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SORBENTS FOR FLUORIDE, METAL FINISHING, AND PETROLEUM SLUDGE LEACHATE CONTAMINANT CONTROL

Municipal Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for preventing, treating, and managing wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for preserving and treating public drinking water supplies, and for minimizing the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research, a most vital communication link between the researcher and the user community.

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

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ABSTRACT

A laboratory evaluation of bottom ash, acidic and basic fly ashes, vermiculite, illite, activated carbon, kaolinite, natural zeolite, activated alumina, and cullite for the removal of contaminants in the leachate and liquid portion of three industrial sludges (calcium fluoride, metal finishing, and petroleum) is presented. Batch and lysimeter studies were carried out to evaluate the static and dynamic sorbent capacity for the constituents present in the leachate. Also, permeability exhibited by these sorbents when contacted with the above industrial sludge leachate was studied. The pH, conductivity, chemical oxygen demand (COD), total organic carbon (TOC), cationic and anionic species in the leachate before and after contact with the sorbent materials, and the coefficient of permeability were determined.

The analysis of the leachate showed that considerable variations exist in composition and concentration of constituents in the leachate prepared from the same industrial sludge, which was collected over the period of this investigation. The results of the batch and lysimeter studies reveal that no single sorbent, but combinations of two, three, or four sorbents, can be used to reduce the concentration of the constituents found in the leachate of a specific sludge. These are acidic and basic fly ashes, kaolinite, and illite for the calcium fluoride sludge leachate; vermiculite, kaolinite, and illite for the metal finishing sludge leachate; basic fly ash, vermiculite, and kaolinite for the petroleum sludge leachate. The combination of the more expensive activated carbon and activated alumina was found to be the more effective combination for treating the calcium fluoride sludge leachate but less effective than the ash and clay combinations in treating the metal finishing sludge leachate and petroleum sludge leachate. The selection of a sorbent combination is sludge leachate specific. In some cases, the most effective sorbents for the removal of the same contaminant in the leachate from different sludges are not the same. Also, significantly greater sorbent capacities for the measured contaminants in the leachates are achieved by the sorbents under dynamic conditions than are achieved under static conditions. In addition, change in pH of the sorbent from acidic to alkaline, such as resulted when alkaline fluoride sludge leachate and metal finishing sludge leachate were passed through the acidic fly ash and illite, was found to favor the removal of cations.

This report was submitted in fulfillment of grant No. R803717 by New Jersey Institute of Technology under partial sponsorship of the U.S. Environmental Protection Agency. This report covers the initial laboratory studies carried out to identify the most promising sorbents that may be used to significantly reduce the concentration of measurable contaminant in calcium fluoride sludge leachate, metal finishing sludge leachate, and petroleum sludge leachate. The study covers the period from June 1975 to May 1977.

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SECTION 1

INTRODUCTION

As a result of the establishment under the Federal Water Pollution Control Act of 1972 of a nonpollutant discharge policy to receiving waters by 1985, industry will be faced with finding feasible techniques for the safe disposal of hazardous and toxic sludges generated during the treatment of their waste streams. Some progress has been made in the development of closed-loop type waste treatment. However, this technology is not expected to significantly reduce the sludge volume in the near future. Currently, the most often used sludge disposal technique for industrial sludges is the "sanitary" landfill. Moreover, the disposal of industrial sludge in landfills can lead to contamination of ground and surface waters through runoff and percolation. Present-day sanitary landfills cannot be considered a panacea for the ultimate disposal of hazardous wastes.

At present, means to accurately predict the leaching potential, direction and rate of flow of the leachate through the soil surrounding the landfill site is lacking. These problems could be overcome by isolating the landfill site from its immediate soil surroundings. By lining the base and sides of the landfill with compacted soil of low impermeablity, horizontal groundwater movement of the leachate is prevented. Polyvinyl chloride and butyl rubber liners have also been used for this purpose. This liner creates a "tub without a drain" unless the rainwater that percolates down through the landfill is provided a route of escape. This could be accomplished by using gravity outlets, such as drainage tiles, or perforated corrugated metal pipe, installed in the lowest portion or along the base of the landfill to remove and collect the leachate. Further treatment of the collected leachate would be required to reduce the pollutants to acceptable discharge levels, assuming that treatment technology is available. In any event, additional construction and operating costs would be required.

It is the intent of this study to establish a design approach for the removal of leachate components at the landfill site using relatively inexpensive natural clays and other sorbents such as fly ash and bottom ash.

This report deals with the results of a laboratory study which has been conducted to evaluate the effectiveness for contaminent removal of ten natural and synthetic sorbent materials on the liquid portion and leachate generated from three different industrial sludges.

The sorbent materials that were used were fly ash, bottom ash, illite, kaolinite, vermiculite, natural zeolite, Ottawa sand, cullite, activated carbon and activated alumina. Activated carbon and activated alumina were

included in this study even though they are far more expensive than the other sorbents because they are generally known to be effective sorbents for the removal of organics, cations and anions from waste streams. Their use may be warranted if the above inexpensive sorbents are not effective in removing a specific component from the leachate. Cullite, which is a synthetic zeolite, was examined because it is widely used in water softening applications. Ottawa sand is included because it is mixed with some of the naturally occurring sorbents to improve their permeabilities. It was found in our preliminary work prior to this study to be relatively inert to the experiments.

Studies exploring possible application of fly ash in this area of wastewater treatment have been investigated by a number of investigators. Deb et al. (1) and Nelson and Guarino (2) reported the use of fly ash for the removal of COD from wastewater. They concluded that the unwashed fly ash added appreciable COD but not BOD to the solution. Ballance et al. (3) investigated fly ash as a coagulant aid in water treatment, reporting that fly ash has certain properties which enhanced chemical coagulation and settling of turbid water.

Soil chemists have shown an interest in ion removal by clay soils for many years. For a complete discussion of chemical reaction and clay mineral structures, the reader is referred to standard works--for instance, Grim (4) and Brown (5). Investigations have dealt, however, in the main, with selected ions, e.g., phosphorous adsorption by Fried and Shapiro (6), Olson and Watanable (7), Ellis and Erickson (8), zinc adsorption by Tiller (9), and Sharpless, Wallihan, and Peterson (10). For ion removal, Bittell and Miller (11) investigated the removal of lead, cadmium, and calcium by montmorillonite, illite, and kaolinite. They found that the cations exhibited consistent preferential sorption characteristics for the three clays. Calcium and cadmium competed evenly, while lead showed favorable sorption over calcium by a factor of 2 to 3. Recently, several investigators have examined the effectiveness of kaolinite, illite, montmorillonite, and soil mixtures in removing pollutants such as heavy metals and organic compounds. Fuller et al. (12) examined eleven soil mixtures, ranging from sandy loam to clay mixtures, mixing with limestone and hydrated Fe_2SO_4, for developing a sanitary landfill liner. Preliminary results indicated both limestone and dehydrated Fe_2SO_4 had a significant retarding influence on migration rate of the cations and anions studied. Another investigation by Griffin et al. (13) examined the effect of pH on removal of heavy metals by kaolinite and montmorillonite. They concluded that both cationic and anionic adsorption on these two clays were pH dependent. The adsorption of the cations was increased as the pH was raised.

The above investigations, however, examined the effectiveness of clays for removing specific contaminant(s) from leachates that were synthesized or modified in the laboratory. Early laboratory work (14) on the chemical and physical reactions of radioactive liquid waste with soils indicated that the removal of radioisotopes from solutions by exchange with the soil is influenced by the concentration of other cations in solutions as well as the total salt concentration. These results indicate that the composition of a leachate could influence the removal of a specific contaminant using a given sorbent. Therefore, our studies were carried out using leachates prepared directly from the industrial sludges without modification to achieve a more realistic eval-

uation of the sorbents for contaminant removal.

The sludges chosen for this study were a calcium fluoride sludge (of the type generated by the electronic and aircraft industries), a metal finishing sludge, and a petroleum sludge. These sludges were selected because their annual production is of a significant magnitude to present disposal problems. Also, the leachate from these sludges contains a cross-section of hazardous organic constituents, heavy metal hydroxides, anions such as cyanide, and substantial amounts of fairly soluble toxic salts such as calcium fluoride. Analysis of the leachate generated from these sludges involved the determination of pH, conductivity, chemical oxygen demand (COD), total organic carbon (TOC), anionic species, and cationic species, before and after contact with sorbent materials.

Static studies were initially conducted to evaluate the capacity of these sorbent materials, using leachate with the maximum concentrations of contaminants that could be obtained from the sludge. These studies were carried out to define the most promising sorbent materials for removal of the constituents in the sludge leachate. The static studies were then followed by lysimeter studies using the most promising sorbent materials to obtain information regarding the dynamic capacity and permeability characteristics of these materials.

SECTION 2

CONCLUSIONS

A number of sorbents have been identified as exhibiting a removal capacity for leachate constituents under flowing conditions from the three types of sludges investigated. No single sorbent material was found to be effective in removing all the objectionable ions from the leachates studied. Two, three, or four different sorbents could be collectively combined to reduce sludge leachate contaminant levels. The combination of acidic fly ash, kaolinite, illite and basic fly ash, respectively, in a layer system may be used for treating the calcium fluoride sludge leachate under flowing conditions. The acidic and basic fly ashes are effective in reducing the magnesium and the organics whereas kaolinite and illite are effective for the calcium, kaolinite for copper and illite and kaolinite for fluoride based upon a comparison of their sorbent capacities. The basic fly ash is recommended, even though it is not as effective as the acidic fly ash, for removal of copper and magnesium because it can retain the copper and magnesium ions that are initially leached from the acidic fly ash. This leaching occurs until the effluent from the acidic fly ash lysimeter becomes basic as a result of prolonged passage of the alkaline fluoride sludge leachate through the column.

Based upon a comparison of all sorbent capacities, the combined use of the relatively expensive sorbents, activated alumina and activated carbon, may be more effective in reducing the above cations, anions, and organics in the calcium fluoride sludge leachate than the inexpensive ashes and clays. The activated alumina reduces the levels of the calcium, copper, magnesium and fluoride and the activated carbon is effective in reducing the organic concentrations. However, the usefulness of the activated alumina for treating this leachate is limited by the marked reduction observed in its permeability as the calcium fluoride sludge leachate flows through this sorbent. A point can be reached where the activated alumina is impermeable to the flow of this sludge leachate.

The combination of illite, kaolinite, and vermiculite, respectively, in a layered system may be used to treat the metal finishing sludge leachate under flowing conditions. Illite and vermiculite are effective for reducing the concentrations of calcium, copper, magnesium, nickel, and the organics. Vermiculite, although not as effective as the illite, is used to retain the calcium and copper ions which are initially leached from the illite. This occurs until the illite becomes alkaline due to prolonged passage of the alkaline metal finishing sludge leachate through this sorbent. The kaolinite is effective for reducing the fluoride ion levels in this leachate.

The combination of the activated alumina and activated carbon can also be

used to treat the metal finishing sludge leachate. The activated alumina is found to be effective in reducing the calcium, magnesium and fluoride ions, and the activated carbon is effective in reducing the copper, nickel and organics. However, the clay sorbent combination, rather than the more expensive activated alumina and activated carbon combination, is more effective in reducing the contaminant levels measured in this leachate.

The combination of basic fly ash, vermiculite, and kaolinite may be used to reduce the measurable contaminants present in the petroleum sludge leachate. Basic fly ash is effective in reducing the copper and the fluoride ion concentrations based upon an examination of the sorbent capacities. Vermiculite is effective for the calcium, zinc, cyanide and the organics, and kaolinite is effective for the magnesium ions. The combination of activated alumina and activated carbon can again be used to reduce the measurable contaminants in the petroleum sludge leachate. The activated alumina is effective for the calcium, copper, magnesium, and fluoride ions, and the activated carbon is effective for the zinc and cyanide ions as well as the organics. However, their sorbent capacities, as was the case for the metal finishing sludge leachate, are again significantly lower than the ash and clay sorbent combinations.

