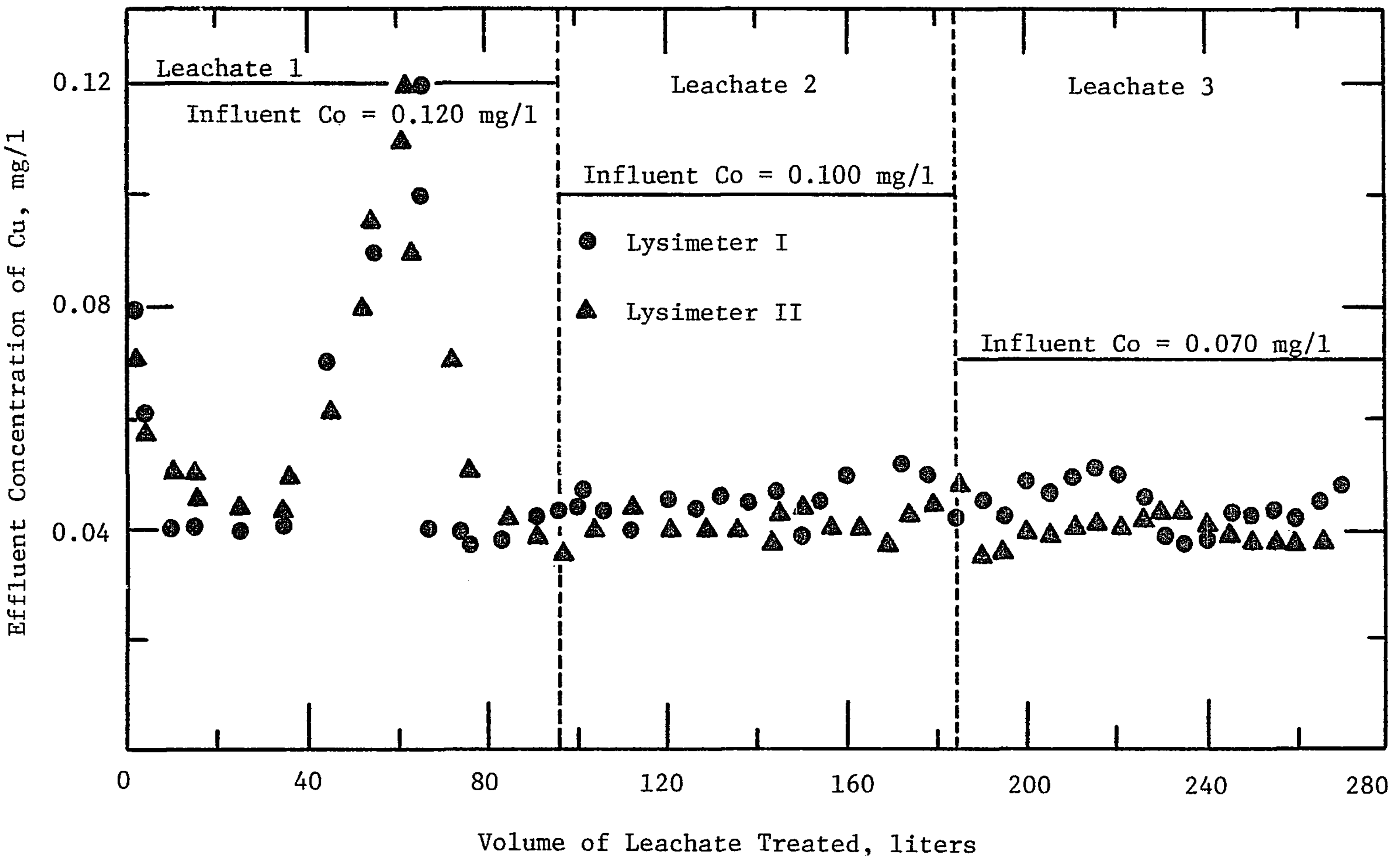

Figure 21. Copper Effluent Concentration in Pilot Scale Lysimeter Study

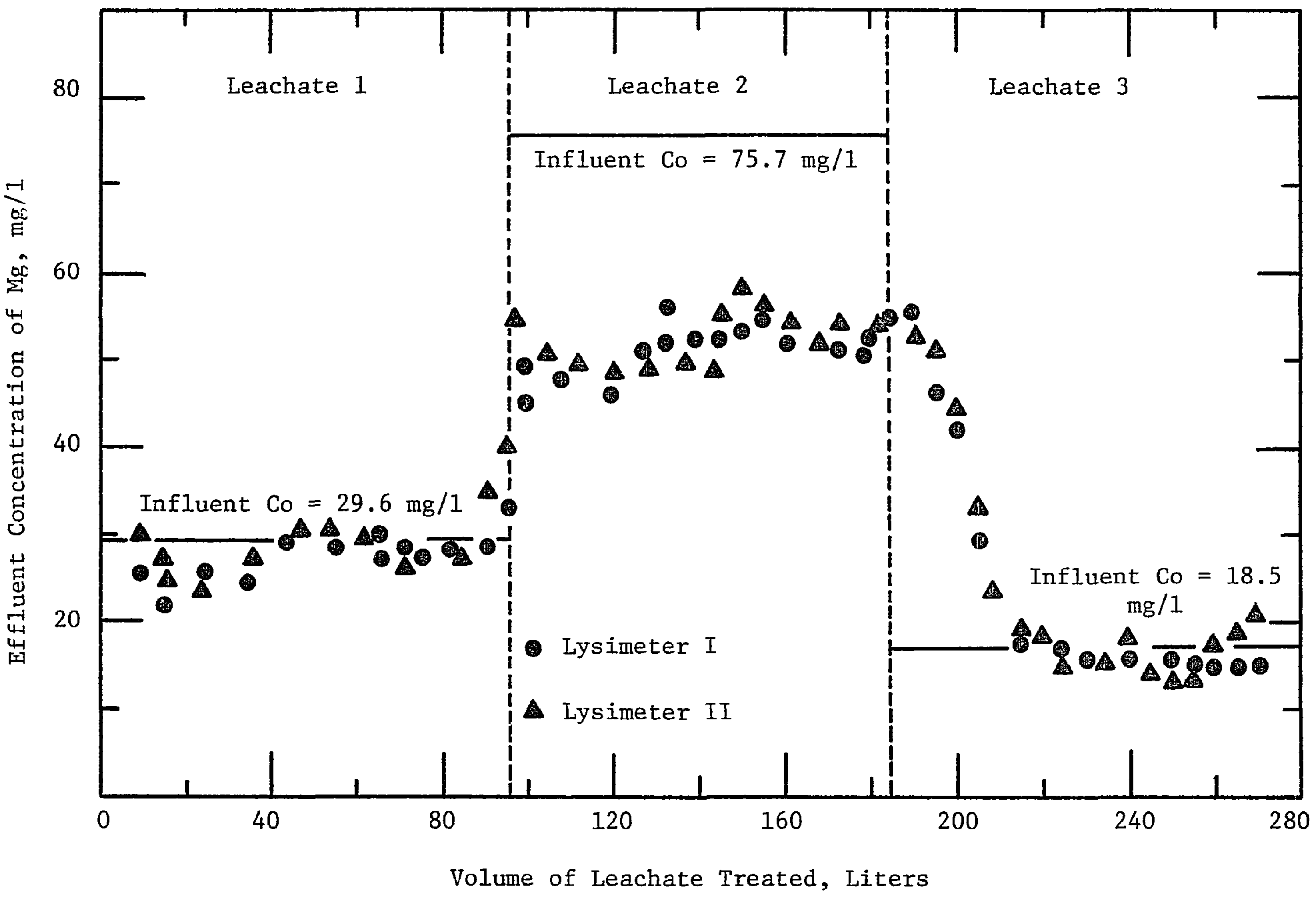

Figure 22. Magnesium Effluent Concentration in Pilot Scale Lysimeter Study

approximately 25 mg/l, 53 mg/l,and 16 mg/l,respectively. One would expect results similar to that observed for the calcium and copper removals which appeared to be independent of the influent concentration. The explanation for these results are unclear at this time.

Effective removal of fluoride was also achieved with this sorbent combination. This was expected since the amount of sorbent and the leachate velocity used were designed for fluoride removal. An effluent concentration of 1 mg/l was achieved with an influent concentration which varied from 10.2 to 15.3 mg/l (see Figure 23). Again, it was shown (as was the case for the calcium and copper results) that the concentration of fluoride ion in the treated leachate was independent of the influent concentration. This also appeared to be true for the removal of the cyanide, where the effluent was significant (i.e., 0.25 and 0.37 mg/l in the first two leachates). The sorbents reduced these concentrations to approximately 0.06 mg/l (see Figure 24). However, 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 could be reduced to with this sorbent combination appeared to be about 0.06 mg/l. However, if the illite, acidic fly ash and basic fly ash sorbent system (2:2:1) was used instead of the illite, acidic fly ash, zeolite combination (2:2:1), the effluent concentration of cyanide would probably be significantly lower than 0.06 mg/l. This is because a greater sorbent removal capacity is achieved with the non-zeolite combination (3.9 mg/g) than the zeolite combination (1.7 mg/g)(see Table 18).