In summary, the removal of organics from the calcium fluoride leachate is best accomplished by the use of activated carbon. However, with regard to the metal finishing and petroleum sludge leachates, illite and vermiculite, respectively, are the most effective for treating the organics.

The behavior of a sorbent with regard to the removal of a particular contaminant varies with the type of leachate being treated. This effect may result from the competitive ion exchange and sorption processes which exist among the constituents of a leachate and the sorbent and cannot be easily predicted on the basis of results obtained from the use of synthetically constituted leachate. This latter point serves to emphasize the choice of an actual industrial sludge leachate rather than a synthetically constituted leachate if one wishes to draw predictive conclusions regarding the effectiveness of sorbents in reducing the contaminants in an industrial sludge leachate.

The experimental conditions, a 2.5 gram of concentrated leachate mixed with 1 gram of sorbent for 24 hours, did not provide results that were in agreement with some of the results obtained under flowing conditions but were useful in indicating promising sorbents. In general, the sorption capacities exhibited by a sorbent for a specific constituent in a leachate, under flowing condition, was significantly higher than that achieved under non-flowing conditions. In some cases no removal of specific constituents by a sorbent was observed under non-flowing conditions but significant removals were observed under flowing conditions.

The pH of the leachate is a factor in the leaching and removal of constituents by a specific sorbent. The pH of the effluent leachate, after prolonged passage through the lysimeter, approaches that of the influent leachate. Some sorbents are more effective in removing specific cations under alkaline conditions than acidic conditions. Acidic fly ash leaches cations into the leachate under acidic conditions, but under alkaline conditions it effectively

removes these constituents. When this occurs, another sorbent, such as basic fly ash, should be used in combination with the acidic fly ash in a layered system to remove the constituents being leached out. This leaching will decrease to insignificant levels when the effluent from the acidic fly ash becomes alkaline.

The permeabilities exhibited by the sorbents are a significant factor in the removal of the contaminants from the three leachates studied. The coefficients of permeability for the clays were so low that mixtures of 20 percent clay and 80 percent sand were used to obtain adequate flows of leachate through the sorbents in the lysimeters.

The coefficients of permeability for most of the sorbents, with the exception of activated alumina, kaolinite, and bottom ash, remained fairly constant for both the calcium fluoride sludge leachate and petroleum sludge leachate. The coefficient of permeability for kaolinite exhibited a decrease but it was not as marked as the decrease in the coefficient of permeability for the activated alumina and bottom ash upon the addition of these leachates. For the cases of the metal finishing sludge leachates, most of the sorbents exhibited a decrease in the coefficient of permeability with the exception of the activated carbon. The coefficient of permeability for this sorbent remained fairly constant for all three types of leachate. The marked decreases in the coefficient of permeabilities may result in ponding when the mixtures containing these sorbents are used to treat the leachate studied unless provisions, such as the addition of inert materials to these sorbents, are made to minimize these decreases in permeability.

The composition and concentration of constituents in the industrial sludges collected over a period of a year show considerable variations leading, in some cases, to wide fluctuations within the leachate. Thus, the selection of sorbents to treat these leachates must take into account the changes in composition and concentrations that can be encountered.

SECTION 3

RECOMMENDATIONS

A test, preferably under non-flowing conditions, must be devised for predicting the effectiveness of the sorbents selected for removing specific constituents from industrial sludge leachates. This may be achieved by identifying the desired properties such as clay type, inorganic composition and carbon content in naturally occurring sorbents located in the vicinity of the landfill. Under flowing conditions, evaluation of a sorbent in a lysimeter is time consuming and requires analysis of a large number of samples.

Means for handling suspended solids present in the leachate must be devised to minimize the clogging of the sorbent bed in the field. In this study, the suspended solids in the leachates (generated from the industrial sludges) were removed prior to treatment.

Each sorbent was evaluated separately in the treatment of the various types of industrial sludge leachates. Since a combination of sorbents must be used in a single bed for treating the leachate, the removal capacity of these combinations in a single column must be evaluated.

The influence of variations in weather conditions such as temperature, pH of precipitations, etc., on the removal processes must be studied. For example, pH has been shown to be a factor in the leaching - removal process. Since it is well known that the pH of precipitation can vary dramatically with locality (15), process development must define and design for this effect.

Since these naturally occurring sorbents show promise for removal of cations, anions, and organics from the leachates studied, an investigation should be carried out using these inexpensive natural sorbents rather than refined sorbents such as activated carbon for tertiary treatment of waste streams. Fly ash has been studied extensively for this purpose, but its use as part of a sorbent mixture has not been examined. Also, the sorbents could be used in sand beds or mixed media filters. The low cost of these sorbents warrants their being discarded rather than being regenerated, as in the case with activated carbon.

The application of sewage treatment effluents to agricultural soils has been handicapped by the presence of trace amounts of toxic cations and anions in this effluent. The naturally occurring sorbents and waste products should be tested with the agricultural soils to determine whether these sorbents can provide an inexpensive means of tying up these toxic substances before they can contaminate ground or surface waters or be incorporated within the vegetation.

The selection of sorbents used in this study was limited by time and financial considerations. Other sorbents should be looked at. For example, in our study, alumina was shown to have a great affinity for a large number of cations and anions; however, its low permeability negated its usefulness as a sorbent. By choosing a naturally occurring soil or waste materials such as red mud, etc. with a high alumina oxide content or by admixing with sand, this permeability problem can be overcome.

Likewise, the choice of industrially generated sludges used in this study led to a limited number of measurable contaminants being encountered in the leachate. Sorbent combinations for the treatment of only calcium, magnesium, copper, nickel, zinc, fluoride cyanide and organics have been defined. Additional industrial sludges whose leachate contains significant concentration of cadmium, chromium, lead, iron, mercury, arsenic, antimony, tin, strontium, etc. should be examined to define the sorbent combinations that can be used to treat these contaminants.

The results of this additional work could provide a list of promising sorbent combinations that may be recommended to industry for treating the heavy metal, toxic anions and organics encountered in their sludge leachate.

SECTION 4

MATERIALS DESCRIPTION

SORBENTS

The sorbent materials that were selected for this study are bottom ash, fly ash, zeolite, vermiculite, illite, kaolinite, activated alumina, cullite, and activated carbon. The selection of these materials was based on the consideration of three factors, namely, (1) economics, (2) availability, and (3) removal potential.

Fly Ash

Fly ash is a waste product of fossil fueled power generating plants and is collected by electrostatic precipitators from the fuel gases before they enter the stacks. This material is generally dark gray in color and is composed of constituents present in coal or their combustion products. Physically, it is a fine gritty substance with the individual particles ranging from 0.5 to 100 microns. The principal chemical constituents of fly ash are silica, alumina, iron oxides, sulfur trioxides, and alkali and alkaline earth metals. Approximately 30 million tons of fly ash is produced annually in this country; only 17.4% is eventually utilized, and the balance is disposed of in landfills. The samples, both acidic and basic, used for this study were supplied by Public Service Electric & Gas Company, Hudson Generating Station, Jersey City, New Jersey.

Bottom Ash

As in the case of fly ash, bottom ash is also a waste product of fossil fueled power generating plants and is collected as a residue of the furnace. This material is generally dark gray in color and is also composed of constituents similar to those present in fly ash. However, the individual particle is much larger than that of fly ash. The samples used for this study were also furnished by Public Service Electric & Gas Company, Hudson Generating Station, Jersey City, New Jersey. The material as received contained grain sizes ranging from 150 microns to 1/2 inch. They were ground to pass a sieve size of 80 mesh before use.

Zeolite

Any mineral belonging to the zeolite family of minerals and synthetic compounds is characterized by an aluminosilicate tetrahedral framework and loosely held water molecules, permitting reversible dehydration. Zeolites

have been extensively studied from theoretical and technical standpoints because of their potential and actual use as molecular sieves, catalysts, and water softeners. Zeolites are low temperature and low-pressure minerals found in aurygdaloidal basalts and also as authigenic minerals in sandstones and other sediments. These materials are usually white in color. After considering potential sorption characteristics, as well as availability, zeolite was selected for the present study. The sample used was from Brickhorn, New Mexico, and was furnished by the Double Eagle Petroleum and Mining Company, Casper, Wyoming. Physically, the material is light tannish-white in color and has a powder-like texture. The sorbent was used as received.

Kaolinite

The structure of kaolinite is composed of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit. It is the principal mineral of the kaolinite group of clay mineral. The mineral kaolinite has a moderately low cation-exchange capacity (5-15 milliequivalent per 100 g). Broken bonds around the edges of the silica-alumina units are the major cause of this exchange capacity. Kaolinite may form under acid conditions at low temperatures and pressures. It is a principal component of lateritic-type soils. Kaolinite has been used extensively in the ceramics industry and in paper products. The selection of this sorbent material was principally due to its importance in clay family as well as its potential sorptive properties and availability. This material was furnished by Georgia Kaolin Company, Elizabeth, New Jersey. Physically, it is tannish-white powder. It was used as received.

Vermiculite

This micaceous mineral exfoliates when heated or subjected to certain chemical reactions. It is a hydrated magnesium aluminum iron silicate. The structure of vermiculite consists of trioctahedral mica sheets separated by double water layers and is unbalanced by substitution of aluminum for tetrahedral layer. The resulting charge deficiency is satisfied by exchangeable cations which occur chiefly between the mica layers. Vermiculites have a high cation-exchange capacity (150 milliequivalents per 100 g). They also adsorb certain organic molecules between the mica layers. It is frequently listed as an alternate product of biolite mica in ancient sediments. Vermiculite is extensively used in many industries, including fireproofing, insulation, fertilizer conditioners, and packing materials. This material was used as received and was obtained from W.R. Grace & Co., Trenton, New Jersey.

Illite

The term illite is used to denote the aluminum, magnesium, and iron rich mica found in the clay fraction of weathered shale in Illinois. The basic structural unit is composed of two silica tetrahedral sheets with a central octahedral sheet. The size of naturally occurring illite particles is very small with well-defined edges. The illites have a moderate cation-exchange capacity (20-30 milliequivalent per 100 g). It is primarily due to broken bonds, but lattice substitution may also be a cause 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 obtained from A.P. Green Refractory Co., Morris, Illinois.

The material received was in rock form and was ground to powder that passed through an 80-mesh screen before use.

Activated Alumina

Activated alumina is a highly porous, granular form of aluminum oxide with preferential adsorptive capacity for moisture and odor. Sizes range from powder to 1.5-inch diameter particles. In this study, particle sizes less than .045 mm and in the size range from 0.147 mm to 0.295 mm were examined. Activated alumina has been used as a desiccant for gases and vapors in the petroleum industry. It is also used as a catalyst or catalyst carrier. The sample studied was furnished by Alcoa, Bauxite, Arkansas.

Activated Carbon

Activated carbon is a manufactured form of carbon with high adsorptivity for gases, vapors, and colloidal solids. It is obtained by the destructive distillation of carbonaceous materials and activated by heating to 800-900°C with steam or carbon dioxide. This results in a porous internal honeycomb-like structure. The specific area of air activated carbon is generally very large, ranging from 600 to 2000 square meters per gram. Although capable of adsorbing large amounts of water vapor, activated carbon finds its major use in solvent recovery, odor and taste removal, and as a catalyst and catalyst carrier. The sample (Grade 718, Granular) was obtained from Witco Chemical, Activated Carbon Division, New York, New York.

Cullite

Cullite is a commercial name of a synthetic zeolite. It is a chemically bound mixture of oxides of sodium, aluminum, and silicon. Physically, it has a white granular form, ranging from 16 to 40 mesh. The primary use of this material is in water softening. This material was selected primarily due to potential capacity as a reference point of synthetic sorbent material. The sample used in this study is called "High Capacity Cullite", abbreviated "Cullite" hereafter. The sample was supplied by Culligan U.S.A., Northbrook, Illinois.

SLUDGE SOURCES

The calcium fluoride sludge used in this study is the result of lime precipitation of fluoride in waste streams from etching processes used in the electronics and aircraft industries. Three samples designated as #1, #2, and #3 were collected over a period of a year to determine how changes in production schedules and process influence the composition of the leachate generated from this sludge.

The metal finishing sludges designated as #1, #2, and #3 were also collected over a year and are the result of alkaline treatment of a waste stream from

a metal finishing plant.

Storage tank bottoms and the API separator were the source of the petroleum sludge #1 and #2 generated by refineries.

SECTION 5

EXPERIMENTAL PROCEDURES

PREPARATION OF SORBENT MATERIALS

All sorbent materials were used as received. Sorbent materials which were not obtained as a powder (illite, bottom ash, and vermiculite) were ground in 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; 13th Ed., 1971, A.P.H.A.) and stored in a desiccator until used.

PREPARATION OF BACKGROUND LEACHATES FROM SORBENTS

Background leachates of all sorbents except vermiculite were prepared using deionized water and dried sorbent material in the ratio of 2.5 ml water per gram of sorbent material and agitated in a Burrell Shaker for 24 hours at ambient temperature. Our studies revealed that saturation of the mixture with respect to total dissolved solids as measured by conductance was achieved in 24 hours. The vermiculite leachate was prepared in ratio of 10 ml of water to one gram of sorbent material because all the water was taken up by the vermiculite and none was available for analysis when the 2.5 to 1 ratio was used. 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-filterable solids. The filtrates (leachates) were then analyzed according to procedures described later.

PREPARATION OF SLUDGE LEACHATES

A sample of each type of sludge was dried at 103°C to constant weight in order to determine its moisture content. In the case of the calcium fluoride and metal finishing sludges, the unaltered sludge was then mixed with deionized water in a ratio of 2.5 ml water per gram of dried sludge (as defined by the above moisture content determination) and mechanically stirred for 24 hours. The above ratio used in the test was arrived at after a series of trial ratios were carried out. This involved decreasing the quantity of water in the mixture until maximum sludge leachate concentrations were achieved.

The petroleum sludge leachates presented a filtration problem because of the extremely high concentration of oils and greases present in the sludge. Thus, a higher mixture ratio (i.e. 10 to 1) of water to sludge was employed. Ratios less than this were extremely difficult to filter. All suspensions,

with the exception of the metal finishing sludge leachate, were filtered through a glass fiber filter (Reeve Angle Type 934A) after stirring. The resultant filtrates were analyzed, stored in screw-capped plastic bottles or carboys at ambient temperatures until used.

The metal finishing sludge leachate was prepared by filtering the suspension with a Trommel Rotary Vacuum Laboratory Filter (Fabricators, Inc., of Piscataway, New Jersey) using newsprint paper, because of the slow rate of settling of the solid encountered with this sludge. This leachate was then passed through a glass fiber filter to remove any nonfilterable residue, analyzed and stored in plastic carboys at ambient temperature until used.

All leachates were analyzed again just before use, even though stored leachate samples failed to exhibit any significant changes in contaminant concentration.

STATIC STUDIES

Into a tared, one liter screw-capped, polypropylene Erlenmeyer flask was placed 100 grams of dried sorbent material. To this was added 250 ml of sludge leachate. To the vermiculite, 1000 ml of sludge leachate was added because the 250 ml amount of leachate initially added was absorbed by this sorbent and none was left for analysis after filtration. The flask was sealed and agitated 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 analyzed. Vermiculite, illite and kaolinite were used as a mixture containing 80 grams of inert Ottawa sand and 20 grams of sorbent (see Tables 3, 7, and 10). These mixtures were required in the dynamic studies to increase the permeability of these sorbents to acceptable levels (see the following section). Thus, these mixtures were used in the static studies to provide a basis for comparing the static results with the lysimeter results.

DYNAMIC STUDIES

In order to simulate dynamic conditions, lysimeter studies were conducted using 500 g of sorbent material, except for activated carbon where 250 g provided approximately the same column height. The sorbents, vermiculite, illite, and kaolinite, were prepared as a mixture consisting of 80 percent inert Ottawa sand and 20 percent clay. This ratio was arrived at after a series of studies established that this would permit adequate flows of leachate through these sorbents. "Pure" clay lysimeters did not exhibit adequate permeability characteristics.

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 laboratory arrangement of the lysimeters are 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

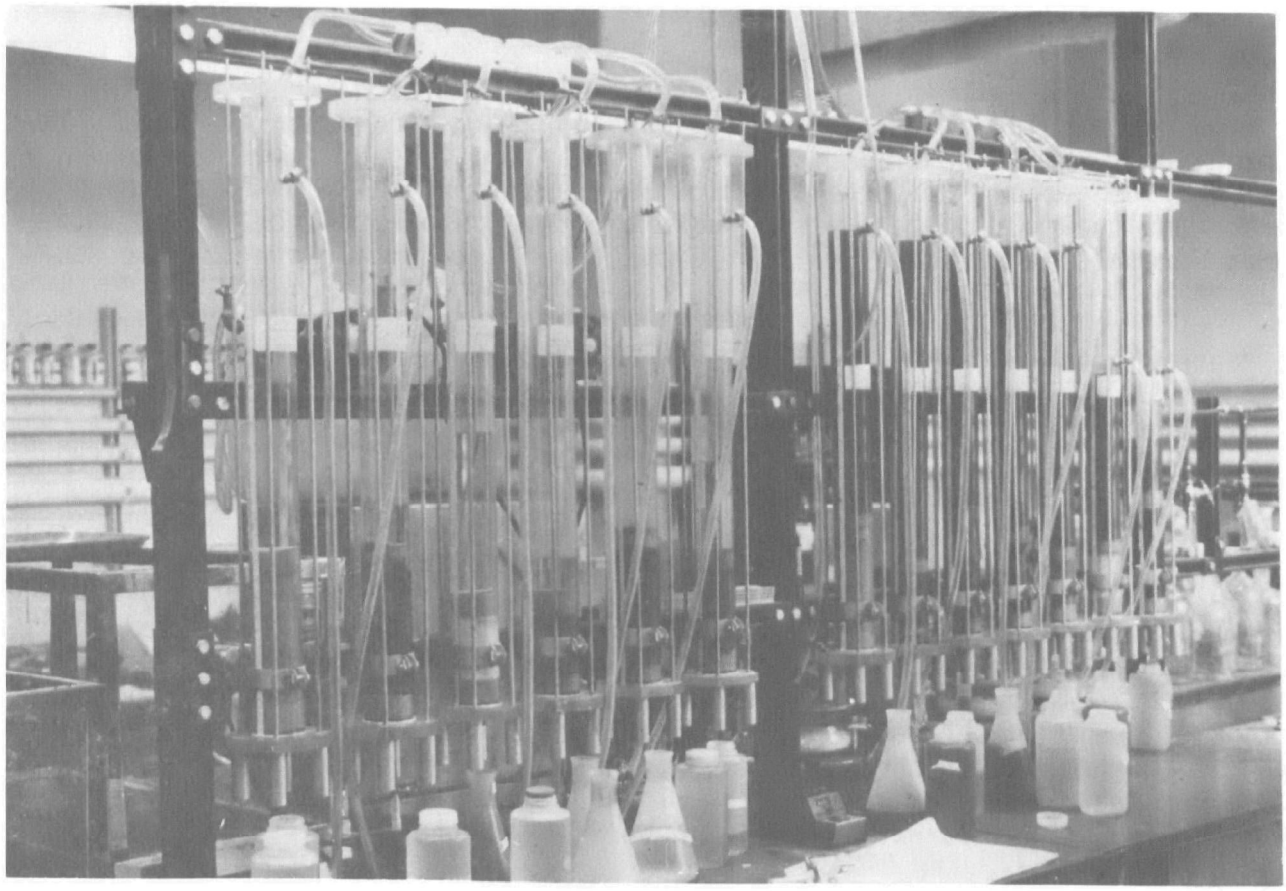

Figure 1. Laboratory Arrangement of Lysimeters

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 then filled with leachate to the level of an overflow drain, which had been trapped into the top side of the column, to permit a constant head condition. Leachate was fed to the top of the column through a valved manifold that distributed the leachate to 10 lysimeters simultaneously, from a central reservoir. The central reservoir, a 100-liter polyethylene carboy, delivered the leachate to the manifold system by means of a gravity syphon feed arrangement. Any overflow from the constant head drains was collected and pumped back up to the central reservoir. All tubing in the system was made of Tygon tubing (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 break-through for all measurable contaminates had occurred or excessively low permeabilities were encountered. Break-through is defined as that condition when the concentration of the species of concern in the collected effluent sample approached or exceeded that in the influent.

ANALYTICAL PROCEDURES

The constituents in the leachate generated from each sludge were initially identified using emission spectroscopy and x-ray fluorescence. Their concentration was then determined using atomic absorption and specific ion probes. The concentration of organics was determined using total organic carbon and chemical oxygen demand measurements. pH and conductivity measurements were also carried out on the leachate to further characterize the samples.

pH Measurements--

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--

Measured using a Beckman conductivity bridge (Model RC16B2) together with a specific conductance cell having a cell constant of 1.

Chemical Oxygen Demand (COD)--

An automated procedure based on the manual method described in "Standard Methods" was employed in the determination of COD. The sample was digested with a potassium dichromate - sulfuric acid digestion mixture, and the depletion of the hexavalent chromium (due to the oxidation reaction with the samples) was measured colorimetrically. This automated analysis was performed using a Technicon Autoanalyzer II (Industrial Method Number 137-71W).

Total Organic Carbon (TOC)--

Measured by use of the Dohrmann Envirotech DC-52D Carbon Analyzer.

Determination of Anionic Species--

The analysis for the anions Cl^-, F^-, CN^- were as follows:

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 1,2-cyclohexylenedinitrilotetraacetic 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. Therefore, total fluoride was measured.

Analysis of cyanide ion--Analysis of cyanide ion was conducted using a cyanide ion electrode (Orion Model 900100) connected to an Orion Model 701 digital pH/mv meter. This electrode responds directly to cyanide ion activity, without regard to sample ionic composition, total ionic strength, pH or complexing species. The free cyanide ion content of a sample solution was determined directly by comparing the electrode potentials obtained using standards of known free cyanide ion content. Semi-logarithmic calibration curves were obtained over the range of 0.01 to 10 ppm using reagent grade sodium cyanide. All solutions were adjusted with 10M NaOH to concentrations of 0.1M in NaOH.

Determination of Metals--

The concentrations of the various metals reported (i.e. Ca, Cd, Cr, Cu, Fe, Mg, Ni, Pb, Zn) were determined using a Varian Techtron Atomic Absorption Spectrometer (Model 1200) according to E.P.A. procedures (16). The reference solutions used to construct calibration curves in these determinations were made up using deionized water with a specific resistence of 18 Megohm-cm (25°C).