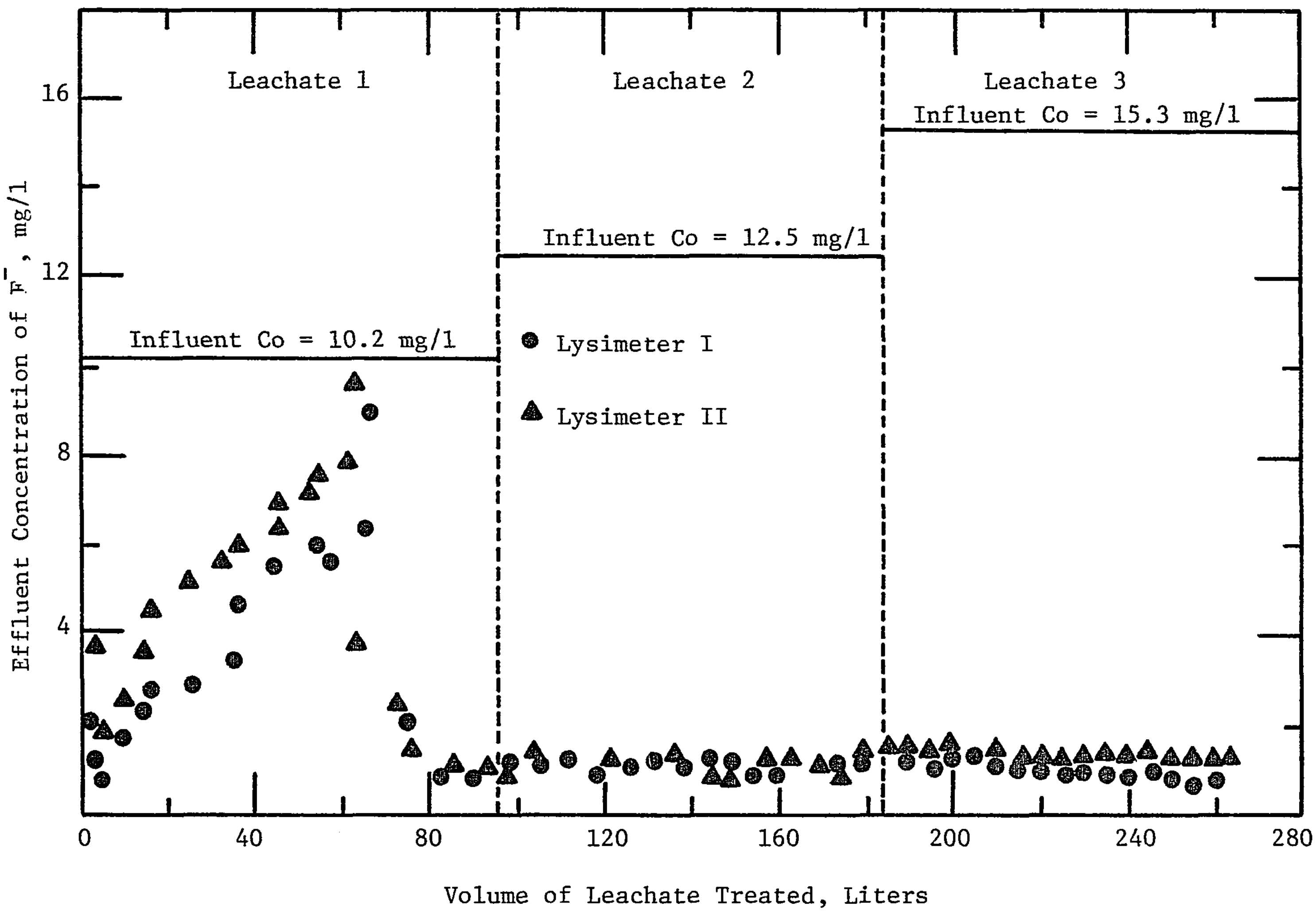

Figure 23. Fluoride Effluent Concentration in Pilot Scale Lysimeter Study

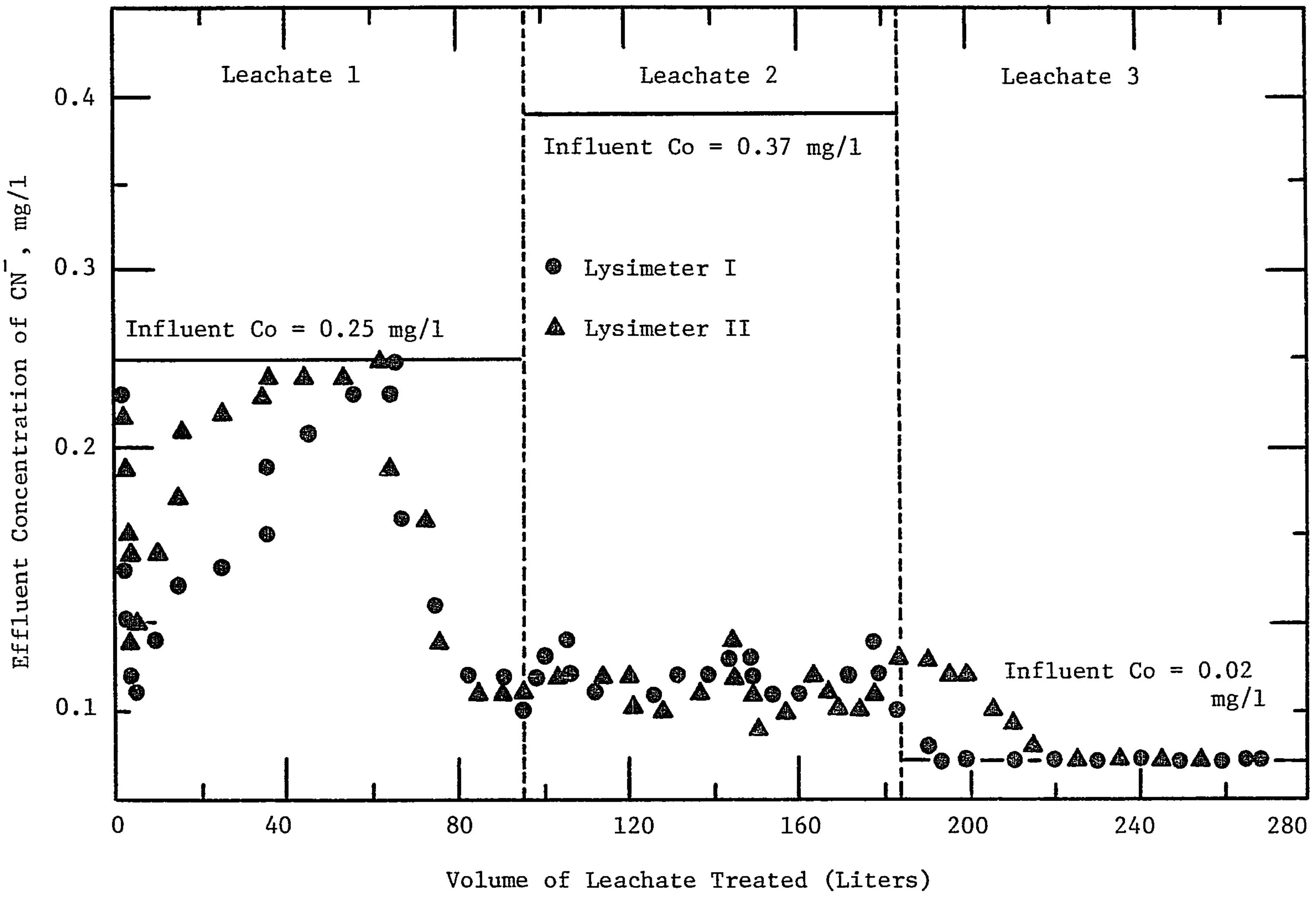

Figure 24. Cyanide Effluent Concentration in Pilot Scale Lysimeter Study

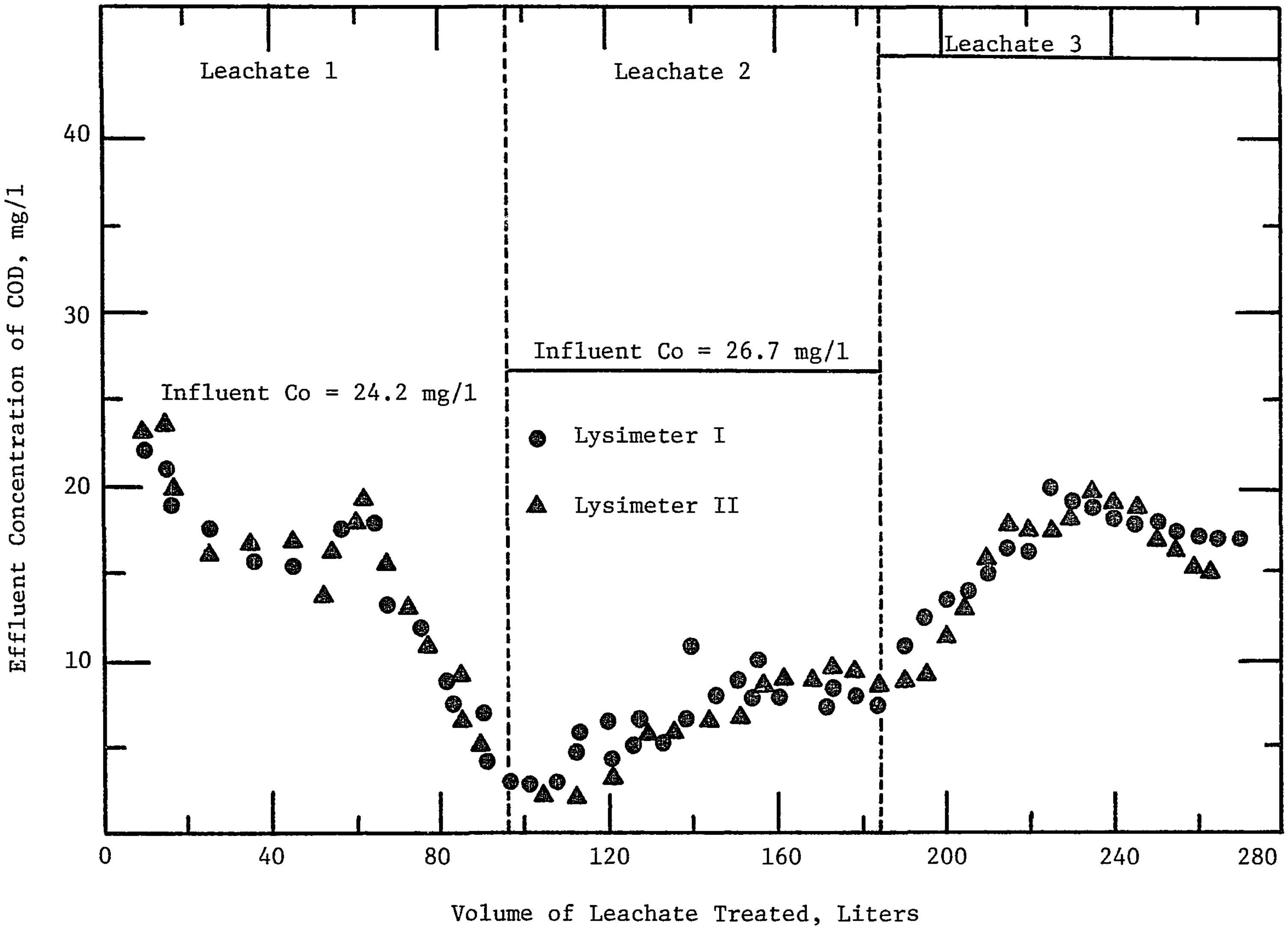

Figure 25 . COD Effluent Concentration in Pilot Scale Lysimeter Study

The minimum effluent concentration of organics achieved with the illite, acidic fly ash, zeolite combination (2:2:1) appears to be dependent on the organic influent concentration. For example, the concentration of organics in the influent increased from 24.2 mg/l 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 (see Figure 25). The overall results indicate that the illite, acidic fly ash and zeolite combination is not only extremely effective in removing the cations and anions, but also the organics present in the neutral calcium fluoride sludge leachate.

OVERVIEW

In Chapter I, it showed that the composition or pH of leachate could be one of the most important parameters in defining a treatment system which uses clay sorbents to treat the leachate contaminant in landfill. The above laboratory and pilot lysimeter studies, however, consistently indicated that the optimum removal of pollutants can be achieved by regulating the pH and flowing velocity of leachate through the sorbent bed, and the composition of sludge leachate does not appear to be a factor. Therefore, with certain specific removal capacities, the natural sorbents encountered in this study can also be used to treat specific pollutants present in other types of sludge leachate provided that the pH and the flowing velocity of leachate are optimized.

V. APPLICATION OF RESULTS TO CONCEPTUAL DESIGN OF DISPOSAL SITES

In order to demonstrate the utilization of experimental results obtained from previous chapters, a conceptual design for treating the calcium fluoride sludge leachate by sorbent system is developed in this chapter.

The results of the pilot study indicate that the use of the combination sorbent capacity (0.148 mg of fluoride removed per gram of sorbent used) (see Table 18), and a leachate velocity of 0.01 cm/min through the illite, acidic fly ash, zeolite combination (2:2:1) is effective in the treatment of all measurable constituents of interest (i.e., Ca, Mg, Cu, F, CN and organics) in 140 gallons of leachate without breakthrough of any of the constituents occurring. In view of these results, two approaches can be proposed for the treatment of leachate. This leachate is assumed to originate from a landfill (205' x 205' x 12') that is designed to contain an estimated 10 years production (27,400 tons) of calcium fluoride sludge. The 12-foot depth is presently being used in a storage pit at the plant where the sludge is generated.

The first approach involves lining the sludge pit with an impermeable liner to prevent ground water intrusion (see Figure 26, Appendix I). A one foot 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 illite, acidic fly ash, and zeolite bed (2:2:1). The dimension of this bed is 28' x 28' x 9'. The bed will contain sufficient sorbent to treat one year's production of leachate at a rate of 7.5 l/min without ponding and still maintain a maximum leachate velocity through the bed of 0.01 cm/min (see calculation in Appendix I). The 7.5 l/min flow rate was determined by assuming an annual average rainfall of 40 inches and that all the rainfall which falls upon the landfill will become leachate.

The second approach 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-foot layer of the illite, acidic fly ash, and zeolite sorbent combination (2:2:1). This layer will be covered with a 1-foot layer of filter media to prevent clogging of the sorbent bed by the suspended solids in the leachate (see Figure 27, Appendix I). The 180' x 180' x 2' layer of sorbent combination will be able to treat 10 years of leachate production containing an average 10 mg/l of fluoride at the flow rate of 7.5 l/min (see calculation in Appendix I). This approach, however, will be used in areas where the ground water table is well below the landfill so that ground water intrusion through the sorbent bed into the landfill will not increase the rate of leachate production beyond 7.5 l/min.

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

The "illite, acidic fly ash, and basic fly ash" sorbent combination (2:2:1), based upon the laboratory studies (see Table 18), offers an alternative for treating the measurable constituents (with the exception of calcium) in the calcium fluoride sludge leachate. The "illite, acidic fly ash, and basic fly ash" combination is a far less expensive approach. If the calcium ion concentration encountered in this leachate (see Table 2) present no significant problems, the sorbent cost for disposing of 1 ton of calcium fluoride sludge decreases to $0.45, with all bed or layer dimensions remaining the same (see calculation in Appendix I). However, there is a disadvantage at the present time to using the "illite, acidic fly ash, and basic fly ash" combination as compared with the "illite, acidic fly ash, and zeolite" combination. The supply of basic fly ash from the power plant is somewhat limited.

VI. CONCLUSIONS

An extremely effective but inexpensive system has been developed for the treatment of leachate arising from industrial sludges disposed of in landfills. The combination of, (a) illite, vermiculite and zeolite, (b) illite, acidic fly ash and zeolite, (c) illite, kaolinite and zeolite have been found to be the most effective in a layered system for removing cations, anions and organics in acidic petroleum sludge leachate, neutral calcium fluoride sludge leachate and basic metal finishing sludge leachate, respectively. The capacities exhibited by these sorbents for the removal of contaminants in these three leachates are comparable to those exhibited by activated alumina and activated carbon. The combinations of natural clay and fly ash were used because no single sorbent could 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 were used in a layered bed can 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 initially induce slightly acidic conditions into the leachate were placed at the top of the layered system followed by those sorbents which induce slightly alkaline conditions in the leachate. This resulted 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. This favors the removal of both the cations in the leachate and the heavy metal cations which are initially leached from specific sorbents at leachate conditions below pH of 6. Either zeolite or basic fly ash was found to be 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 organic, which was removed by a single sorbent, was 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 could be treated with maximum removal was regulated by the velocity of leachate through the sorbent bed. This leachate velocity could be regulated by adjustment of the sorbent bed height and defines the leachate volumetric flow rate through sorbent bed, under specified hydraulic conditions. It can also be effected by varying the amount of inert material added to the clays in order to regulate their permeability, or by varying the particle size of the sorbents in the bed.

With the exception of magnesium, the "illite, acidic fly ash, and zeolite" sorbent combination (in the weight ratio of 2:2:1) was found to be effective in the treatment of the measurable contaminants in a calcium fluoride sludge leachate using a pilot scale. A calcium ion concentration of over 300 mg/l in the leachate was reduced to 80 mg/l, copper ion concentration of 0.12 mg/l was reduced to 0.04 mg/l, the fluoride ion concentration was reduced from 15 mg/l to 1 mg/l, the total cyanide was reduced from 0.37 mg/l to about 0.06 mg/l and the COD was reduced from about 45 mg/l to 15 mg/l. Magnesium ion concentration was reduced from 76 mg/l down to only about 53 mg/l. In addition, with the exception of the magnesium and the COD, the resultant effluent concentration were found to be independent of influent concentrations.

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 ten year period of working the landfill was estimated to be $1.37 per ton of sludge disposed of in the landfill. This cost is based upon an annual rainfall of 40 inches and assumes that all of the rainfall that fall upon the landfill becomes leachate. However, this cost could be reduced to only $0.45 per 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 upon the laboratory lysimeter results, the "illite, acidic fly ash, and basic fly ash" combination also appears to be equally promising for the treatment of the contaminants present in the leachate.

VII. RECOMMENDATIONS

While this study has developed an effective sorbent treatment process of controlling hazardous leachate from industrial sludge landfills, there are still many other areas which need further investigations. To assist in further developing a fully commercial scale system based on this sorbent system, the following recommendations are considered:

a) By passing leachate upward through a bed of sorbent at a velocity sufficient to suspend the solid particles of sorbent bed problems of fouling, plugging and increasing pressure drop can be eliminated. It is possible to use sorbent of smaller particle size in an expanded bed, and thus take advantage of the high sorption rate which obtain for smaller particles in an upward flow bed.

b) 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 these constituents were below measurable levels in the leachates that were examined in this study. 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 will provide data for potential users and enable them to set up pilot scale studies in order to obtain the engineering data necessary for field use.

c) A project should be undertaken to demonstrate the use of fly ash-clay sorbent combinations for treatment of industrial sludge leachates containing fluoride ion 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 will be evaluated. The most economical system will be defined for the control of fluoride, cyanide, and heavy metal pollution of ground and surface waters by leachate from the operation of regionalized landfills or specific sites by industry. This system in operation would be available for inspection by other potential users. However, prior to initiation of this project, a pilot scale evaluation of the illite, acidic fly ash and 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 the zeolite combination.

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APPENDIX I.

DESIGN OF SORBENT TREATMENT SYSTEM

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

Annual sludge production estimated by sludge producer:

2740 tons = 2.74×10^{10} g

10 years production = 2.74×10^{11} g

2. Volume of Sludge Pit

Assume the compacted sludge density = 110 $\mathrm{lb/ft^3}$ or 1.76 $\mathrm{g/cm^3}$

Therefore, the sludge pit volume for 10 years = 2.74×10^{10} g/1.7 $\mathrm{gm/cm^3}$

= 1.55×10^{10} $\mathrm{cm^3}$ = 5.49×10^{5} $\mathrm{ft^3}$

3. Calculation of Surface Area of Sludge Pit

Depth of sludge in existing storage pit = 12 ft

Mean surface area required = $(5.49 \times 10^5\ \mathrm{ft^3})/12$ ft

= 3.74×10^4 $\mathrm{ft^2}$

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 (ft) x a (ft)

and bottom dimension = b (ft) x b (ft)

then $(a^2 + b^2)/2 = 3.74 \times 10^4$

$a = b + 12 \times 2$

the top and bottom areas will be:

a x a = 205 ft x 205 ft = 4.20×10^4 $\mathrm{ft^2}$

b x b = 180 ft x 180 ft = 3.24×10^4 $\mathrm{ft^2}$

4. Volume of Sludge Leachate Generated by Rainfall

Assuming the annual rainfall is 40 inches per year, the annual leachate generated is:

$(40/12)^{ft^2} \times 4.2 \times 10^4 = 1.4 \times 10^5$ ft^3 $= 3.96 \times 10^9$ cm^3

Assuming that all the rainfall that falls upon the sludge becomes leachate, the amount of sludge leachate generated in 10 years

$= 1.4 \times 10^6$ ft^3 or 3.96×10^{10} cm^3

5. Total Sorbents Required for Each Year

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

System 1: Using combination (2:2:1) the sorbent removal capacity of fluoride is 0.148 mg/g; therefore, amount of sorbent required annually

$= 3.96 \times 10^9 \times 10^{-3}\ 10 \div 0.148 = 2.68 \times 10^8$ g/yr

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

$= 3.96 \times 10^9 \times 10^{-3} \times 10 \div 0.128 = 3.09 \times 10^8$ g/yr

6. Average Flowrate of Leachate to be Treated

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

7. Required Sorbent Bed Area to Avoid Ponding

$K = Ql/Ah$ (assume $l = h$)

The permeability of clay will be adjusted by mixing with inert material (i.e., sand) to provide a coefficient of permeability $K = 1.8 \times 10^{-4}$ cm/sec (i.e., exhibited by the fly ash)

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

$= 6.97 \times 10^5\ \text{cm}^2 = 750\ \text{ft}^2 = 27.4\ \text{ft} \times 27.4\ \text{ft}$, or 28 ft x 28 ft

8. Volume of Sorbent Bed

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

amount of sorbents = 2.680×10^8 g

sand for illite = 0.429×10^8 g

sand for zeolite = 0.429×10^8 g

Total amount of materials = 3.54×10^8 g

Total Volume = $2.01 \times 10^8\ \text{cm}^3 = 7.10 \times 10^3\ \text{ft}^3$

$= 28\ \text{ft} \times 28\ \text{ft} \times 9\ \text{ft} = 7.06 \times 10^3\ \text{ft}^3$

Packing density = 110 lb/ft^3 or 1.76 g/cm

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

amount of sorbents = 3.09×10^8 g

sand for illite = 4.94×10^7 g

Total amount of materials - 3.58×10^8 g

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

$= 7169\ \text{ft}^3 = 28\ \text{ft} \times 28\ \text{ft} \times 9\ \text{ft}$

$= 7.06 \times 10^3\ \text{ft}^3$

9. Cost of Sorbents

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

Illite cost = \$10/ton

Zeolite cost = \$50/ton

Fly ash cost = \$0

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

$+ 2.68 \times 10^{8} \times 0.2 \times 10^{-6} \times 50 = \$3752$

or \$3752/2740 ton of sludge produced annually

Sorbent cost per ton of sludge = \$1.37

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

Illite cost = \$10/ton

Fly Ash cost = \$0

Total sorbent cost = $3.09 \times 10^{8} \times 0.4 \times 10^{-6} \times 10 = \$1240$

or \$1240/2740 ton = \$0.45/ton of sludge produced annually

Sorbent cost per ton of sludge = \$0.45

DESIGN OF LINER BED

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

total sorbent volume = 7169 ft^3

the depth of sorbent bed = $\frac{7169 \times 10}{180 \times 180} = 2.2$ ft

System 2: Using the illite, acidic fly ash and basic fly ash combination, total sorbent volume = $7.10 \times 10^{3}\ \text{ft}^{3}$

the depth of sorbent bed = $\frac{7.10 \times 10^{3} \times 10}{180 \times 180} = 2.2$ ft

Sorbent Cost

System 1: The illite, acidic fly ash, and zeolite combination

weight of sorbents required for 10 years

Fly Ash (acidic)	= 1072 tons	x $0/ton	=	0
Illite	= 1072 tons	x $10/ton	=	$10,720
Zeolite	= 536 tons	x $50/ton	=	$26,800
TOTAL	2680 tons		=	$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

Fly Ash (basic)	= 620 tons	x 0/ton	=	0
Fly Ash (acidic)	= 1240 tons	x 0/ton	=	0
Illite	= 1240 tons	x $10/ton	=	$12,400
TOTAL	2100 tons			$12,400

Tons of sludge produced in ten years = 27,400

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

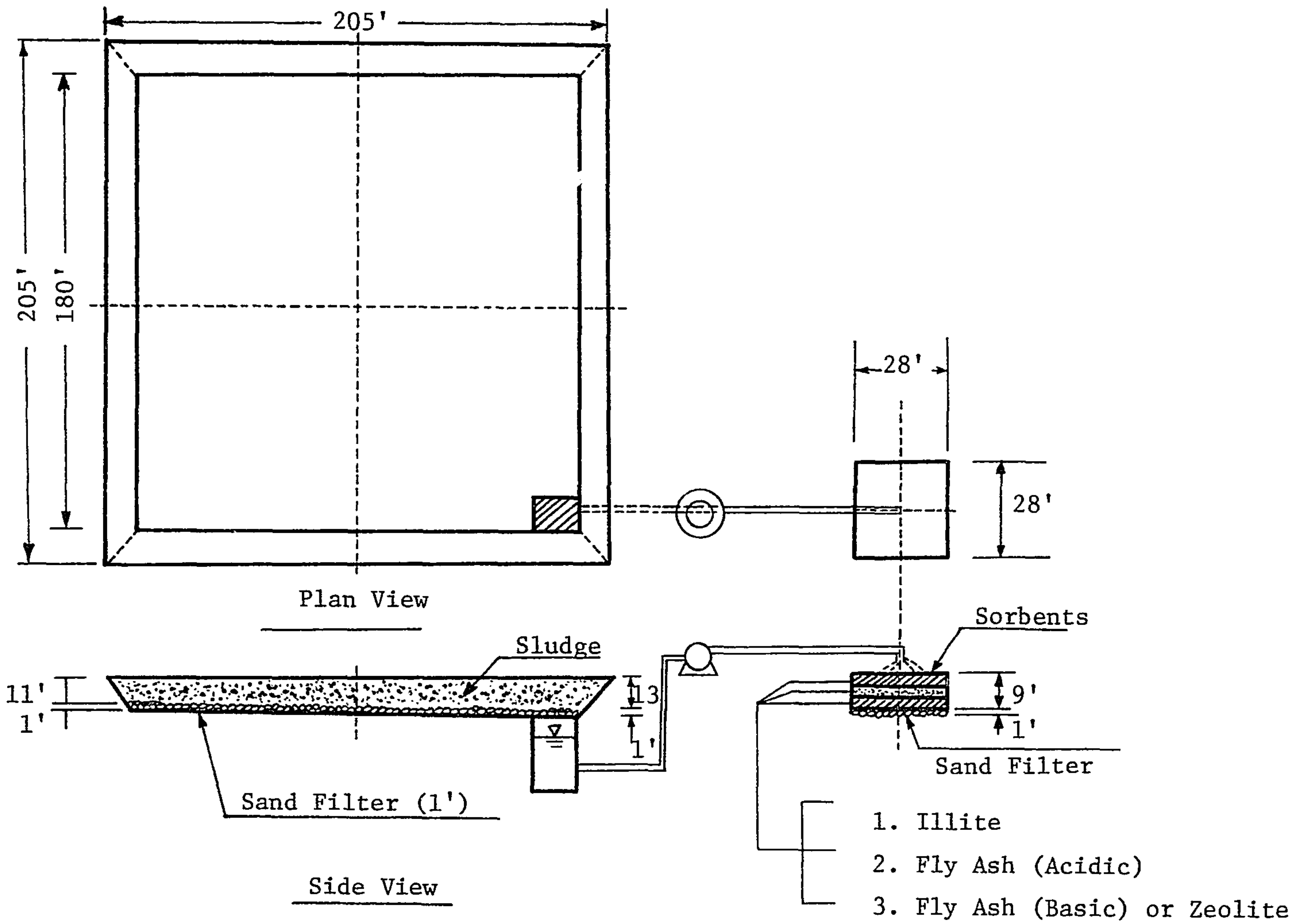

Figure 26. Design of Sorbent Treatment System

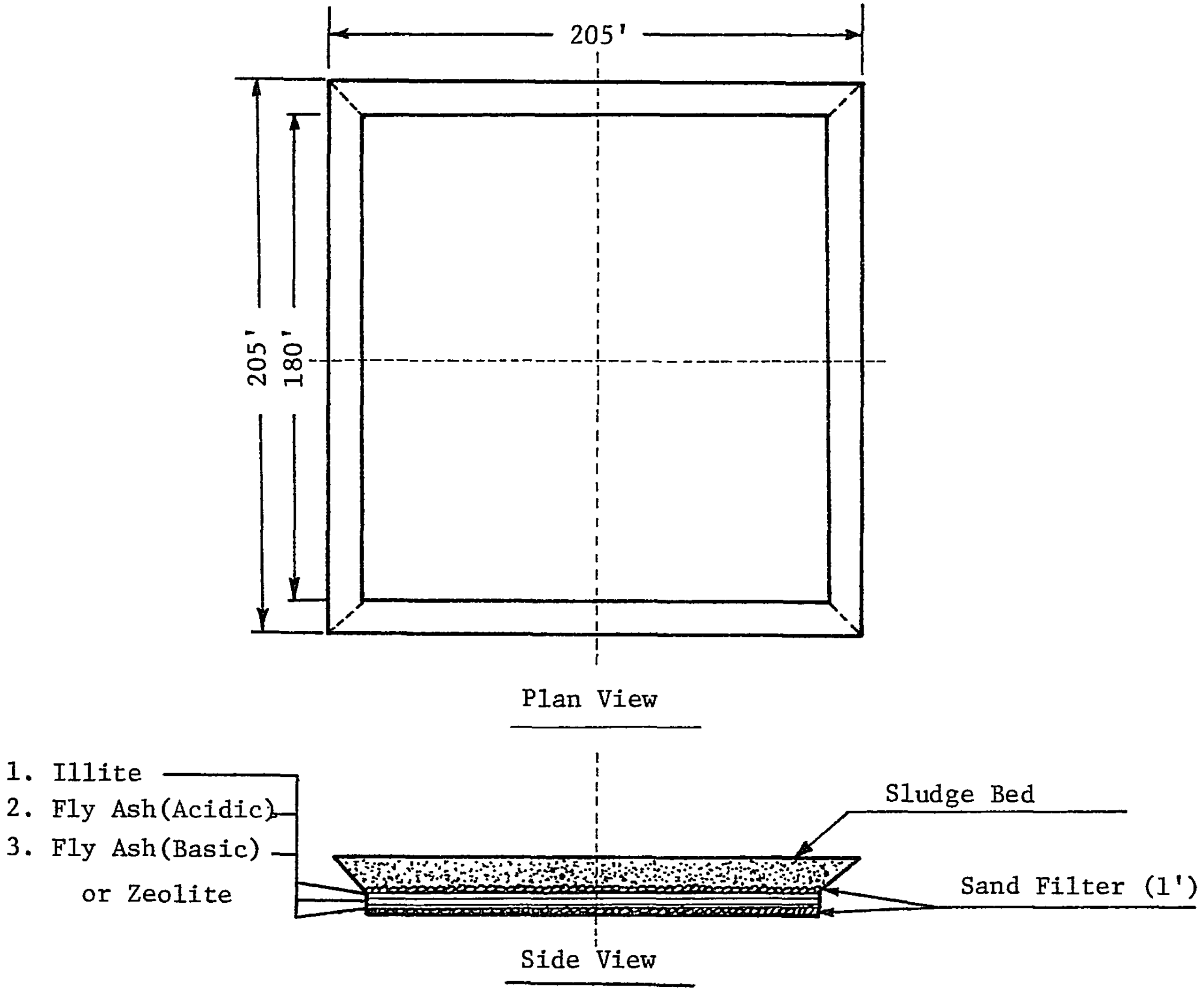

Figure 27. Design of Liner Bed

APPENDIX II

PERMEABILITY CHARACTERISTICS OF SORBENT MATERIALS

	Sorbent Material	e	K_1(cm/sec)	K_2(cm/sec)	K_1/K_2	d_{10}(mm)	Cu	Specific Gravity,G_s
	A. Calcium Fluoride Sludge Leachate							
1.	Illite (20%) mixed with Ottawa Sand (80%)	0.52	2.2×10^{-5}	3.7×10^{-5}	0.6	0.016	37.5	2.68
2.	Vermiculite (20%) mixed with Ottawa Sand (80%)	1.83	5.8×10^{-5}	6.4×10^{-5}	0.9	0.20	3.0	2.52
3.	Fly Ash (Acidic)	1.41	1.5×10^{-4}	1.3×10^{-5}	1.2	0.0041	2.0	2.13
4.	Fly Ash (Basic)	1.38	1.1×10^{-4}	9.9×10^{-5}	1.1	0.010	1.4	2.25
5.	Bottom Ash	0.69	3.3×10^{-4}	3.8×10^{-5}	8.7	0.028	6.4	2.69
6.	Kaolinite (20%) mixed with Ottawa Sand (80%)	0.79	7.1×10^{-5}	2.1×10^{-5}	3.4	0.028	21.4	2.67
7.	Activated Alumina	2.07	7.7×10^{-4}	2.1×10^{-5}	36.7	0.075	1.3	3.24
8.	Activated Carbon	1.66	5.2×10^{-2}	6.4×10^{-2}	0.8	1.1	1.8	1.26
	B. Metal Finishing Sludge Leachate							
1.	Illite (20%) mixed with Ottawa Sand (80%)	0.49	9.2×10^{-4}	2.7×10^{-4}	3.4	0.016	37.5	2.68
2.	Vermiculite (20%) mixed with Ottawa Sand (80%)	1.81	1.4×10^{-4}	1.1×10^{-5}	12.7	0.20	3.0	2.52
3.	Fly Ash (Acidic)	1.50	2.1×10^{-4}	4.7×10^{-5}	4.5	0.0041	2.0	2.13
4.	Fly Ash (Basic)	0.84	9.4×10^{-5}	1.3×10^{-5}	7.2	0.010	1.4	2.25
5.	Kaolinite (20%) mixed with Ottawa Sand (80%)	0.53	2.5×10^{-5}	1.2×10^{-5}	2.1	0.028	21.4	2.67
6.	Activated Alumina	2.29	1.4×10^{-3}	4.5×10^{-6}	311.	0.075	1.3	3.24
7.	Activated Carbon	1.45	7.2×10^{-2}	8.6×10^{-2}	0.84	1.1	1.8	1.26
	C. Petroleum Sludge Leachate							
1.	Illite (20%) mixed with Ottawa Sand (80%)	0.44	1.2×10^{-4}	7.5×10^{-5}	1.6	0.016	37.5	2.68
2.	Vermiculite (20%) mixed with Ottawa Sand (80%)	2.01	8.5×10^{-5}	6.3×10^{-5}	1.4	0.20	3.0	2.52
3.	Fly Ash (Acidic)	1.50	2.7×10^{-4}	3.1×10^{-4}	0.9	0.0041	2.0	2.13
4.	Fly Ash (Basic)	1.01	1.3×10^{-4}	1.8×10^{-4}	0.7	0.010	1.4	2.25
5.	Bottom Ash	0.64	4.4×10^{-4}	1.5×10^{-6}	293.	0.028	6.4	2.69
6.	Kaolinite (20%) mixed with Ottawa Sand (80%)	0.40	1.4×10^{-5}	3.0×10^{-6}	4.7	0.028	21.4	2.67
7.	Activated Alumina	2.20	1.2×10^{-3}	1.7×10^{-6}	706.	0.075	1.3	3.24
8.	Activated Carbon	1.50	6.7×10^{-2}	6.7×10^{-2}	1.0	1.1	1.8	1.26

REMARKS:

e = Void Ratio

K_1 = Initial Coefficient of Permeability

K_2 = Terminal Coefficient of Permeability

d_{10}(mm) = Grain Size Diameter at 10% finer

Cu = Coefficient of Uniformity

APPENDIX III.

BREAKTHROUGH CURVES OF SORBENTS IN LYSIMETER STUDY FOR THREE INDUSTRIAL SLUDGE LEACHATES.

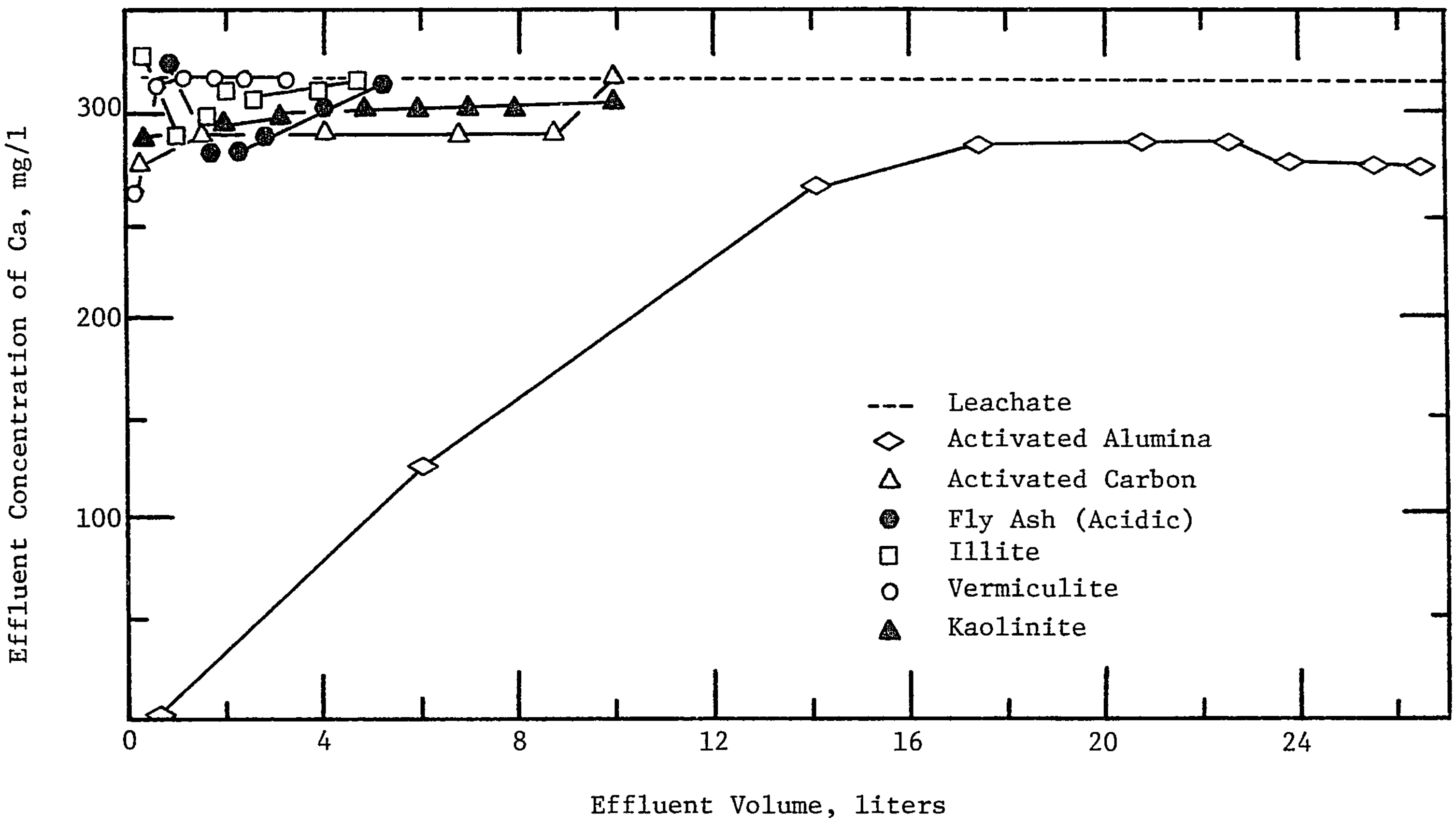

Figure 28. Lysimeter Studies of Calcium-ion in Calcium Fluoride Sludge Leachate.

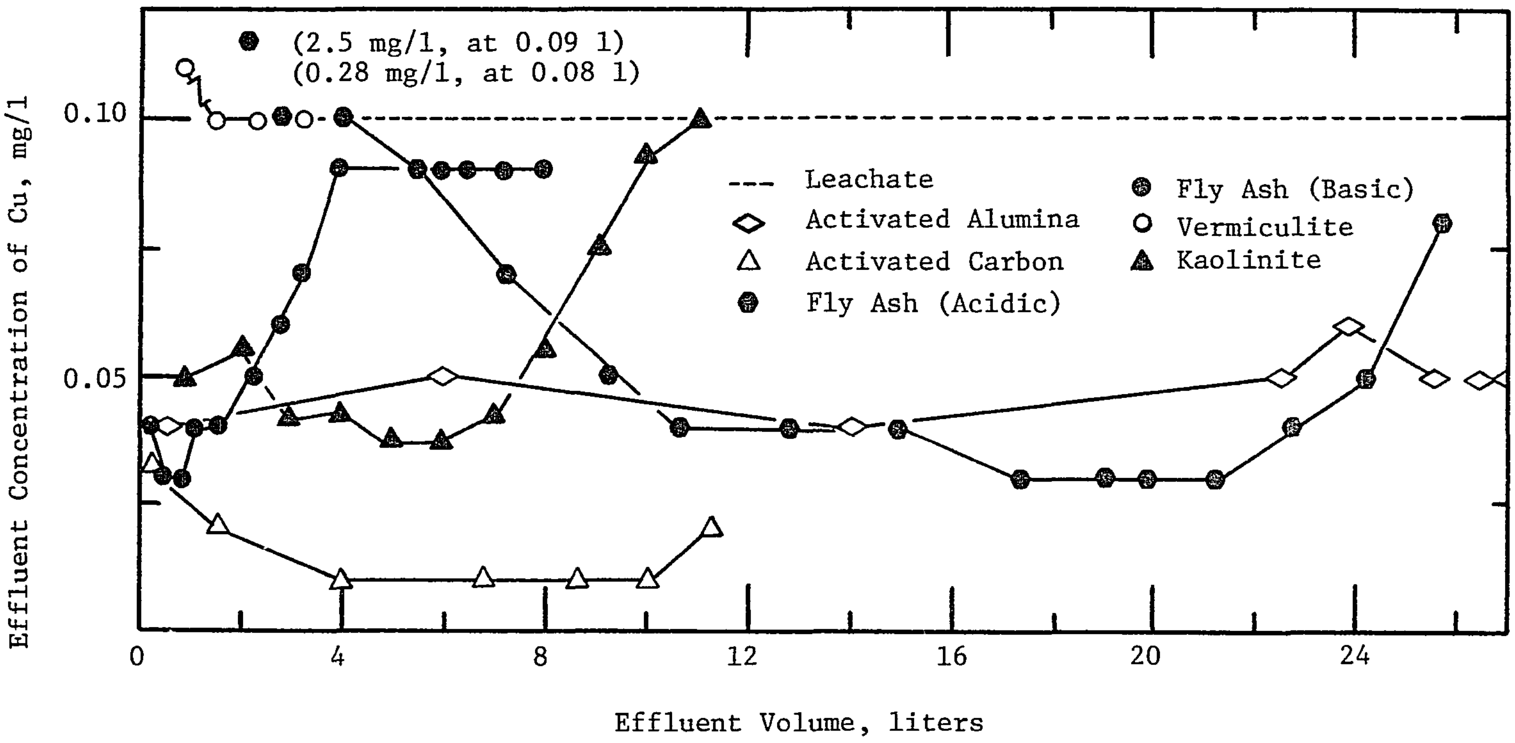

Figure 29. Lysimeter Studies of Copper-ion in Calcium Fluoride Sludge Leachate.