PERMEABILITY STUDIES

After a steady flow condition through the column was established, volume throughput per second was recorded. The permeability coefficient, k, was then calculated by means of the following equation (17):

$$k = (QL)/(aht)$$

where a = Cross-sectional area of soil column

Q = Total quantity of water which flowed through the soil column in elapsed time, t.

h = Total hydraulic head, i.e., distance from the bottom drain to the top of the leachate level corresponding to the level of the top overflow drain.

l = Length of soil sample in the lysimeter.

t = Total elapsed time in seconds for quantity collected, Q.

Permeability tests were conducted each day, until break-through had been achieved. In certain cases, where the flow through the lysimeters ceased, the studies were discontinued even though leachate analysis indicated that the sorbtive capacity of the soil column was not yet exhausted.

GRAIN SIZE DETERMINATION

The test procedure for grain size determination follows: For large grain

sorbents (i.e. >200 mesh) sieve analysis was performed. For those sorbents of a fine particle size (<200 mesh) the hydrometer test was used to determine grain size. For mixed size composition a combined analysis was used.

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 were specified according to ASTM.

Hydrometer Analysis--

The hydrometer analysis is based upon Stokes' law, which relates the terminal velocity of a sphere falling freely through a fluid to the diameter. It is assumed that Stokes' law is valid to a mass of dispersed solid particles of various diameter and shapes. The hydrometer is used to determine the percentage of dispersed particles remaining in suspension at a given time. The grain size equivalent to a spherical particle is computed for each hydrometer reading using Stokes' law.

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 2). The grain size distribution curve was obtained by plotting particle diameter on the logarithmic abscissa and the percent finer by weight on the arithmetic ordinate. The grain diameter whose size is greater than that of 10 percent of the particles by weight is called the effective diameter because of the influence of the smaller grain sizes on soil properties. 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 such samples of poorly graded materials. The reader is referred to standard texts of soil mechanics for a more detailed explanation (17).

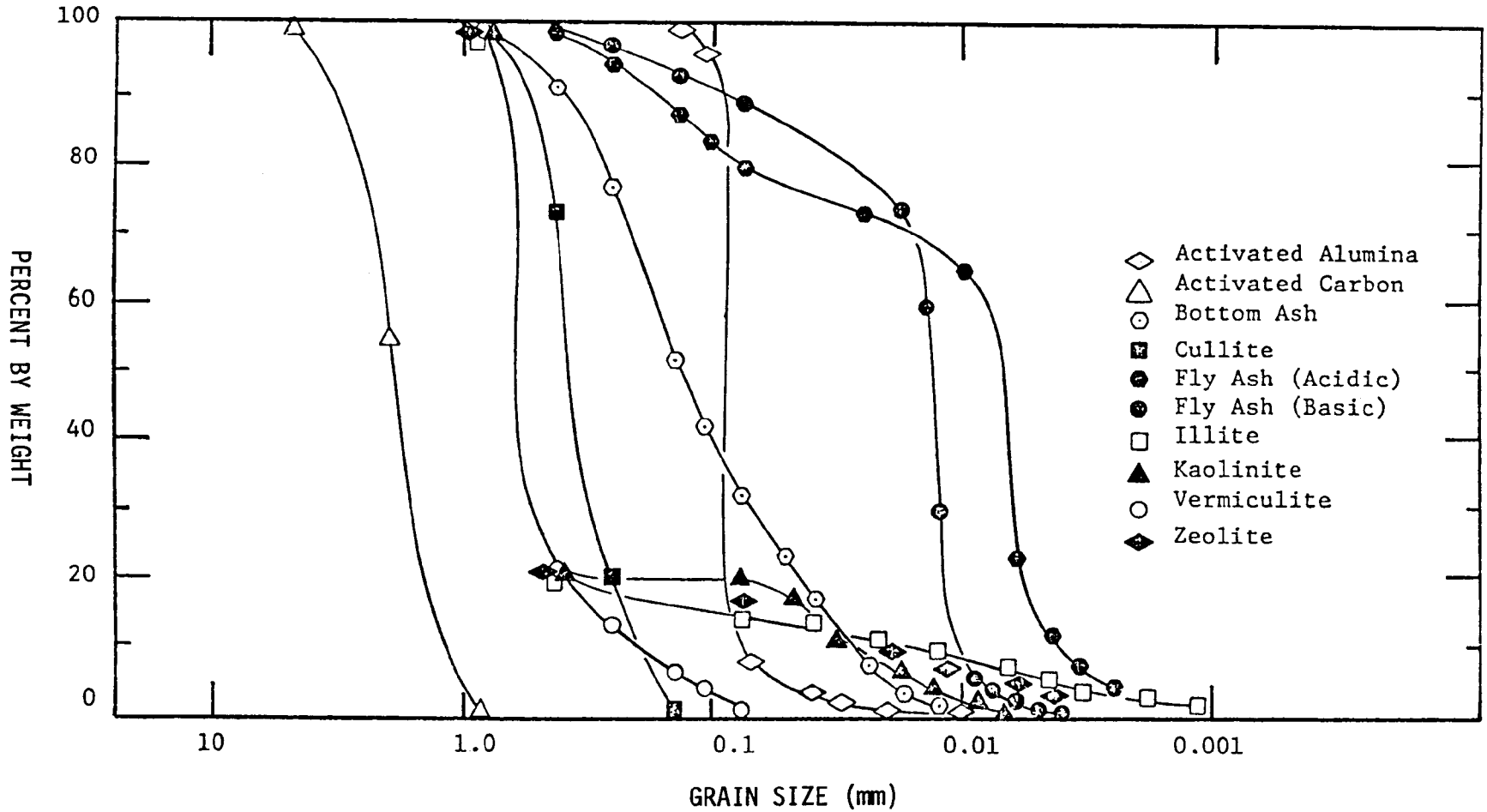

Figure 2. Grain-Size Distribution of Sorbents.

SECTION 6

RESULTS AND DISCUSSION

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 schedules and manufacturing processes. Comprehensive analyses were performed in accordance with "Standard Methods" on leachates generated from these sludges. Petroleum sludges were collected from two separate sources, a storage tank bottom and API gravity separator, to determine the effect of two different sources of petroleum sludge on the composition and concentration of the constituents in their respective leachates.

The heavy metals present in the leachates from the different sludges were found to be copper, chromium, cadmium, iron, nickel, lead, and zinc. Their concentrations are listed in the first column of Tables 1 to 3, 5 to 7, 9, and 10. The concentrations of calcium and magnesium were also measured because they contribute to the hardness in water. The concentrations of chloride, fluoride, and cyanide ions were also determined because their presence in water in sufficient concentrations can lead to its rejection as potential drinking water. As described earlier, this study is divided into two phases; namely, the static study and dynamic study.

RESULTS OF STATIC STUDIES

Calcium Fluoride Sludge Leachate

Analysis of the leachate prepared from the three calcium fluoride sludge samples collected over a period of one year indicated that most variations in concentrations of the measured constituents are within a factor of two with the exception of cyanide (see Tables 1 to 3). Cyanide was not found in significant quantities in sludge sample #3 (see Table 3), the most recent one collected, because the use of cyanide in the production processes was discontinued during the study year period. This was established through discussions with plant personnel at the place where the sludge was obtained after it was determined that amounts of cyanide found in the leachate prepared from sludge sample #3 were significantly lower than those encountered in sludge leachates #1 and #2.

Further examinations of the concentration levels of the constituents in the leachate prepared from the fluoride sludges reveal that the calcium, magnesium, copper, nickel, fluoride, and cyanide and organic concentrations (as indicated by COD and TOC) are significant. However, cadmium (with the

exception of sludge #1 leachate) iron, lead, chromium, and zinc are found at concentration levels that do not differ significantly from the minimum concentration levels that can be readily measured using the atomic absorption spectrometer and specific ion probes.

The sorbent capacity of eleven natural and refined sorbents for the removal of constituents in the leachate is represented in Tables 1 to 3 for each of the constituents that exist in the leachate at measurable levels. This data was obtained by subtracting the amount of each constituent remaining in the leachate after treatment with sorbent, from its initial concentration and dividing by the amount of sorbent used. Both acidic fly ash and activated carbon were not evaluated using leachate #1 (see Table 1) and leachate #2 (see Table 2) but were examined using leachate #3. During our static studies on leachate #1 and leachate #2, only the basic fly ash was available. Also, our limited supply of activated carbon was depleted due to the unanticipated large amounts required for these studies. Since we had collected a limited amount of sludge, we were unable to prepare leachate #1 and leachate #2 to evaluate the activated carbon and acidic fly ash once we obtained sufficient supplies of these sorbents.

An examination of the static study data (see Table 1, Table 2, and Table 3) resulting from the mixing of eleven sorbents with three types of leachate suggests the following observations: The sorbent exhibits a capacity for a specific contaminant and may be used to remove this contaminant from the leachate. The sorbent exhibits no capacity for a contaminant in the leachate but the amount of this contaminant that is leached from the sorbent when it is mixed with the leachate is significantly less than the amount obtained when it is mixed with water (see sorbent capacities designated as L). Finally, the sorbent exhibits no capacity for the contaminant and no reduction in leaching is observed when it is mixed with the leachate. For example, the acidic fly ash (see Table 3) exhibits a sorbent capacity of 105 mg of COD removed per gram of acidic fly ash used. For the case of the calcium, copper and fluoride ions, this sorbent exhibits no removal capacity but the concentration of these ions after treatment is significantly less than the mathematical sum of the concentration of these ions in the influent sludge leachate and that which is leached from the sorbent with water. Perhaps, the addition of a slightly alkaline leachate or the presence of contaminants in the leachate reduces the leaching potential of the calcium, copper, and fluoride ions from the sorbent. The acidic fly ash exhibited no removal capacity for the nickel ion since the sum of the nickel ion concentration in the sludge leachate and that which can be leached from the sorbent is equal to the effluent concentration level of nickel ion after treatment.

The sorbent capacities are listed in Table 4 for both the static and the lysimeter tests. The sorbent capacities are considered to include the removal capacities related to such processes as ion exchange, adsorption, etc. A study of the specific removal processes such as the determination of exchange capacities or generation of sorption isotherms was not carried out in this investigation because it would be necessary to modify the sludge leachate by altering the contaminant concentration to obtain this data.