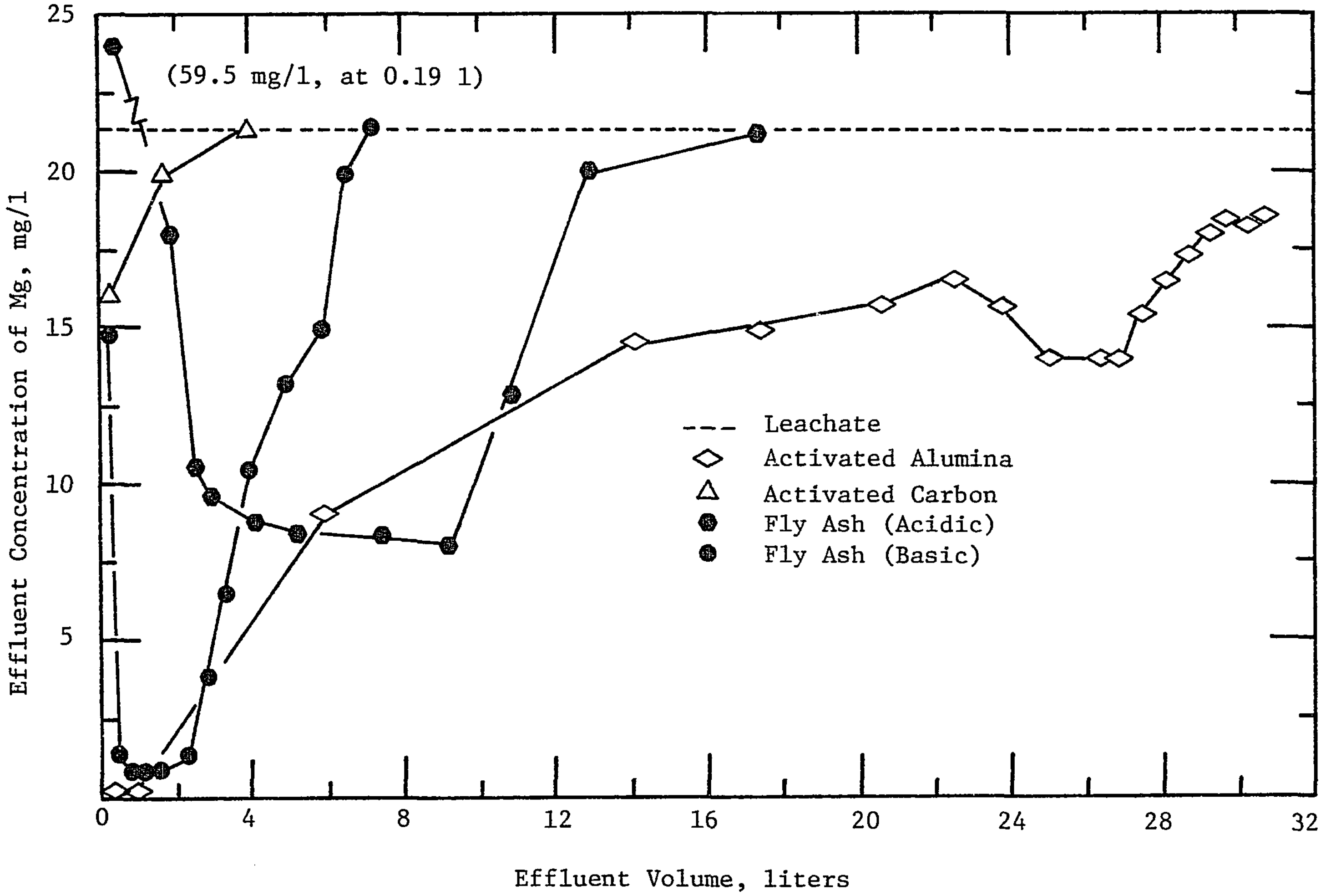

Figure 30. Lysimeter Studies of Magnesium-ion in Calcium Fluoride Sludge Leachate.

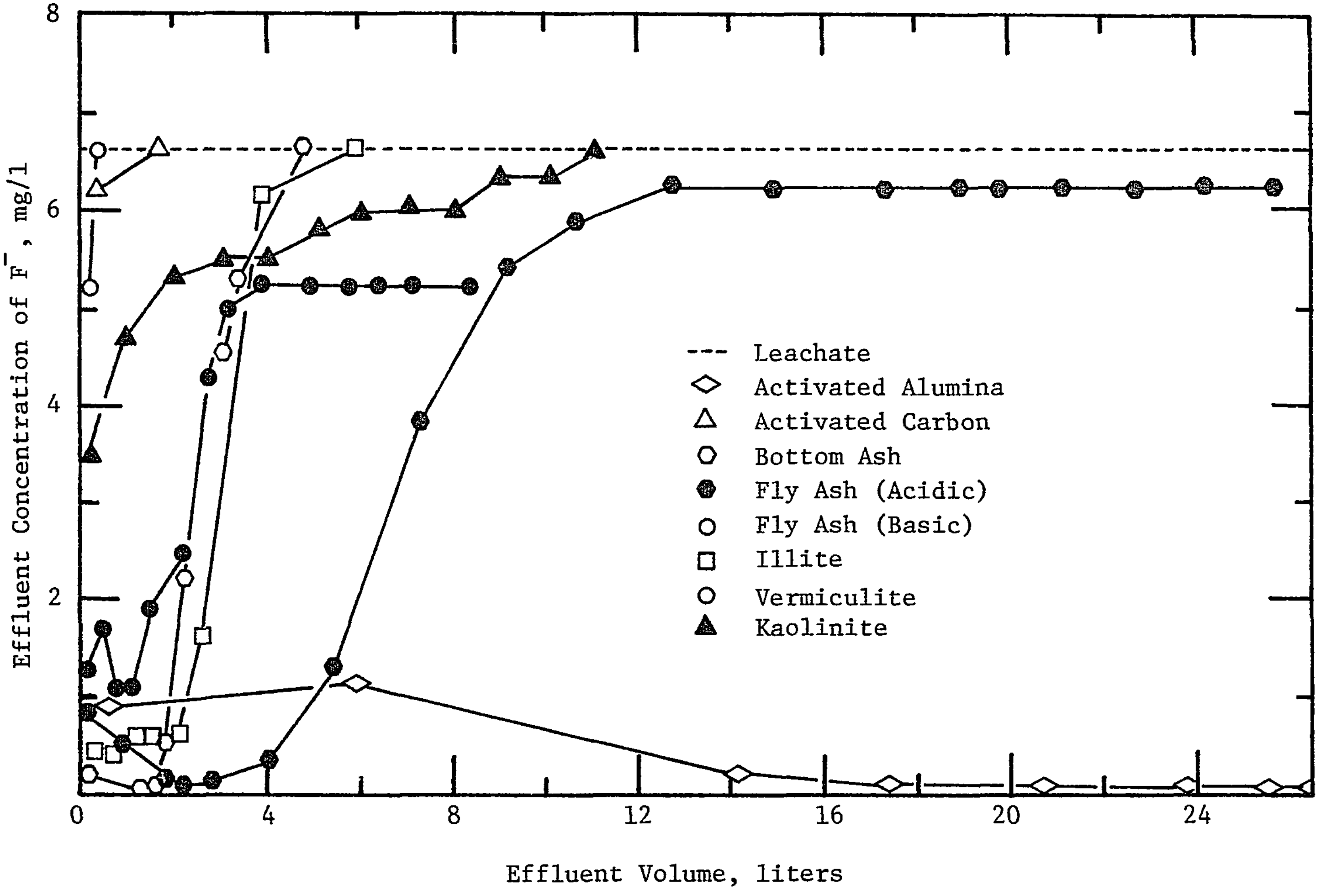

Figure 31. Lysimeter Studies of Fluoride-ion in Calcium Fluoride Sludge Leachate.

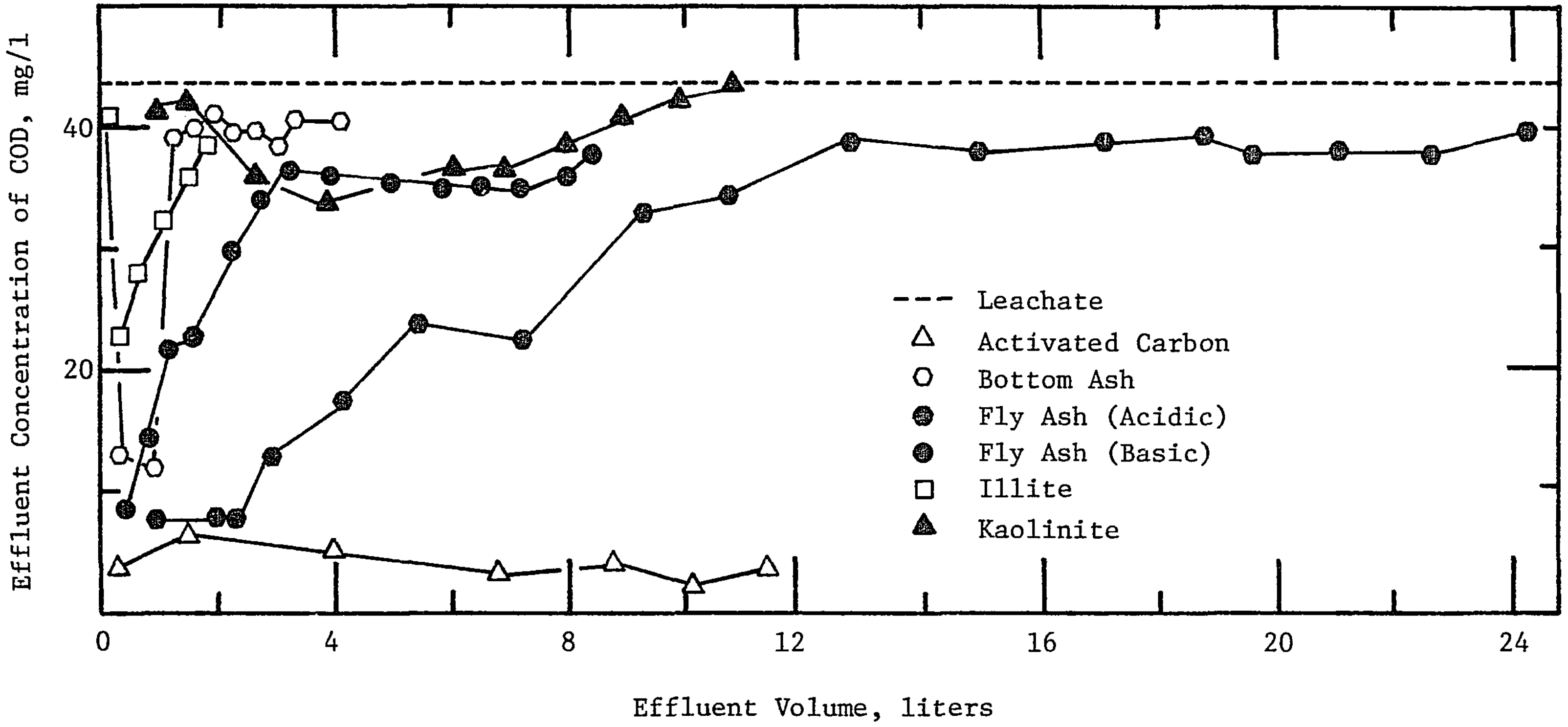

Figure 32. Lysimeter Studies of COD in Calcium Fluoride Sludge Leachate.

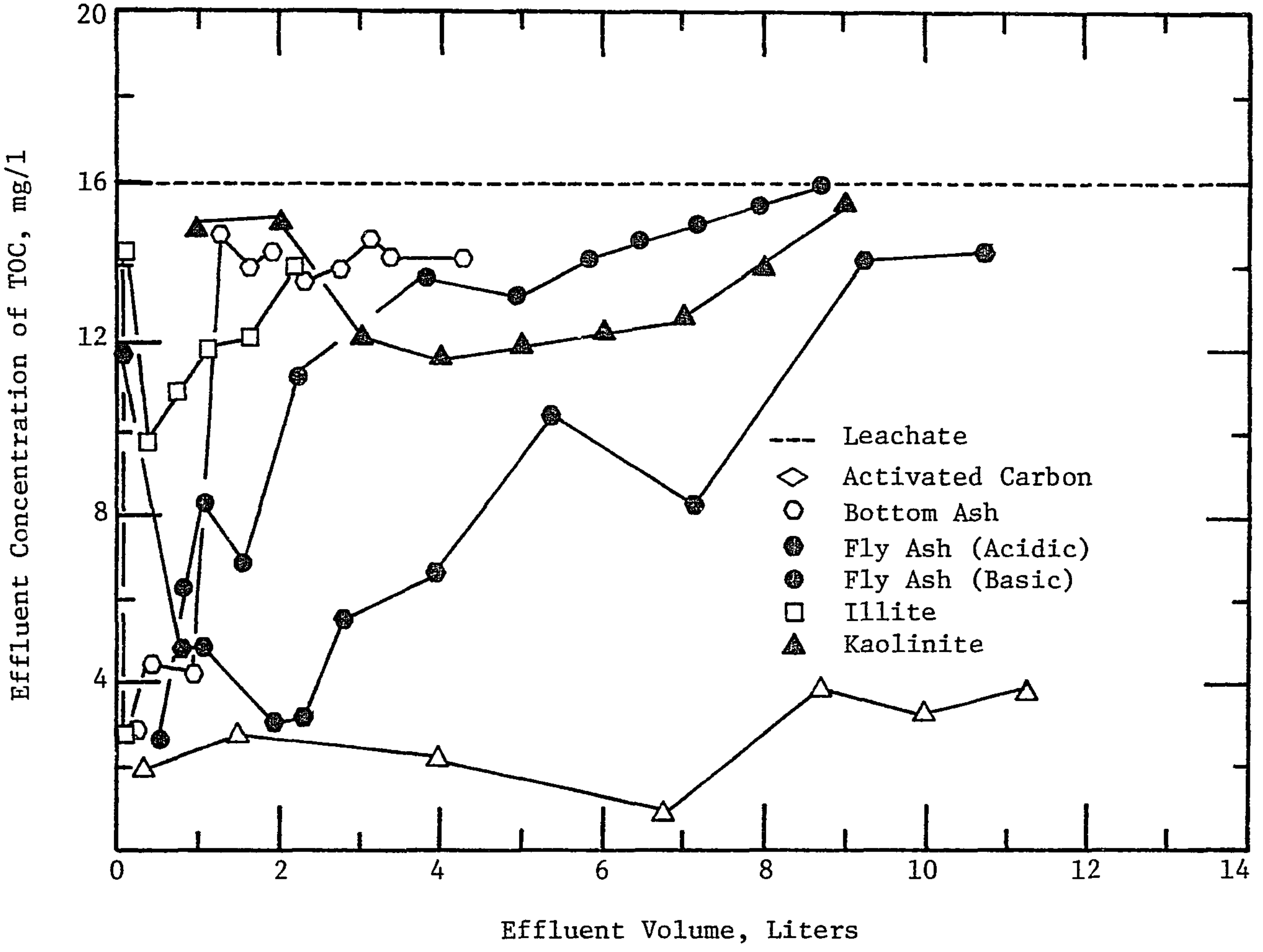

Figure 33. Lysimeter Studies of TOC in Calcium Fluoride Sludge Leachate.

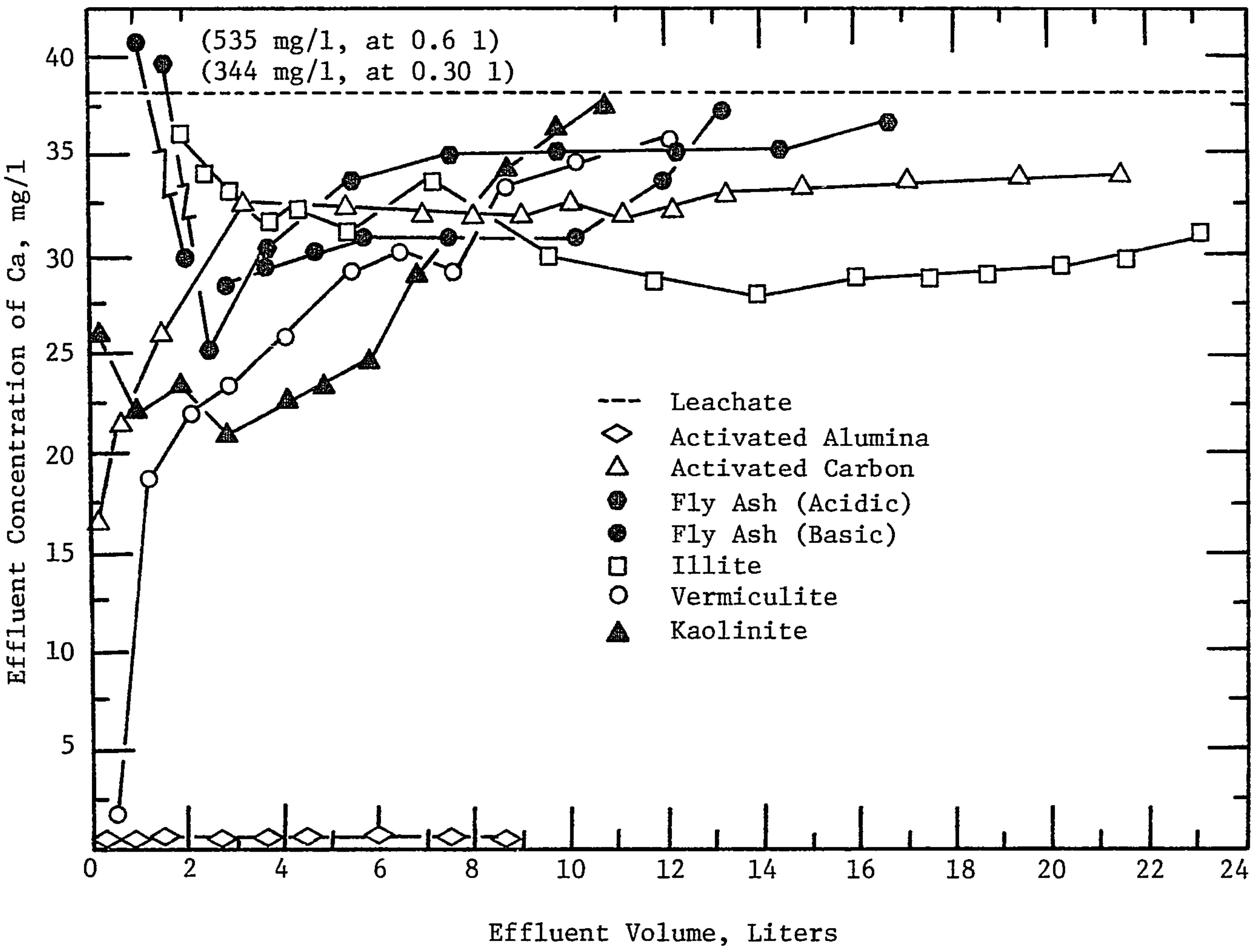

Figure 34. Lysimeter Studies of Calcium-ion in Metal Finishing Sludge Leachate.

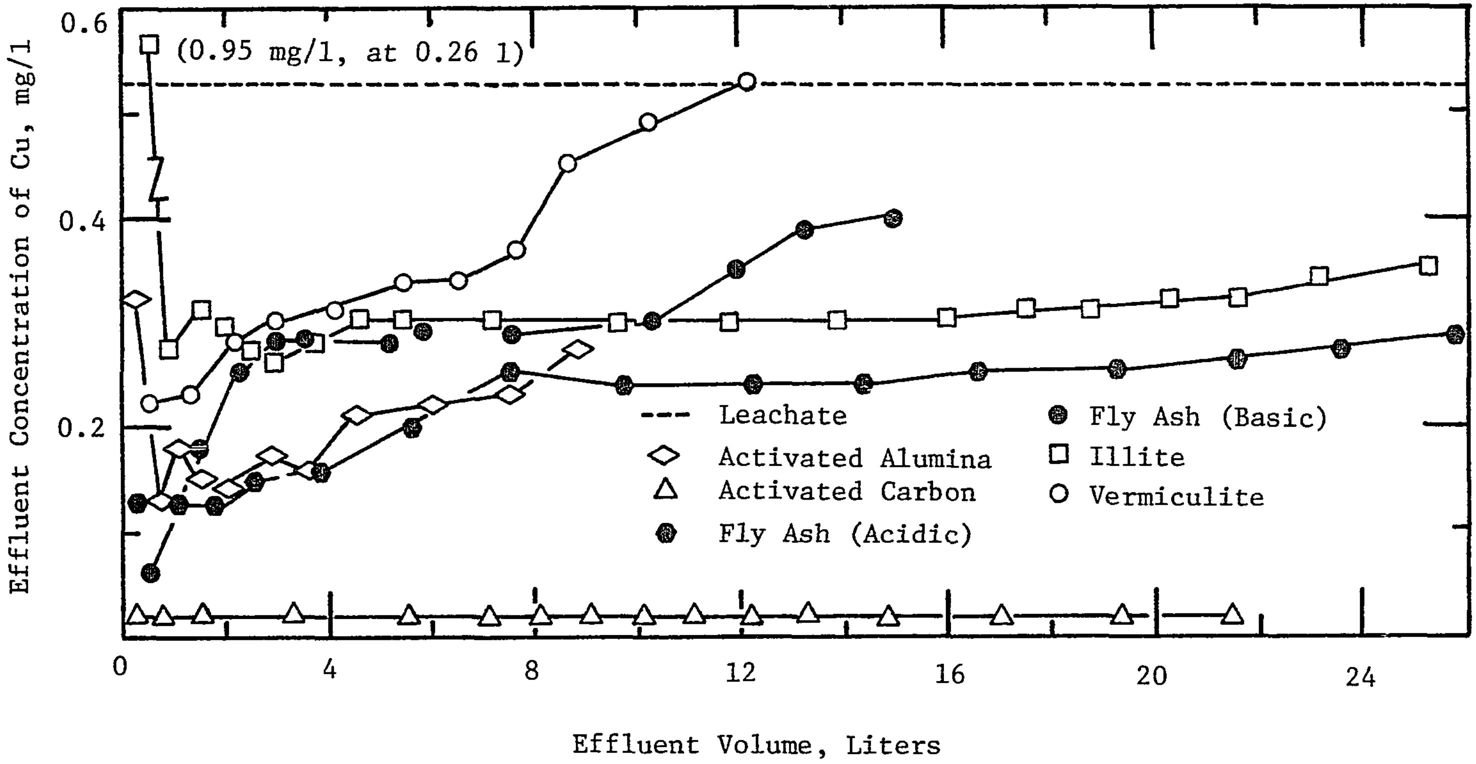

Figure 35. Lysimeter Studies of Copper-ion in Metal Finishing Sludge Leachate.

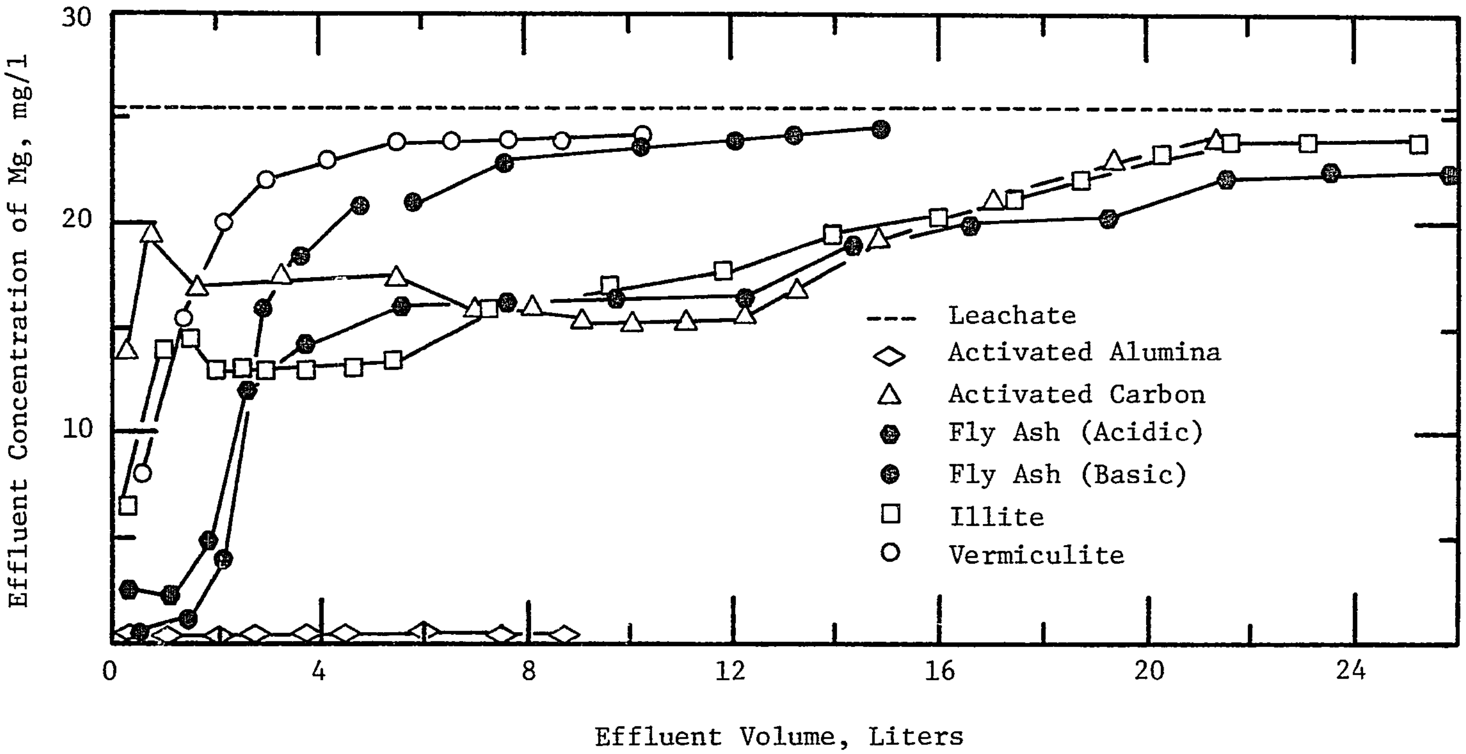

Figure 36. Lysimeter Studies of Magnesium-ion in Metal Finishing Sludge Leachate.

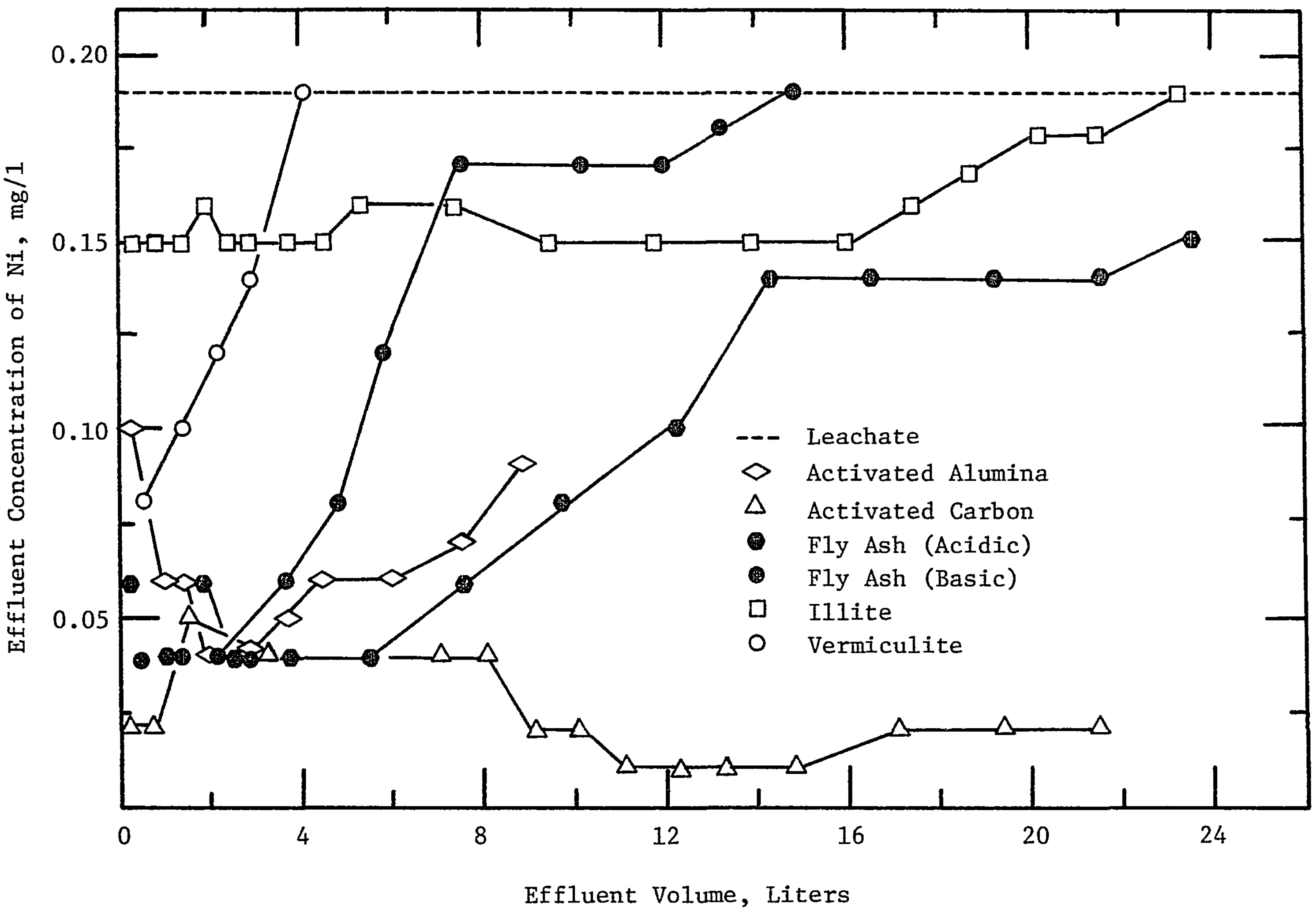

Figure 37. Lysimeter Studies of Nickel-ion in Metal Finishing Sludge Leachate.

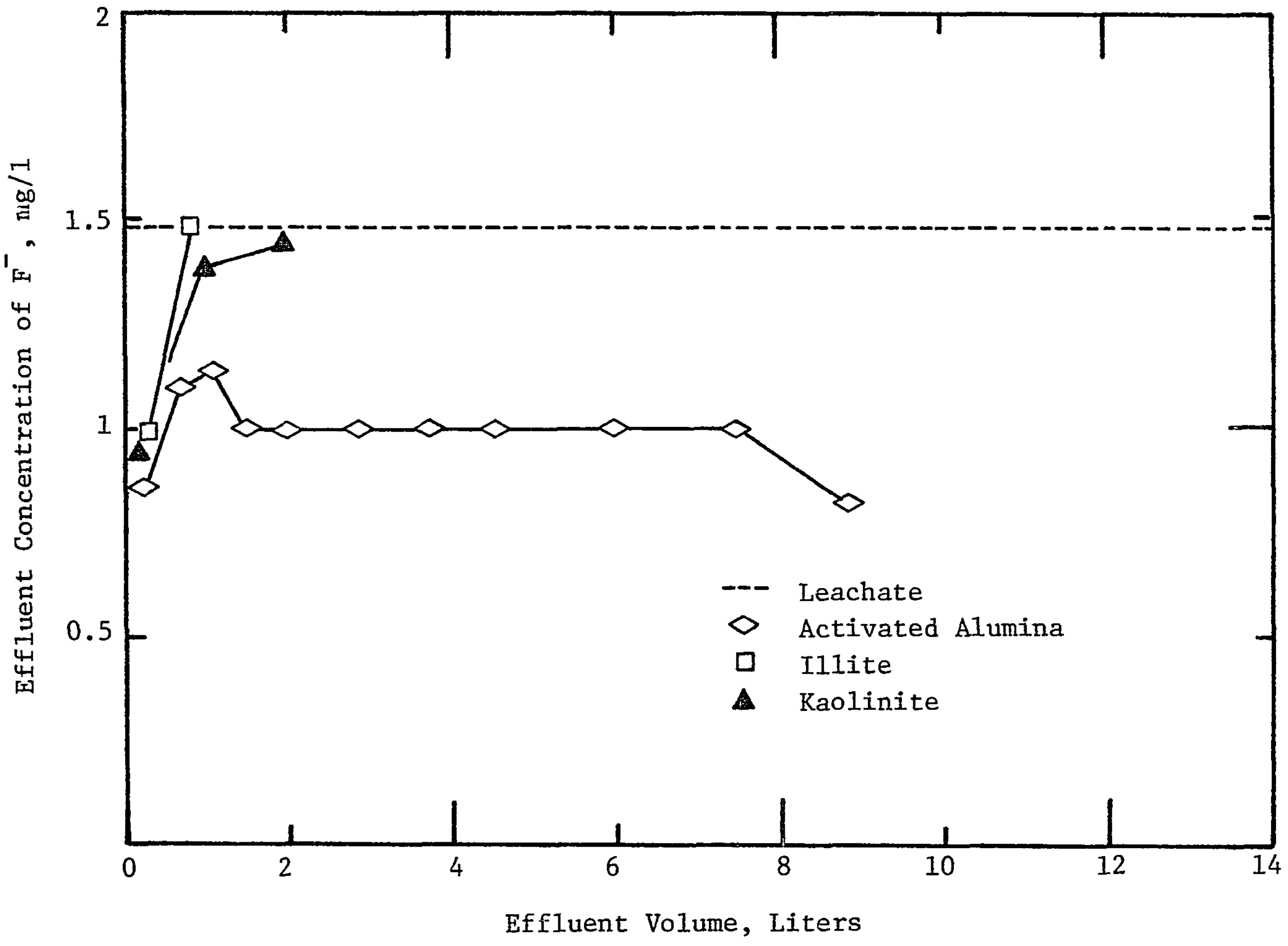

Figure 38 . Lysimeter Studies of Fluoride-ion in Metal Finishing Sludge Leachate.