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

Measured Parameters	Initial Condition 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	1.5	2.5	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)	0	4.1	0	2.7	0	15.5	37.6	84.0	40.1	-
		(2)	16.3	0	16.4	10.9	0	26.0	16.3	60.4	17.5	
		(3)	0	41.3	0	5.6	41.3	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 2 : STATIC STUDY RESULTS OF CALCIUM FLUORIDE SLUDGE LEACHATE #2

Measured Parameters	Initial Condition of Leachate	Description*	Bottom Ash	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina(I)	Activated Alumina(II)	Cullite	Minimum Detectable Value
pH	7.5	(1)	7.1	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/l)	365	(1)	20.0	300	6.0	1.5	2.5	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/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	<0.01	<0.01	0.07	<0.01	<0.01	<0.01	<0.01	
		(3)	-	-	-	-	0	-	-	-	-	
Cr (mg/l)	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/l)	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/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	2.2	<0.05	<0.05	<0.05	0.20	
		(3)	-	-	-	-	0	-	-	-	0	
Mg (mg/l)	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/l)	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/l)	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/l)	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/l)	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/l)	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/l)	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/l)	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/l)	8.5	(1)	0	4.1	0	2.7	0	15.5	37.6	84.0	40.1	-
		(2)	8.5	0	8.3	8.0	0	18.5	8.3	57.5	10.8	
		(3)	0	21.3	0	0.5	21.3	L	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 3 : STATIC STUDY RESULTS OF CALCIUM FLUORIDE SLUDGE LEACHATE #3

Measured Parameters	Initial Condition of Leachate	Description*	Bottom Ash	Fly Ash (Acidic)	Fly Ash (Basic)	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Carbon	Minimum Detectable Value
pH	7.2	(1)	7.2	5.1	10.1	9.3	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	1.5	2.5	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	>0.50	<0.20	
		(3)	-	-	-	-	-	-	-	-	
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	0.10	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	0.74	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	0.04	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)	0	0.50	4.1	2.7	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

TABLE 4 : COMPARISONS OF SORBENT CAPACITIES* IN STATIC AND LYSIMETER TESTS

(CALCIUM FLUORIDE SLUDGE LEACHATE)

Measured Parameters	Description*	Bottom Ash	Fly Ash (Acidic)	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon
Ca	Static Test #1	37.5	-	L**	663	0	163	113	998	1000	1000	-
	Static Test #2	260	-	L	693	47.0	163	335	913	913	912	-
	Static Test #3	108	L	L	-	65.0	0	85.0	795	-	-	275
	Lysimeter Test	-	350	0	-	84.8	630	1190	6300	-	-	547
Cd	Static Test #1	0.18	-	0.18	0.13	0.70	0.05	0.18	0.18	0.18	0.15	-
	Static Test #2	-	-	-	-	-	0	-	-	-	-	-
	Static Test #3	-	-	-	-	-	0	-	-	-	-	-
	Lysimeter Test	-	-	-	-	-	-	-	-	-	-	-
Cu	Static Test #1	0.30	-	0.48	0.43	0.15	L	L	0.48	0.48	L	-
	Static Test #2	0.73	-	0.83	0.73	0.20	L	0	0.70	0.70	0.18	-
	Static Test #3	L	L	0.10	-	0	L	0	0.15	-	-	0.25
	Lysimeter Test	-	2.2	0.49	-	0	0	8.9	2.9	-	-	2.0
Mg	Static Test #1	L	-	25.0	L	L	L	L	26.0	24.8	20.0	-
	Static Test #2	L	-	4.3	0	0	L	0	11.9	12.4	11.5	-
	Static Test #3	L	0	43.3	-	0	L	0	53.0	-	-	21.3
	Lysimeter Test	0	250	172	-	0	0	0	534	-	-	19.0
Ni	Static Test #1	0.18	-	0.30	0.18	0.09	L	0	0.43	0.35	0.03	-
	Static Test #2	0.13	-	0.13	0.13	0.05	L	0.13	0.13	0.13	0.13	-
	Static Test #3	0	0	0.25	-	0	L	0.25	0.25	-	-	0.25
	Lysimeter Test	-	-	-	-	-	-	-	-	-	-	-
F^-	Static Test #1	9.0	-	9.8	11.0	0.2	13.7	7.5	11.3	10.5	10.3	-
	Static Test #2	8.5	-	9.0	9.5	0.5	12.5	6.0	11.5	10.8	10.0	-
	Static Test #3	9.3	L	13.0	-	L	79.9	79.8	13.8	-	-	3.8
	Lysimeter Test	35.4	109	57.0	-	2.4	205	183	348	-	-	0.60
Cl^-	Static Test #1	L	-	L	0	2.5	46.3	21.3	L	L	0	-
	Static Test #2	L	-	0	0	0	20.0	10.0	L	L	0	-
	Static Test #3	0	0	48.8	-	5.0	313	188	L	-	-	0
	Lysimeter Test	-	-	-	-	-	-	-	-	-	-	-
CN^-	Static Test #1	0.30	-	0.10	0.15	0.10	1.1	L	0.30	0.15	0	-
	Static Test #2	0	-	0	0	0	0.65	L	0	L	0	-
	Static Test #3	L	0.03	0.05	-	0.02	0.25	0	0	-	-	0.05
	Lysimeter Test	-	-	-	-	-	-	268	-	-	-	-
COD	Static Test #1	L	-	93.5	L	22.8	70.0	0	L	0	L	-
	Static Test #2	L	-	91.0	L	21.5	121	0	L	0	L	-
	Static Test #3	0	105	73.0	-	4.1	264	44.0	L	-	-	104
	Lysimeter Test	100	704	232	-	0	250	102	0	-	-	956
TOC	Static Test #1	0	-	41.3	0	5.6	41.3	0	L	0	L	-
	Static Test #2	0	-	21.3	0	0.50	21.3	L	L	0	L	-
	Static Test #3	0	38.3	20.0	-	0	71.3	L	L	-	-	36.8
	Lysimeter Test	42.0	156	62.4	-	0	88.0	-	0	-	-	325

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

\- Indicates data not obtained for specific sorbent.

**L Represents no sorbent capacity and a reduction in leaching of contaminant when sorbent is mixed with leachate.

In Table 4 a comparison of the magnitude of the micrograms of constituents removed per gram of sorbent used between the various sorbents indicates which sorbents are the most effective for removing a specific constituent. Chromium, iron, lead, and zinc are omitted from this table because their concentrations in the leachate are not significantly greater than the minimum detectable value. There is no single sorbent material which is effective in removing all measured parameters. However, either a combination of the natural sorbents basic fly ash, kaolinite, vermiculite, and illite or the refined sorbents, activated alumina and activated carbon, can be used to treat all the measurable ions found in the calcium fluoride sludges provided that leaching of ions from the sorbents does not exceed the sorbent's capacity for removing these ions. The natural sorbents, basic fly ash and illite, exhibit leaching of specific ions in the presence of water which may reduce the effectiveness of these sorbents for treating the calcium fluoride sludge leachate. The basic fly ash leaches significant amounts of calcium whereas the illite leaches significant amounts of copper and magnesium ions (see Tables 1, 2, and 3). However, this leaching is reduced when these sorbents are placed in contact with the slightly alkaline leachate. This is indicated by the effluent concentration of the above ions being significantly less than the concentration level that is defined by the mathematic sum of the concentration of the ion in the leachate and the background of sorbent material. These were obtained with leachates that contained magnesium ion concentrations of 5.0 mg/l, 11.0 mg/l and 21.3 mg/l.

The above reason however doesn't explain the results where significant sorbent capacities are obtained for the removal of a specific ion in one or two leachates but not in the third leachate. The calcium ion concentration in all three fluoride leachates is above 300 ppm (see Tables 1, 2, and 3). Yet, the illite exhibits significant sorbent capacities for calcium in leachate #1 and leachate #2 but no sorbent capacity for calcium in leachate #3. The reason for these results is not clear at the present time. However, removal capacities may be highly pH dependent, and a slight difference in the leachate pH will give different results. That is, the pH of leachates #1 and #2 was 7.5, and that of #3 was 7.2.

Of 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 best able to reduce fluoride levels. Calcium and copper removal was best accomplished with activated alumina. Regarding the natural sorbents, kaolinite could be used for calcium and basic fly ash for copper removal. Basic fly ash and activated alumina were the most effective for magnesium and nickel removal. Vermiculite was the most effective for removing cadmium.

Marked variations in the sorbent capacity for the removal from the three leachates of specific contaminants can be observed in Table 4. One of the possible reasons 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. For example, the sorbent capacities exhibited by the basic fly ash for the magne-

sium ion in the three leachates are 25.0, 4.3, and 43.3.

Metal Finishing Sludge Leachate

Analysis of the leachate prepared from the three metal finishing sludges collected over a period of a year showed much greater variations in particular contaminant concentrations than those encountered with the calcium fluoride sludge leachate. Here, the concentration in some cases varied by at least a factor of six when a specific constituent within the three leachates was compared. For example, the calcium concentration ranged from 6.5 mg/l to 38 mg/l (see Tables 5 to 7).

The analysis of the metal finishing sludge leachates indicated the presence of significant concentrations of calcium, copper, magnesium, nickel, fluoride, chloride, as well as organics (see Tables 5 to 7). The concentrations of chromium, cadmium, iron, lead, cyanide, and zinc did not differ significantly from the minimum measurable levels that can be determined using the atomic absorption spectrometer and specific ion probes.

The sorbent capacity of the eleven natural and refined sorbents, with respect to each of the measurable constituents in the leachate, is represented in Tables 5 to 7. The sorbent capacities for the natural zeolites, the synthetic activated alumina II and cullite were again evaluated using only the metal finishing sludge leachate #1 and leachate #2. The sorbent capacities for acidic fly ash and activated carbon were determined using leachate #3. The sorbent capacities were obtained according to the calculations described earlier.

A comparison of the sorbent capacities (see Table 8) indicates the most effective sorbent material for removing specific constituents. Cadmium, chromium, iron, lead, and zinc were omitted from this table because their concentrations in the leachate were at levels that could not be measured. The natural sorbent, illite, was found to exhibit the largest sorbent capacity for the organics and fluoride ion. Kaolinite exhibited the largest capacity for calcium; vermiculite for magnesium, nickel and copper. Vermiculite and illite exhibited a capacity for chloride removal.

As in the case of the calcium fluoride sludge leachates, there is no single sorbent material which is effective in removing all ions from the leachates examined. However, a combination of vermiculite, illite and kaolinite shows promise for treating the metal finishing sludge leachate provided that the leaching of ions from one of the sorbents does not exceed the other sorbent's capacity for removing these ions. The vermiculite exhibits the best capacity for magnesium, copper, and nickel; kaolinite for calcium; illite and vermiculite for the organics and chloride; and illite for fluoride.

A significant reduction in the copper leaching from illite, as was the case for the fluoride sludge leachate, was only observed for leachate #3 (see Table 7). The lack of this reduction in copper when the illite was mixed with leachate #1 and leachate #2 is not understood at the present time.

TABLE 5 : STATIC STUDY RESULTS OF METAL FINISHING SLUDGE LEACHATE #1

Measured Parameters	Initial Condition 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	1.5	2.5	42.0	<0.10	<0.10	<0.10	
		(2)	22.0	295	10.0	7.1	25.5	<0.10	0.17	0.23	<0.10	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	
		(2)	0.02	<0.01	<0.02	<0.01	0.06	<0.01	<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	
		(2)	<0.20	0.50	<0.20	<0.20	<0.20	<0.20	1.1	0.60	0.30	0.20
		(3)	-	0	-	-	-	-	0	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	
		(2)	0.22	0.14	0.09	0.05	3.6	0.19	0.05	0.07	0.53	0.03
		(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	
		(2)	<0.05	<0.05	<0.05	<0.05	2.1	<0.05	<0.05	<0.05	0.20	0.05
		(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	
		(2)	42.0	17.0	53.0	20.0	48.0	2.0	0.17	0.23	0.75	0.05
		(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	
		(2)	0.15	0.08	0.16	0.08	0.68	<0.05	0.08	0.08	0.20	0.05
		(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	
		(2)	<0.20	0.28	0.29	<0.20	<0.20	<0.20	<0.20	<0.20	<0.30	0.20
		(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	
		(2)	0.02	<0.01	0.05	0.02	1.50	0.12	<0.01	<0.01	0.06	0.01
		(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	
		(2)	1.4	1.4	1.8	1.8	0.34	0.34	2.0	1.3	0.43	0.02
		(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	28.0	7.4	
		(2)	510	135	245	105	76.0	95.0	170	150	130	2.0
		(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	
		(2)	0.05	0.07	0.04	<0.03	<0.03	0.05	0.11	0.17	<0.03	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)	96.5	58.0	109	77.0	50.0	122	132	146	138	2.0
		(3)	1.3	97.5	L	200	118	0	0	0	0	
TOC (mg/l)	39.9	(1)	0	4.1	0	2.7	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 6 : STATIC STUDY RESULTS OF METAL FINISHING SLUDGE LEACHATE #2

Measured Parameters	Initial Condition 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	1.5	2.5	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	0.85	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)	0	4.1	0	2.7	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 7 : STATIC STUDY RESULTS OF METAL FINISHING SLUDGE LEACHATE #3

Measured Parameters	Initial** Condition 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	10.1	9.3	3.0	5.1	9.8	9.4	-
		(2)	7.5	6.6	8.9	8.4	3.8	8.0	9.3	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	1.5	2.5	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	<0.20	<0.20	<0.20	0.30	<0.20	0.60	<0.20	
		(3)	-	-	-	-	0	-	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	0.60	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	0.36	<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)	0	0.50	4.1	2.7	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.