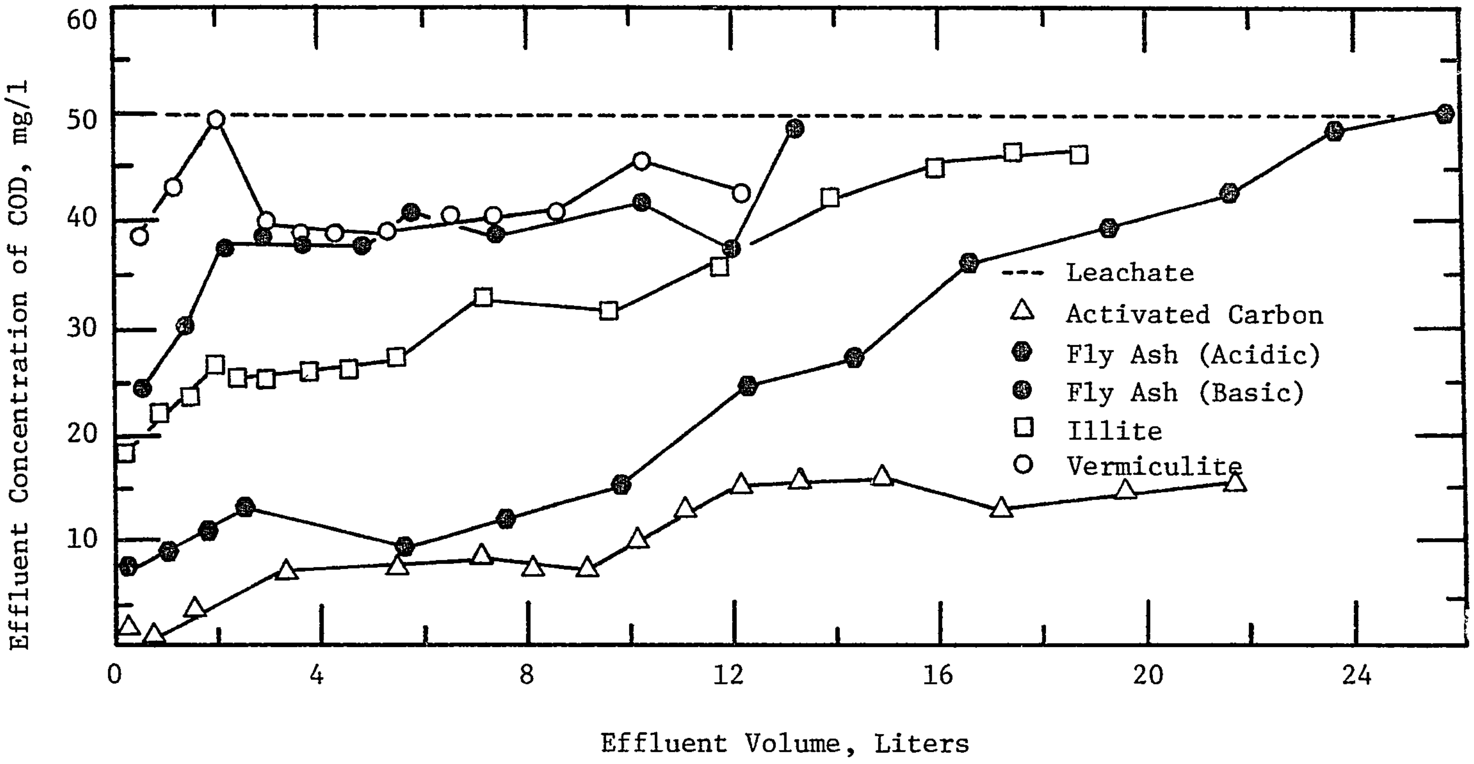

Figure 39. Lysimeter Studies of COD in Metal Finishing Sludge Leachate.

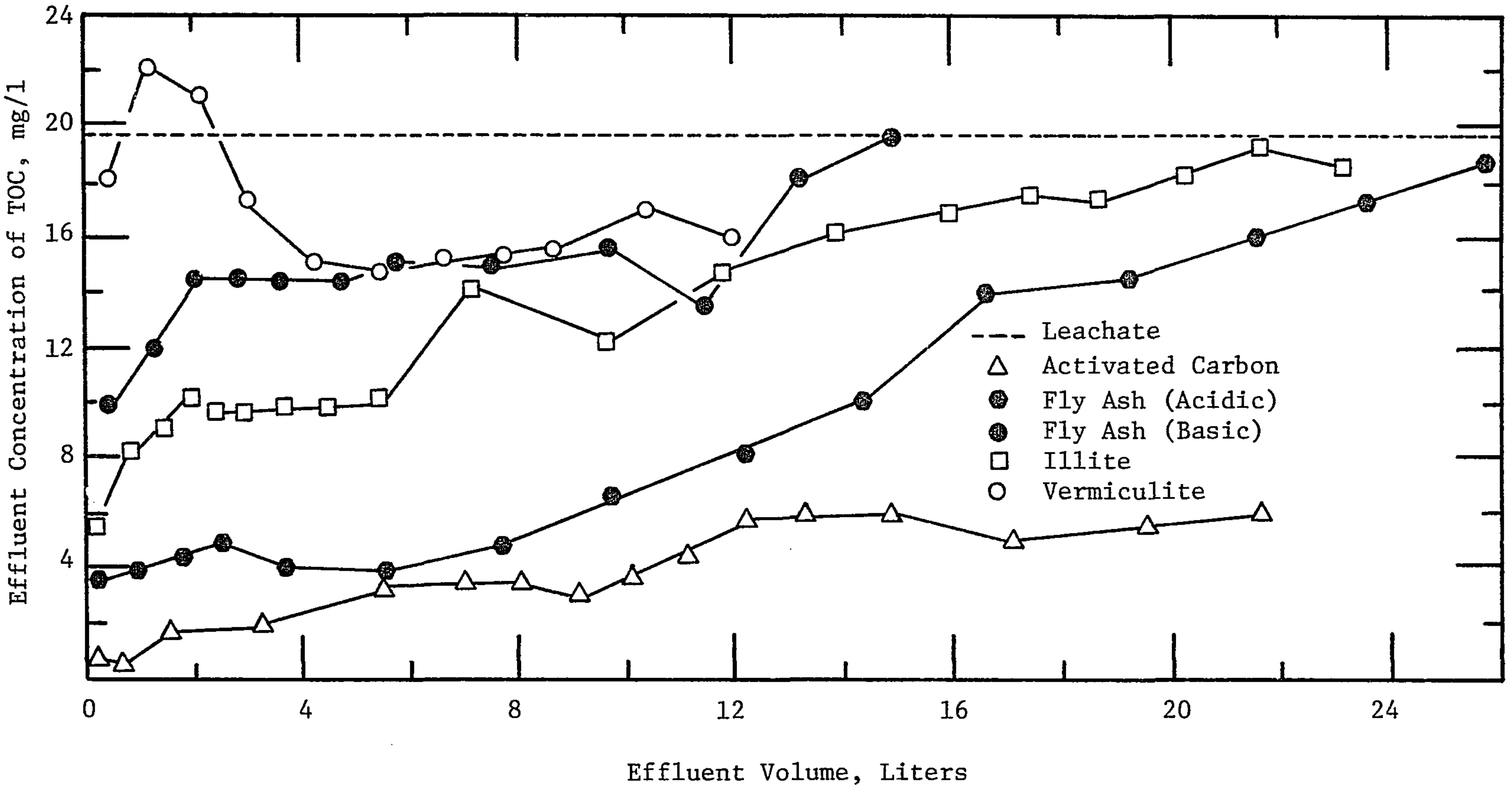

Figure 40. Lysimeter Studies of TOC in Metal Finishing Sludge Leachate.

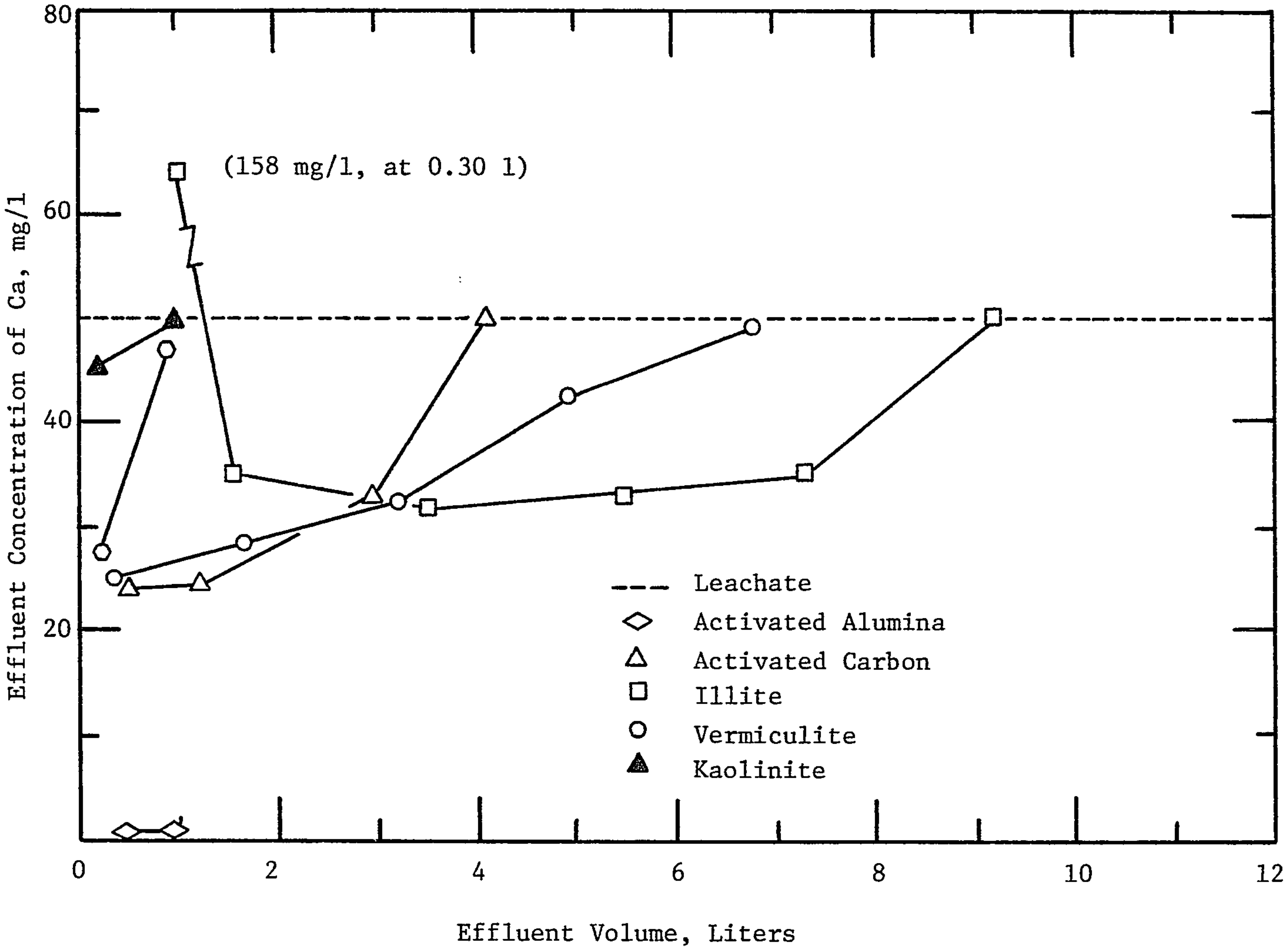

Figure 41. Lysimeter Studies of Calcium-ion in Petroleum Sludge Leachate.

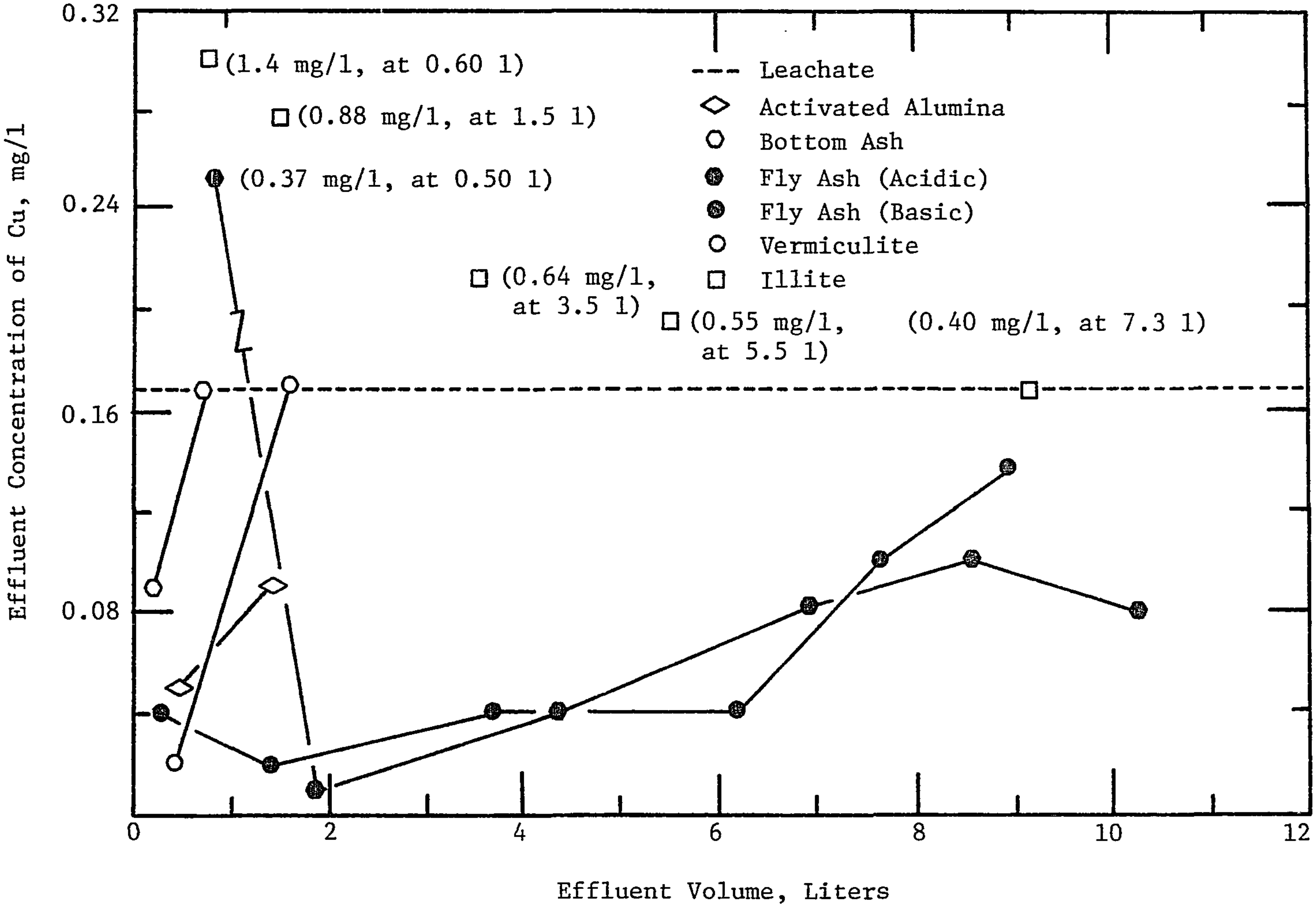

Figure 42. Lysimeter Studies of Copper-ion in Petroleum Sludge Leachate.

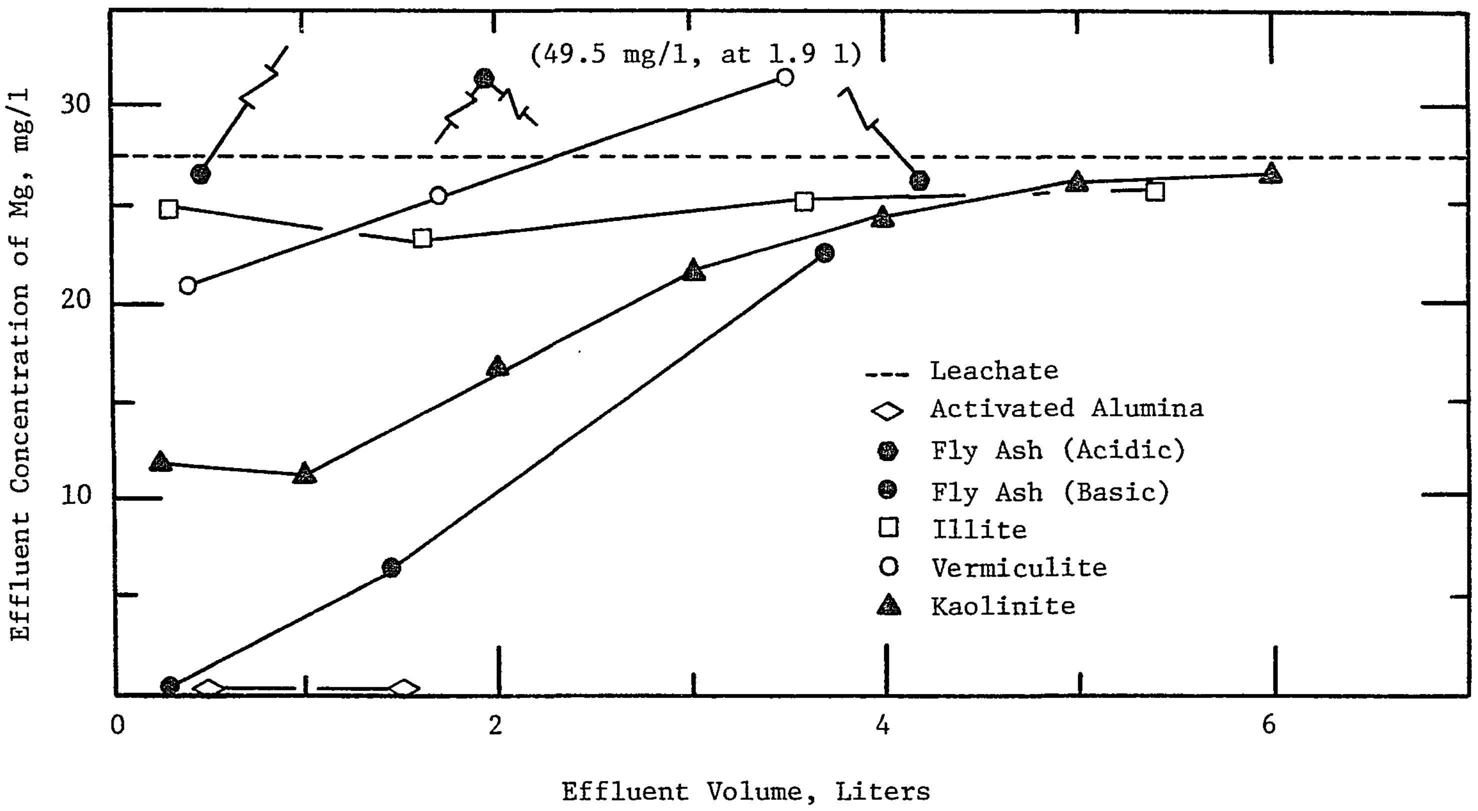

Figure 43. Lysimeter Studies of Magnesium-ion in Petroleum Sludge Leachate.

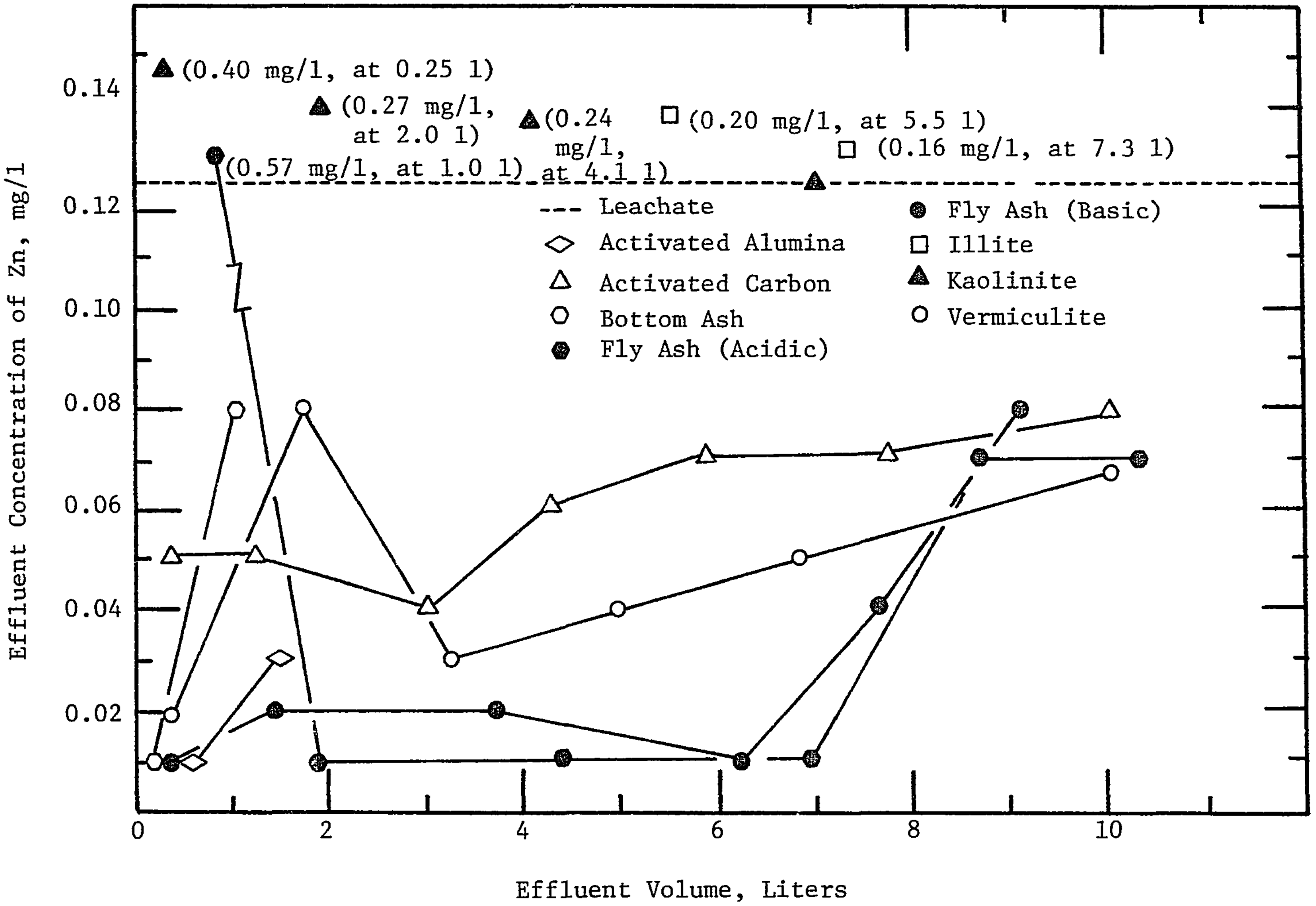

Figure 44 Lysimeter Studies of Zinc-ion in Petroleum Sludge Leachate.

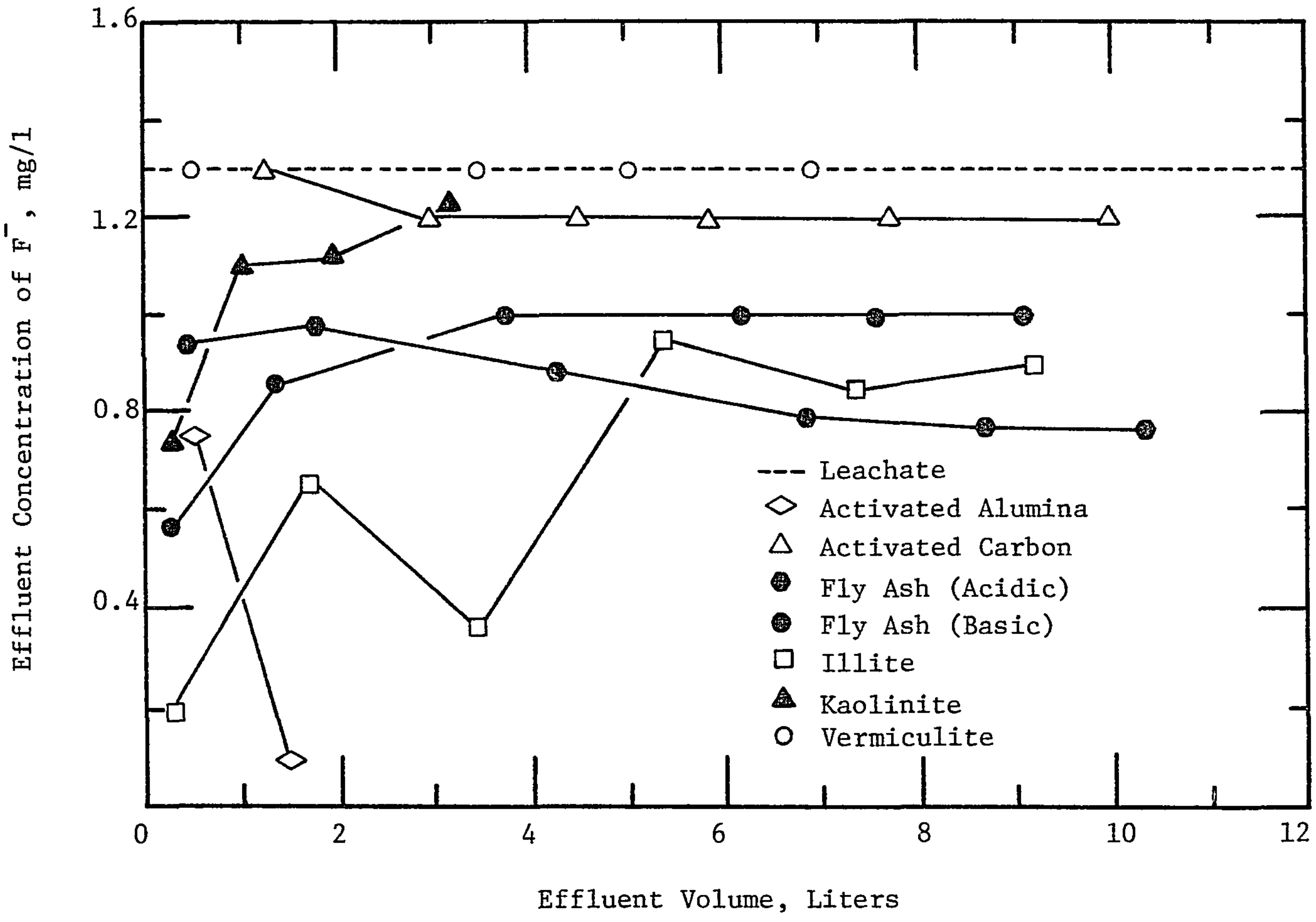

Figure 45. Lysimeter Studies of Fluoride-ion in Petroleum Sludge Leachate.

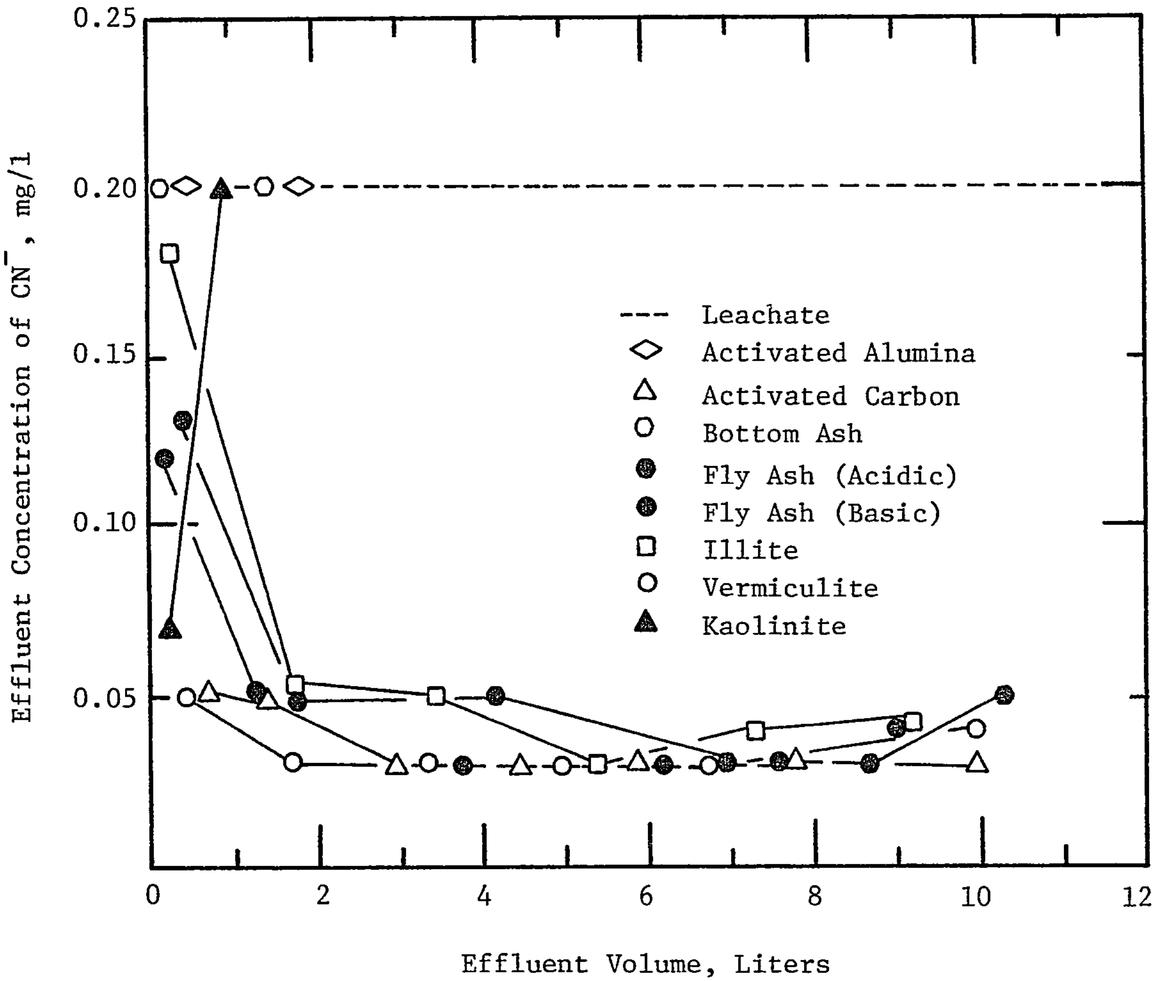

Figure 46. Lysimeter Studies of Cyanide-ion in Petroleum Sludge Leachate.

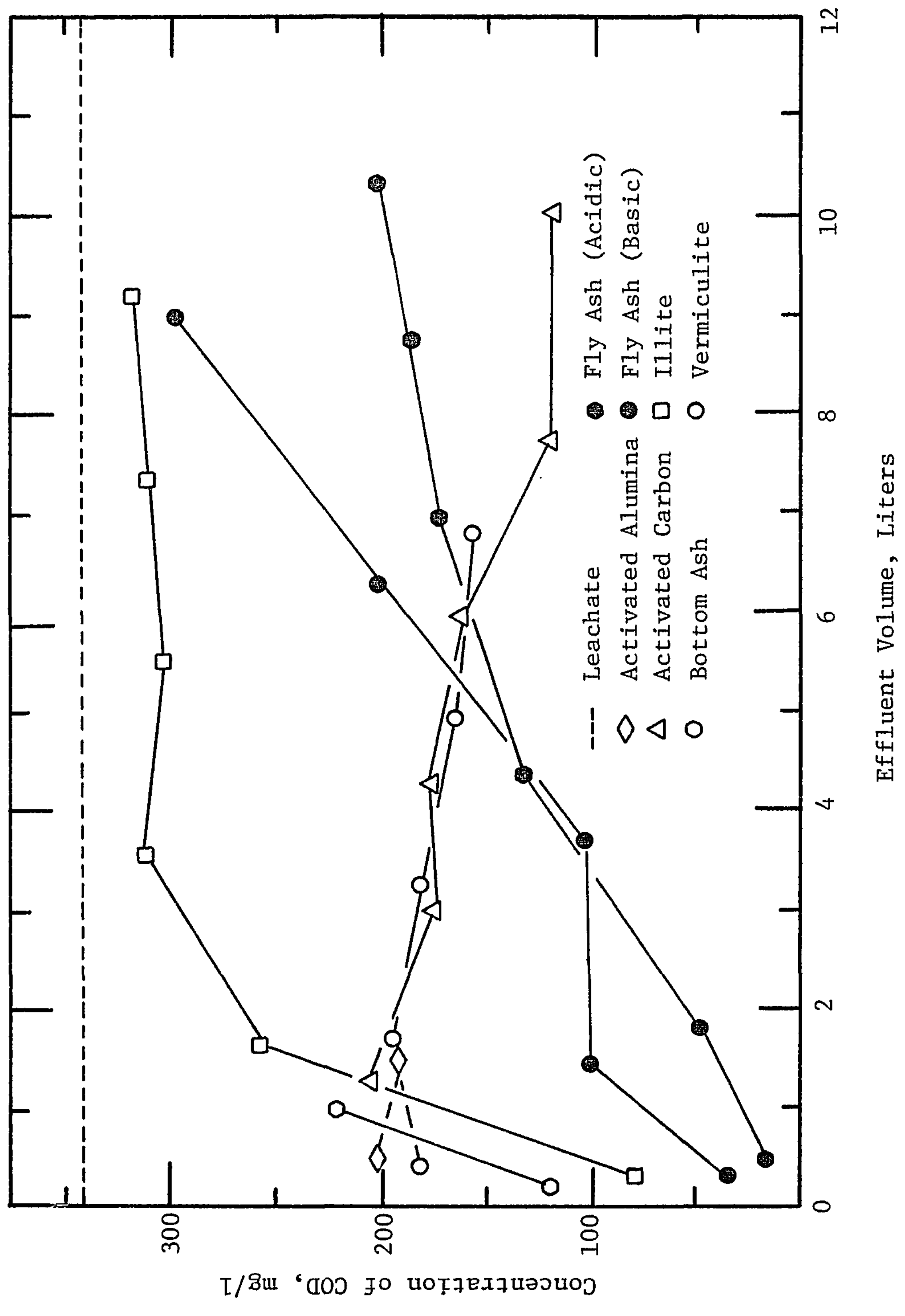

Figure 47. Lysimeter Studies of COD in Petroleum Sludge Leachate.