TABLE 8 : COMPARISONS OF SORBENT CAPACITIES IN STATIC AND LYSIMETER TESTS

(METAL FINISHING SLUDGE LEACHATE)

Measured Parameters	Description*	Bottom Ash	Fly Ash (Acidic)	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon
Ca	Static Test #1	L**	-	L	L	L	0	64.0	15.8	15.7	16.0	0
	Static Test #2	L	-	L	L	55.0	0	100	33.5	33.5	33.5	-
	Static Test #3	19.0	0	0	-	273	0	383	95.3	-	-	79.0
	Lysimeter Test	-	123	146	-	1280	1828	930	737	-	-	283
Cu	Static Test #1	L	-	L	0.13	0.90	0	L	0.23	0.18	0	-
	Static Test #2	0	-	0	0	0.20	0	L	0.03	0.05	0	-
	Static Test #3	0.35	1.0	0.93	-	4.6	L	3.1	0.98	-	-	1.3
	Lysimeter Test	-	16.5	7.5	-	20.5	57.5	-	6.3	-	-	23.0
Mg	Static Test #1	L	-	2.5	L	L	L	40.0	44.6	44.4	43.1	-
	Static Test #2	L	-	40.0	L	50.0	L	45.3	49.8	47.9	48.1	-
	Static Test #3	L	25.5	58.3	-	88.8	6.3	30.6	63.5	-	-	58.5
	Lysimeter Test	-	448	200	-	485	1840	-	495	-	-	314
Ni	Static Test #1	0	-	0.18	0	0.70	L	1.0	0.18	0.18	0	-
	Static Test #2	0	-	0.05	0	0.40	L	0	0.15	0.18	0	-
	Static Test #3	L	0	0.23	-	1.4	0.50	1.4	0.33	-	-	0.23
	Lysimeter Test	-	4.9	2.0	-	3.0	7.3	-	2.5	-	-	7.2
F^-	Static Test #1	L	-	L	0	0	8.6	8.6	L	L	1.9	-
	Static Test #2	L	-	L	0	L	10.5	2.0	L	L	2.6	-
	Static Test #3	1.4	L	0.88	-	L	12.6	10.0	1.2	-	-	0
	Lysimeter Test	-	0	0	-	0	2.7	3.6	11.4	-	-	0
Cl^-	Static Test #1	L	-	0	0	200	123	375	0	0	0	-
	Static Test #2	L	-	0	L	340	325	0	0	0	0	-
	Static Test #3	0	50.0	93.8	-	313	369	438	37.8	-	-	47.8
	Lysimeter Test	-	-	-	-	-	-	-	-	-	-	-
COD	Static Test #1	1.3	-	97.5	L	200	470	0	0	0	0	-
	Static Test #2	195	-	130	688	2130	2880	1880	L	0	150	-
	Static Test #3	0	75.0	58.5	-	300	258	244	0	-	-	115
	Lysimeter Test	-	1228	320	-	1048	3060	0	0	-	-	1476
TOC	Static Test #1	0	-	41.5	0	71.0	368	0	0	0	0	-
	Static Test #2	50.0	-	20.0	260	60.0	1381	971	0	0	0	-
	Static Test #3	0	32.8	19.3	-	115	143	143	0	-	-	38.3
	Lysimeter Test	-	519	148	-	444	1430	0	0	-	-	589

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

\- Indicates data not obtained for specific sorbent.

**L Represents no sorbent capacity and a reduction in leaching of contaminant when sorbent is mixed with leachate.

Petroleum Sludge Leachate

Analyses of the leachates prepared from the tank bottom sludge and the A.P.I. gravity separator sludge indicated significant concentrations of calcium, copper, iron, magnesium, nickel, zinc, fluoride, chloride, cyanide, and organics (see Tables 9 and 10). However, marked differences in the concentrations of constituents in each leachate were observed. The leachate prepared from the tank bottom sludge contained a greater number of constituents of higher concentration levels than those present in the A.P.I. separator sludge leachate. For example, the organics in the tank bottom sludge leachate are some four times higher than found in the separator sludge leachate. The cyanide concentration in the bottom sludge leachate is 40 times higher than in the separator sludge leachate. Also, the tank bottom sludge leachate contained significant levels of iron and nickel whereas the levels of these metals in the separator sludge leachate were not significantly higher than the minimum detectable values observed using the atomic absorption spectrometer and the specific ion probes.

The sorbent capacities exhibited by eleven sorbents for the removal of constituents in the leachate is represented in Tables 9 and 10. The sorbent capacities of the zeolite, cullite, and activated alumina II were determined with the tank bottom sludge leachate. The acidic fly ash capacity was only determined with the A.P.I. sludge leachate because we depleted our supply of the tank bottom sludge leachate.

The sorbent capacities are listed in Table 11. Here, a comparison of the sorbent capacities indicates the most effective sorbent for removing a specific constituent. Cadmium and chromium were omitted because their concentration levels in the leachate were not significantly different from the minimum measurable concentrations.

In the natural sorbent category, illite appears to be effective for removing magnesium and fluoride. Illite and vermiculite are effective for chloride and the organics. Vermiculite is more effective than illite for removing the cyanide ion in the tank bottom leachate but the reverse is true for the A.P.I. sludge leachate where the cyanide ion concentration is lower. Illite exhibits a greater sorbent capacity than the kaolinite for the calcium in the tank bottom sludge leachate where high leachate concentrations of calcium are encountered (see Table 9). On the other hand, kaolinite exhibits a greater sorbent capacity for the calcium in the A.P.I. sludge leachate where the calcium leachate concentration is significantly lower. Activated carbon is the best sorbent in the refined category for the removal of the chloride, cyanide, fluoride, and organics. Vermiculite exhibits the best sorbent capacities for copper in the A.P.I. sludge leachate, iron in the tank bottom sludge leachate, and zinc in both leachates. Basic fly ash exhibits a capacity for nickel for both leachates. Thus, combination of basic fly ash, kaolinite, vermiculite, and illite shows promise for treating the constituents present in both petroleum sludge leachates provided that the leaching of ions from one sorbent does not exceed the other sorbent's capacity for removing these ions. For the case of the refined sorbents, activated alumina and activated carbon show promise for treating both leachates.

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

Measured Parameters	Initial Condition 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	1.5	2.5	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	0.67	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	<0.03	<0.03	<0.03	<0.03	0.25	0.06	
		(3)	L	0	0	0	0.15	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	903	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)	0	4.1	0	2.7	0	15.5	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 Condition 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	10.1	9.3	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	1.5	2.5	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	0.60	0.20	
		(3)	-	-	-	-	-	-	0	-	
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	0.23	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)	0	0.50	4.1	2.7	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.

TABLE 11 : COMPARISONS OF SORBENT CAPACITIES IN STATIC AND LYSIMETER TESTS

(PETROLEUM SLUDGE LEACHATE)

Measured Parameters	Description*	Bottom Ash	Fly Ash (Acidic)	Fly Ash (Basic)	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon
	Static Test #1	0	-	L	0	0	415	300	812	811	765	728
Ca	Static Test #2	0	0	L	-	0	0	100	125	-	-	92.8
	Lysimeter Test	157	0	0	-	1010	1110	14.0	200	-	-	160
	Static Test #1	L	-	0	0	0	0.15	0.15	0.15	0.15	L	0.08
Cu	Static Test #2	0.35	L	0.28	-	1.8	0.	L	0.28	-	-	0.23
	Lysimeter Test	0.04	2.7	2.5	-	1.6	0	0	0.39	-	-	0
	Static Test #1	0.15	-	0.38	0	1.0	0	0	0.38	0.38	0	0.38
Fe	Static Test #2	-	-	-	-	-	0	-	-	-	-	-
	Lysimeter Test	-	-	-	-	-	-	-	-	-	-	-
	Static Test #1	L	-	7.5	110	100	70.0	37.5	996	995	903	468
Mg	Static Test #2	L	L	58.8	-	0	25.6	18.8	68.0	-	-	43.8
	Lysimeter Test	0	0	140	-	90.0	180	753	107	-	-	10.0
	Static Test #1	0	-	0.10	0	0.20	0	0	0.25	0.23	0.03	0.15
Ni	Static Test #2	L	0	0.13	-	0	L	0.25	0.13	-	-	0.13
	Lysimeter Test	-	-	-	-	-	-	-	-	-	-	-
	Static Test #1	0.08	-	0.08	0.05	0.30	0	L	0.10	0.05	0.05	0.10
Zn	Static Test #2	0.30	L	0.30	-	1.5	L	1.5	0.30	-	-	0.30
	Lysimeter Test	0.23	2.0	2.0	-	6.4	0	0	0.43	-	-	1.3
	Static Test #1	1.5	-	0.50	1.3	1.0	3.2	3.3	2.7	1.9	1.6	3.3
F^-	Static Test #2	0.90	L	0.25	-	L	10.1	L	L	-	-	0.50
	Lysimeter Test	0	9.9	7.2	-	0	12.1	4.3	3.4	-	-	1.3
	Static Test #1	10630	-	11980	10630	49600	19780	17280	11530	11630	13730	20490
Cl^-	Static Test #2	L	40.0	75.0	-	313	1750	350	15.0	-	-	288
	Lysimeter Test	-	-	-	-	-	-	-	-	-	-	-
	Static Test #1	12.5	-	7.5	12.3	45.0	16.3	6.5	6.5	4.8	1.8	19.0
CN^-	Static Test #2	0.33	0.43	0.35	-	1.8	2.1	0	0	-	-	0.43
	Lysimeter Test	0	3.3	3.3	-	13.0	15.5	4.2	0	-	-	2.9
	Static Test #1	628	-	628	703	2850	1628	465	575	448	420	2985
COD	Static Test #2	588	825	712	-	2900	3526	3200	308	-	-	753
	Lysimeter Test	495	4545	5125	-	12555	5525	795	556	-	-	3000
	Static Test #1	208	-	225	175	810	618	213	253	180	108	1055
TOC	Static Test #2	224	318	273	-	1124	1325	1240	125	-	-	289
	Lysimeter Test	219	1813	983	-	4995	2620	273	248	-	-	1270

* Sorbent Capacities are expressed in g of ion removal per g of sorbent used.

\- Indicates data not obtained for specific sorbent.

**L Represents no sorbent capacity and a reduction in leaching of contaminant when sorbent is mixed with Leachate.

DISCUSSION OF STATIC RESULTS

The results of the static tests on the three types of leachates (i.e., calcium fluoride, metal finishing, and petroleum) indicate that constituents present in these leachates in some cases can be removed by the same sorbent, and in other cases, different sorbents must be used to remove the same constituent in the leachate. The fluoride, chloride, cyanide, and organics in all three types of leachate can be treated with illite. Vermiculite exhibits removal capacities for the copper in the metal finishing sludge leachate and petroleum sludge leachate whereas basic fly ash exhibits the highest capacity for copper ion in the fluoride sludge leachate. Magnesium in the calcium fluoride sludge leachate can be best treated with basic fly ash. In the petroleum sludge leachate, illite is the most effective for magnesium whereas vermiculite is most effective in treating the magnesium in two of the three metal finishing sludge leachates. Calcium in the fluoride and metal finishing sludge leachates can be treated with kaolinite. On the other hand, the illite is more effective than the kaolinite in removing the calcium ion in the tank bottom sludge leachate. Nickel, in the fluoride sludge leachate and petroleum sludge leachate, may be treated with basic fly ash and in the metal finishing sludge leachate, with vermiculite.