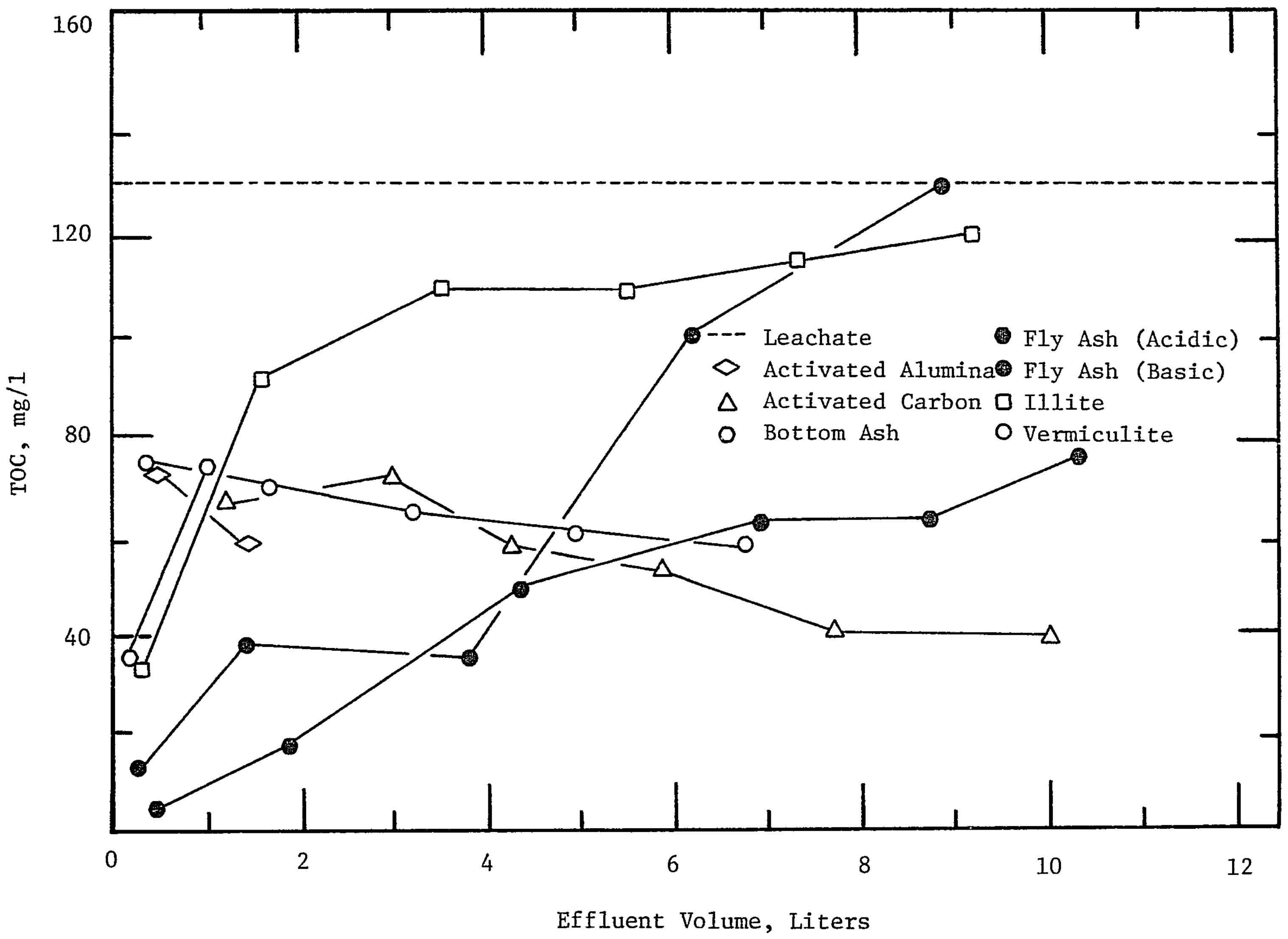

Figure 48. Lysimeter Studies of TOC in Petroleum Sludge Leachate.

APPENDIX IV.

PERMEABILITY CURVES OF SORBENT MATERIALS IN LYSIMETER STUDIES FOR THREE INDUSTRIAL SLUDGE LEACHATES.

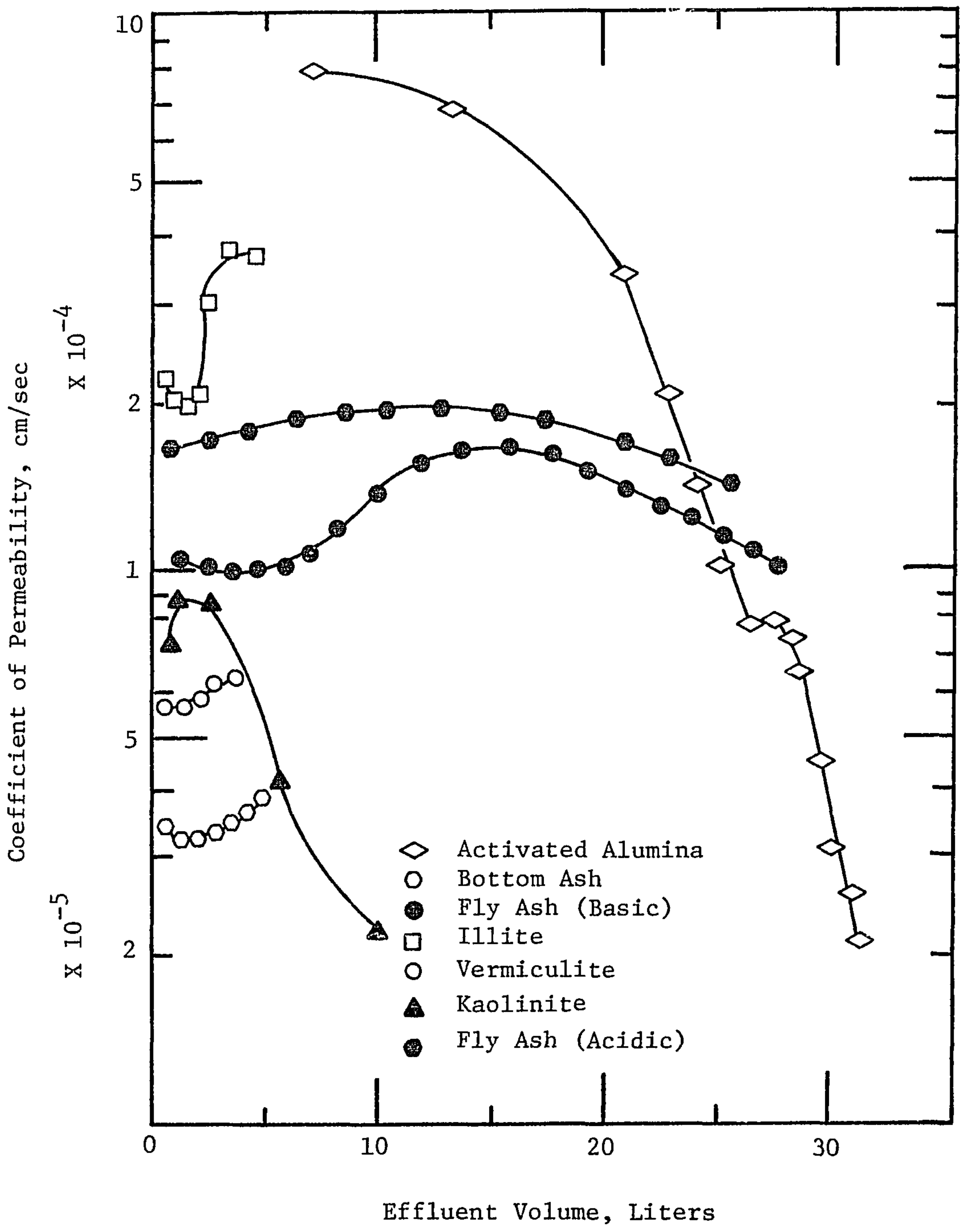

Figure 49 . Permeability Studies of Sorbent Materials with Calcium Fluoride Sludge Leachate.

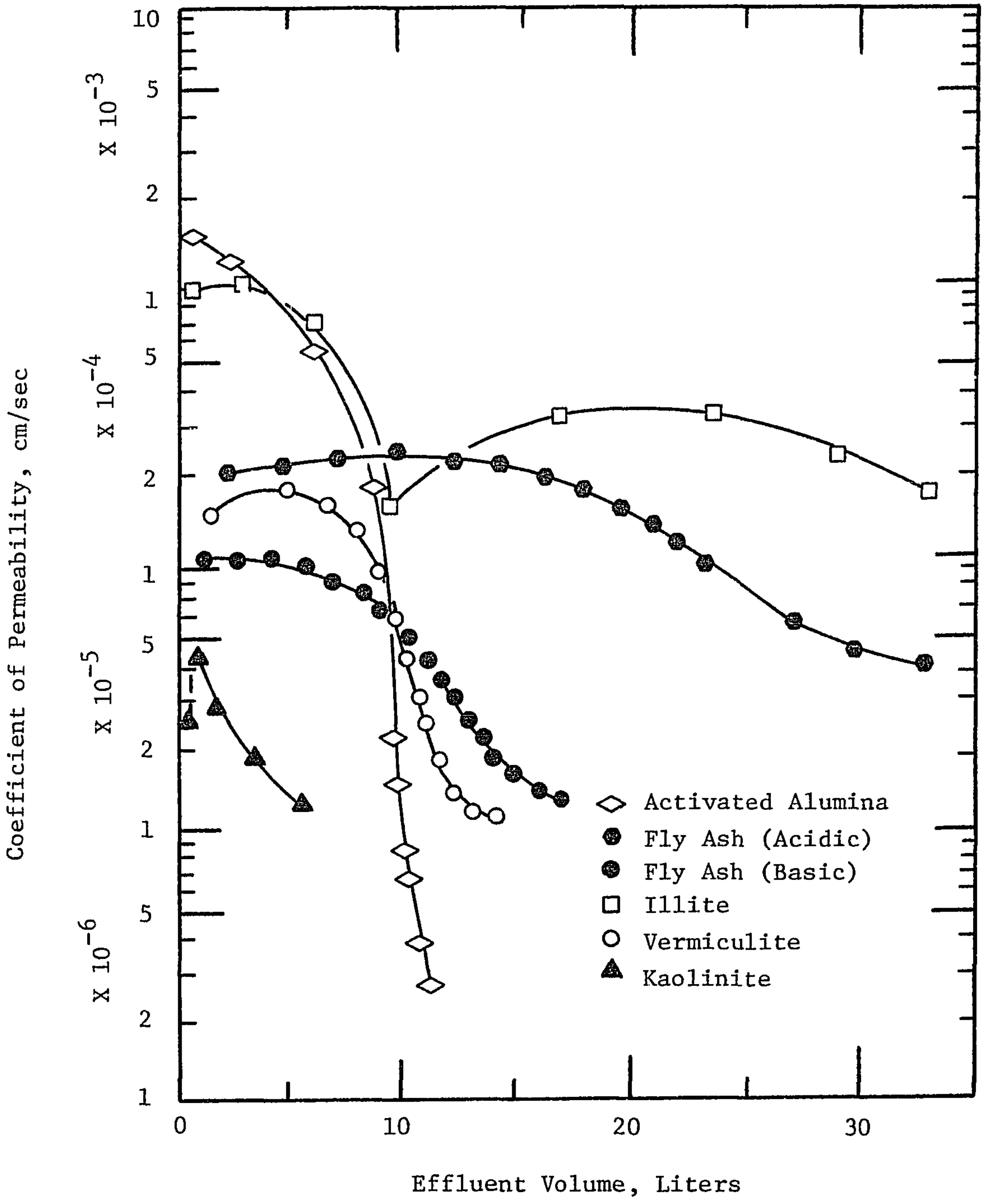

Figure 50. Permeability Studies of Sorbent Materials with Metal Finishing Sludge Leachate.

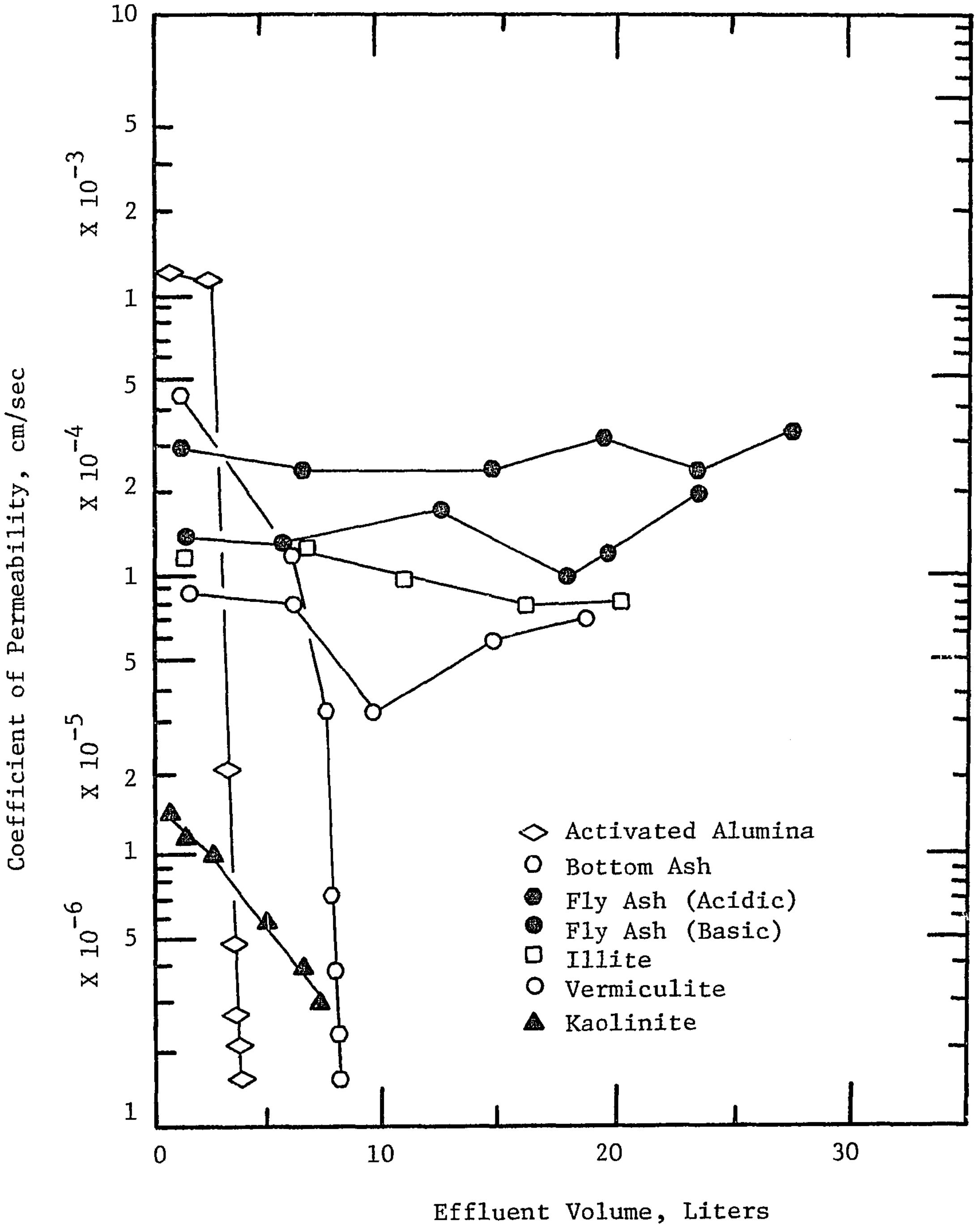

Figure 51. Permeability Studies of Sorbent Materials with Petroleum Sludge Leachate.

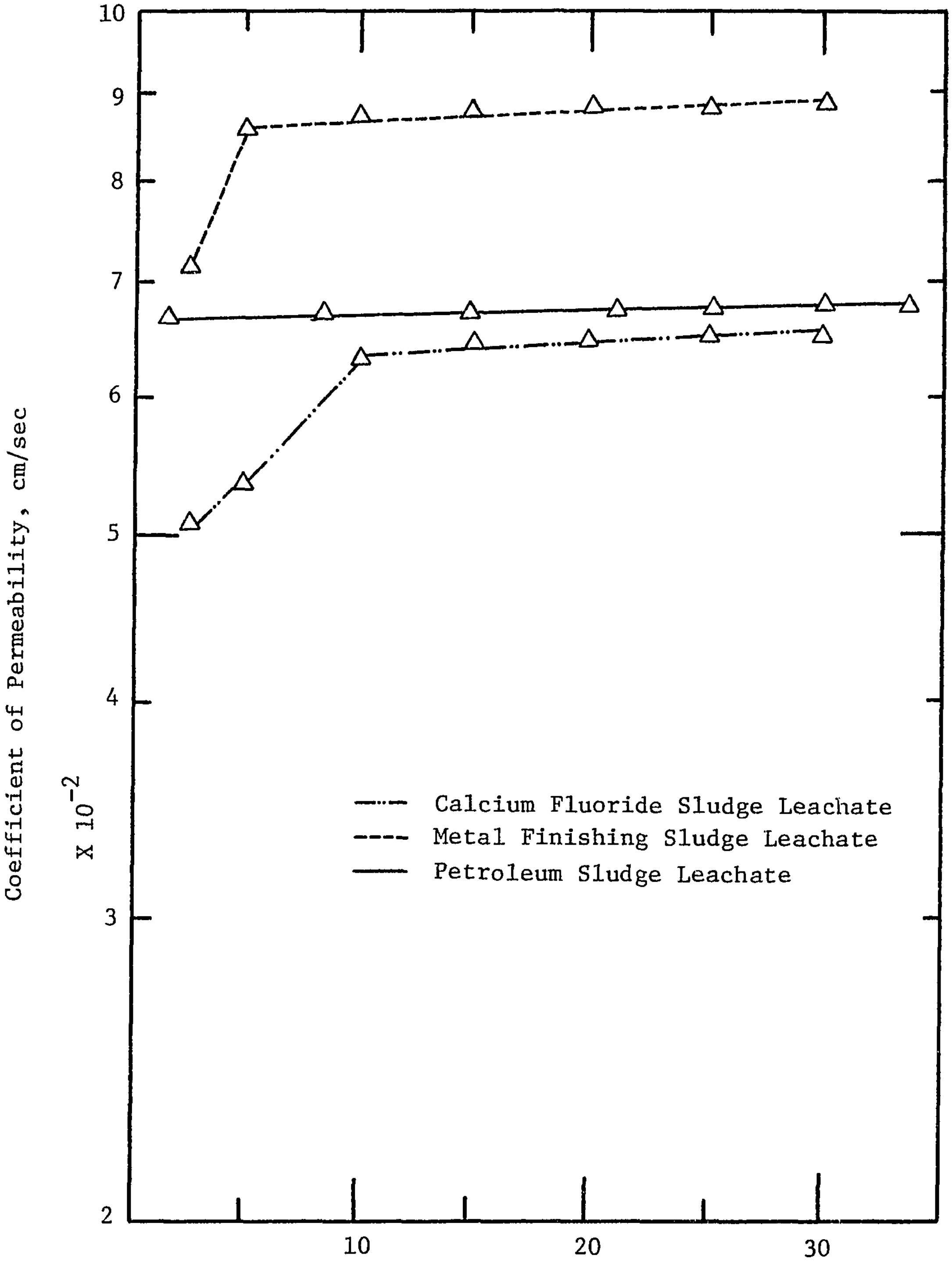

Figure 52. Permeability Studies of Activated Carbon.