The reason for the above differences in behavior of the sorbents toward the same constituents in different leachates is not known at this time. However, it is believed that the effectiveness of a specific sorbent for removal of a contaminant may be influenced by the other contaminants present in the leachate because of competition for available sorbent sites. Thus, some of the constituents may tend to bind more readily to the active sites on the sorbents than others.

RESULTS OF THE LYSIMETER STUDIES

As a result of the static studies using the leachates prepared from the three industrial sludges, the natural sorbents (i.e., basic fly ash, vermiculite, illite, kaolinite) and the refined sorbents (i.e., activated alumina and activated carbon) showed the most promise for treating the constituents found in the three leachates. Although bottom ash and acidic fly ash were not as effective in the static studies, they are also included in the lysimeter studies because preliminary examinations under flowing conditions indicate a greater removal than under static conditions.

The vermiculite, illite, and kaolinite used in these lysimeter studies consisted of a mixture of 20 percent sorbent and 80 percent inert Ottawa sand because the permeability exhibited by the "pure" sorbents was so low that virtually no flow was obtained. The results of a series of permeability studies using different mixtures of sand and clay indicated that the above clay-sand mixture would provide the minimum flow of leachate through the solids that could be measured within a reasonable time.

In these lysimeter studies, only the leachates prepared from the calcium fluoride sludge #3, metal finishing sludge #3, and the petroleum sludge from the gravity separatory were used. There was not enough of the calcium fluoride sludges #1 and #2, metal finishing sludges #1 and #2 and the petroleum

tank bottom sludge remaining after the static studies to permit the preparation of the 50 gallons of each leachate required for the lysimeter studies.

In view of the large number of measurements required for the lysimeter studies, the analyses for the constituents in the effluent from the lysimeter were performed only on those constituents whose concentrations were significantly higher than the minimum measurable concentration or exceeded the acceptable concentration for raw water standards (18). The analysis for the calcium, copper, magnesium, fluoride, and organics were carried out with the calcium fluoride sludge leachate. Cadmium, chromium, iron, and lead were excluded because the concentrations in leachate #3 were below the measurable levels (see Table 3). Both zinc and chloride were not determined because their concentrations in the leachate were below raw water standards.

The analysis for calcium, copper, magnesium, nickel, fluoride, and the organics were performed on the metal finishing sludge leachate #3. The cadmium, chromium, iron, lead, and cyanide were excluded because their concentrations were below measurable levels (see Table 7). Both zinc and chloride were below raw water standards.

The analysis for the calcium, copper, magnesium, zinc, fluoride, cyanide, and the organics were performed on the A.P.I. separatory sludge leachate. The cadmium, chromium, and iron were excluded because their concentrations were below measurable levels (see Table 11). Chloride was excluded because its concentration was below raw water standards.

Calcium Fluoride Sludge #3 Leachate

The effectiveness of selected sorbents for removing calcium, magnesium, copper, fluoride, and the organics under flowing conditions was determined by measuring the concentration of these constituents in the leachate before and after it had been percolated through the sorbent. The pH of the leachate before and after it passed through the sorbent was also monitored. The results are represented in Figures 3 through 9. Here, the concentration of the constituent remaining in a sample collected, after a known volume of leachate was passed through the column, is plotted against this volume of leachate. The background of the sorbents were not evaluated using water under flowing conditions because leaching from the sorbent was indicated when the effluent concentration exceeded the influent leachate concentration of a particular contaminant.

The pH of the specific leachate samples collected from the lysimeter changed as leachate is passed through the columns (see Figure 3). The pH values of the effluent leachate collected initially are defined by the pH of the sorbent. For example, the pH of the leachate sample collected initially from the illite-sand mixture is 3. This sorbent, when mixed with water, exhibits a background pH of 3 (see Table 3). However, after 4 liters of leachate were passed through the sorbent, the pH of the effluent approached that of the leachate. This is observed for all the sorbents studied.

Calcium Removal--

Kaolinite, activated alumina, activated carbon, illite, vermiculite, and

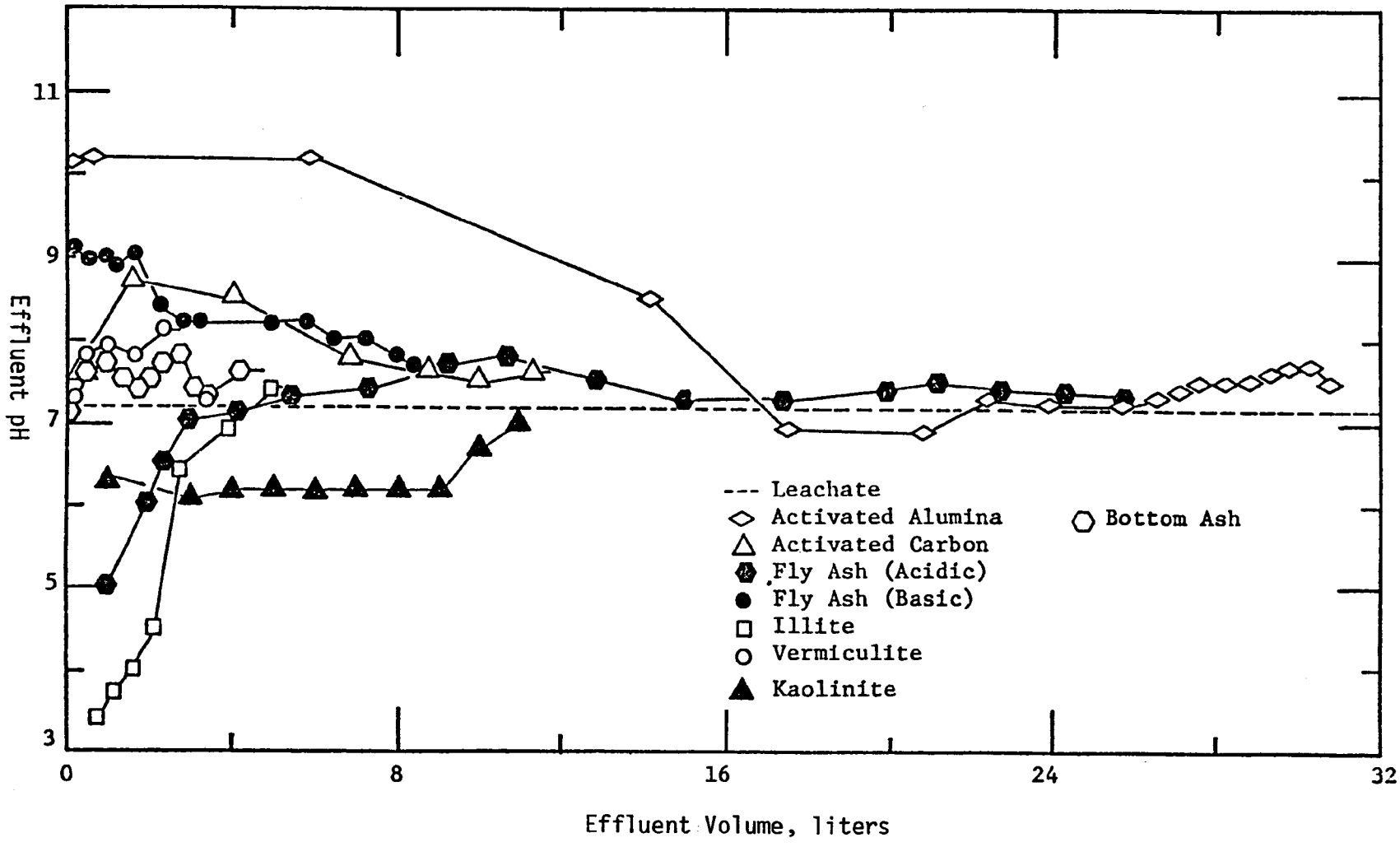

Figure 3. Lysimeter Studies of pH in Calcium Fluoride Sludge Leachate.

acidic fly ash were examined in the lysimeter for their ability to remove calcium under dynamic conditions. Leachate was passed through these columns until the concentration of calcium in the sample effluent leachate approached that of the influent leachate or excessively low permeability was encountered.

The results indicate that activated alumina is the most effective for treating the calcium in the calcium fluoride sludge #3 leachate up to the addition of 29 liters of leachate (see Figure 4). Beyond this point, the permeability of the activated alumina became excessively low (see Figure 10). For the inexpensive sorbents, kaolinite-sand mixture is the most effective with break-through occurring after 10 liters of leachate had been passed through this sorbent.

The sorbent capacities that are exhibited by each sorbent for a specific contaminant in the calcium fluoride sludge leachate #3 were determined from the curves in Figure 4. The area under each lysimeter curve, which also includes that portion where (in some cases) the concentration of contaminant exceeds that in the influent, was integrated and multiplied by the total volume of effluent collected until break-through was achieved or the permeability exhibited by the sorbent became excessively low. (Break-through is defined as the point where the concentrations of a specific contaminant in the influent and effluent leachates are comparable and there is no longer any significant removal of a specific contaminant by the sorbent.) This provides the total amount of contaminant added to the lysimeter; the result is equal to the total amount of contaminant removed by the sorbent. This latter value is determined by multiplying the concentration of the contaminant in the influent leachate by the volume of leachate used. The sorbent capacity is determined by dividing the total amount of contaminant removed by the amount of sorbent used in the lysimeter.

The sorbent capacities for activated alumina, activated carbon, acidic fly ash, illite, vermiculite and kaolinite are presented in Table 4. Here, it is shown that activated alumina exhibits the largest capacity followed by kaolinite, illite, and then activated carbon.

A comparison of the sorbent capacities exhibited by the acidic fly ash and illite under static and dynamic condition reveals that calcium is only removed from the leachate under flowing conditions. These results are probably due to the greater increase in pH that occurs as the slightly alkaline leachate flows through these sorbents than is achieved under static conditions. The initial fraction of leachate effluent collected shows that calcium is being leached from both sorbents (see Figure 4). The pH of the acidic fly ash and illite effluents collected initially are 5 and 3.2 respectively (see Figure 3) and are comparable or slightly more acidic than the pH of those effluents collected under static conditions (see Table 3). The analysis of the next effluent fraction collected from the acidic fly ash and illite lysimeters show removal of the calcium ion from both leachates. The pH of these fractions are 6.0 and 3.8 respectively.

There are significant variations in the concentration of calcium ion in the initial effluent fractions collected from the lysimeters containing the

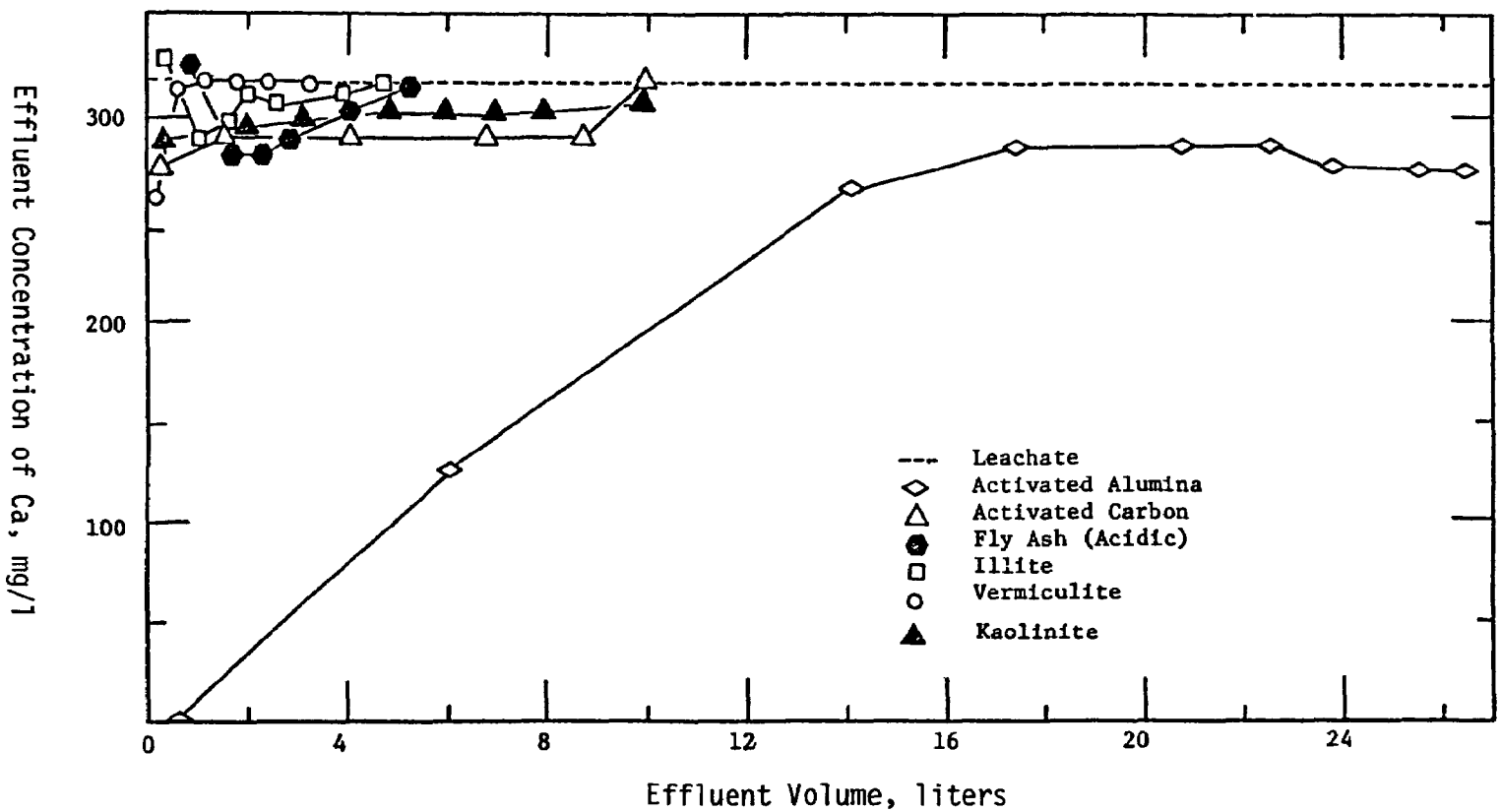

Figure 4. Lysimeter Studies of Calcium Ion in Calcium Fluoride Sludge Leachate.

different sorbents. This is presumably due to the different amounts of calcium leached from the various sorbents.

Copper Removal--

The sorbents which are effective for removing copper, based on the static results, from the calcium fluoride sludge #3 leachate are basic fly ash, activated alumina, and activated carbon. Their removal capacities were 0.10, 0.15, and 0.25 micrograms removed per gram of sorbent used, respectively (see Table 4). Thus, these sorbents were examined for removal of the copper under flowing conditions. The kaolinite, vermiculite, and acidic fly ash were also examined.

The effective sorbents for the treatment of copper were found to be acidic fly ash, activated alumina, activated carbon, and kaolinite (see Figure 5). The vermiculite-sand mixture showed no removal of copper under flowing conditions. Acidic fly ash and kaolinite-sand mixture were found to be effective for copper treatment under flowing conditions even though their static tests showed no sorbent capacity for copper. pH may be a factor, in both cases. As leachate is added to the acidic fly ash in the lysimeter, the pH is raised from 4 to slightly above 7 after 4 liters have passed through the column (see Figure 3). When the effluent leachate becomes slightly alkaline, the copper is removed. The concentration of copper in the effluent leachate now falls below the dotted line which represents the initial concentration of copper in the untreated leachate. For the case of the kaolinite the pH of the initial kaolinite effluent collected is significantly more alkaline than the pH of the kaolinite effluent obtained under static conditions. The pH of this effluent remains relatively constant at slightly greater than 6 and becomes neutral when break-through occurs (see Figure 5).

Considerable variations of the copper ion concentration is observed in the initial fractions of effluent collected from the different lysimeters. This is probably due to the different amounts of copper that are leached from the various sorbents. In fact, the concentration of copper in the first 0.09 liters of effluent collected from the acidic fly ash is 2.5 mg/l. This is far in excess of the background concentration of 0.06 mg/l obtained in the static studies (see Table 3).

These excessive concentrations, when compared to the static data, occur because the leachate to sorbent ratio for the initial effluent collected from the lysimeters is equivalent to only 0.2 to 1, as opposed to the water to sorbent ratios of 2.5 to 1 used for the determination of background of sorbent material in the static studies.

These results indicate that the maximum amount of copper that can be leached from the acidic fly ash was not achieved (as defined by the conductance measurements) using the water to sorbent ratio of 2.5 to 1 or that the lower pH of 4.2 exhibited by this effluent fraction resulted in greater leaching of the copper than had occurred in the static studies where a pH of 5.4 was encountered.

The sorbent capacities for the removal of copper by the acidic fly ash, kaolinite-sand mixture, activated alumina and activated carbon are 2.2, 8.9, 2.9,

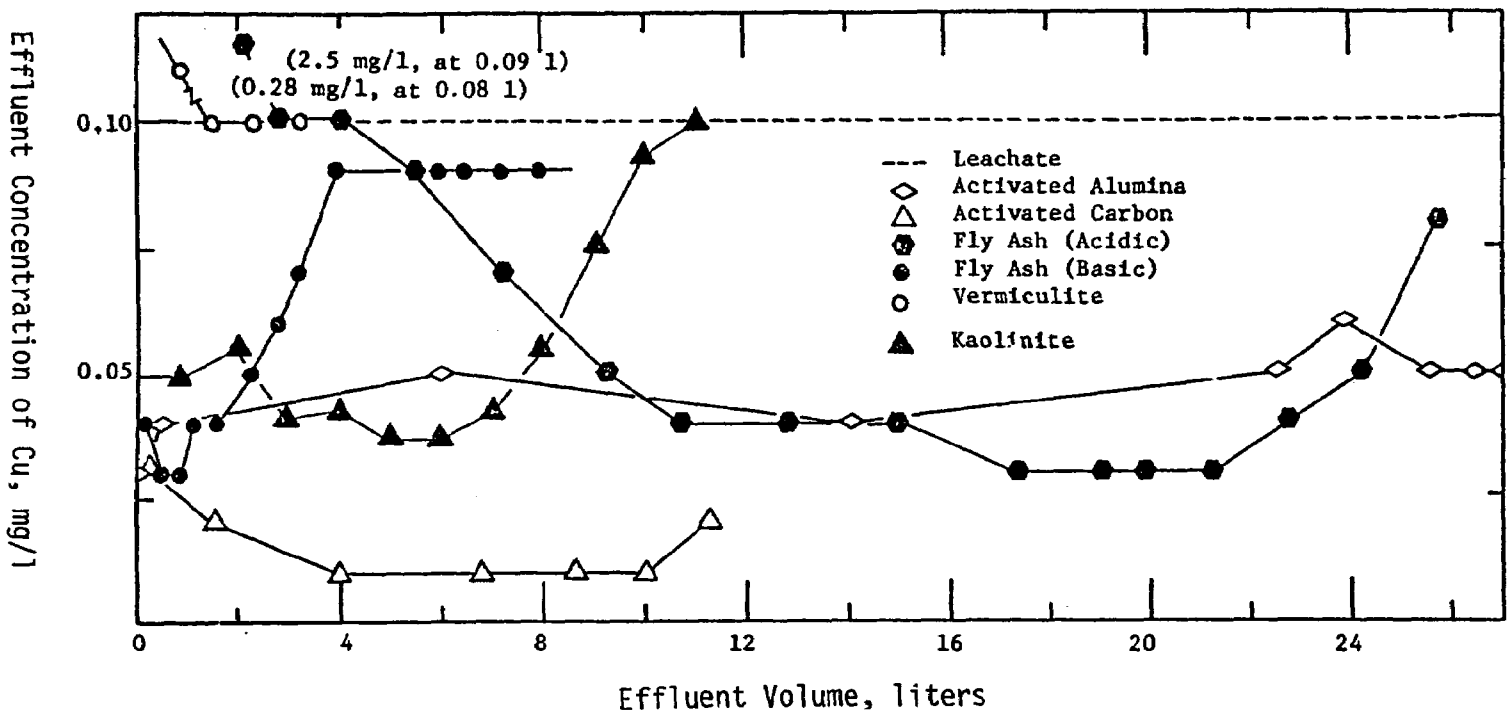

Figure 5. Lysimeter Studies of Copper Ion in Calcium Fluoride Sludge Leachate.

and 2.0 micrograms of copper removed per gram of sorbent used. The sorbent capacity for the kaolinite-sand mixture is significantly greater than the other sorbents, even though it is not apparent from a comparison of the curves in Figure 5 because the amount of kaolinite used in the lysimeter is only 20 percent of the weight of the other sorbents used.

The kaolinite-sand coefficient of permeability shows a significant decrease with the addition of leachate to the lysimeter. However, this levels off at the point of copper break-through (see Figure 10). This reduction in coefficient of permeability for the kaolinite-sand mixture is not as significant a problem as would occur if the next best sorbent, activated alumina, were used. The coefficient of permeability for the activated alumina shows no leveling off. Thus, a point could be reached where the activated alumina could form an impermeable barrier.

Magnesium Removal--

Acidic and basic fly ash, activated alumina, and activated carbon were examined for removing the magnesium from the leachate under flowing conditions. The results indicate that basic fly ash and activated alumina are effective sorbents for treating the magnesium in the leachate (see Figure 6). Acidic fly ash was found to be effective for removing the magnesium after the pH of the leachate became alkaline. This occurs after approximately 2 liters of leachate has been passed through this sorbent. Prior to this, magnesium was continuously leached from acidic fly ash. Thus, basic fly ash should be used with the acidic fly ash in a layered system to remove the magnesium during this initial leaching period.

The activated alumina appears to exhibit the greatest capacity for removal of magnesium ion and is capable of handling the largest volume of leachate (30 liters). Beyond this, its permeability becomes excessively low.

The sorbent capacities for acidic and basic fly ashes, activated alumina, and activated carbon were determined to be 250, 172, 534, and 19 micrograms of magnesium removed per gram of sorbent used. This order of effectiveness for removing the magnesium ion is also apparent from the lysimeter curves (see Figure 6) since all the lysimeters contain 100% of the sorbent.

Fluoride Removal--

The effectiveness of acidic and basic fly ashes, bottom ash, illite, vermiculite, kaolinite, activated alumina, and activated carbon were investigated for the treatment of fluoride sludge #3 leachate. The results show that the refined sorbent, activated alumina, is the most effective for removing the fluoride (see Figure 7) even after 26 liters of leachate was added to the lysimeter. Acidic fly ash appears to be the most effective natural sorbent for fluoride removal. The illite-sand mixture and bottom ash exhibit similar types of removal curves. Both vermiculite and activated carbon are least effective.

The sorbent capacities for the bottom ash, acidic and basic fly ashes, vermiculite-sand mixture, illite-sand mixture, kaolinite-sand mixture, activated alumina, and activated carbon are listed in Table 4. Illite and activated alumina, which proved to be the most effective in treating fluoride

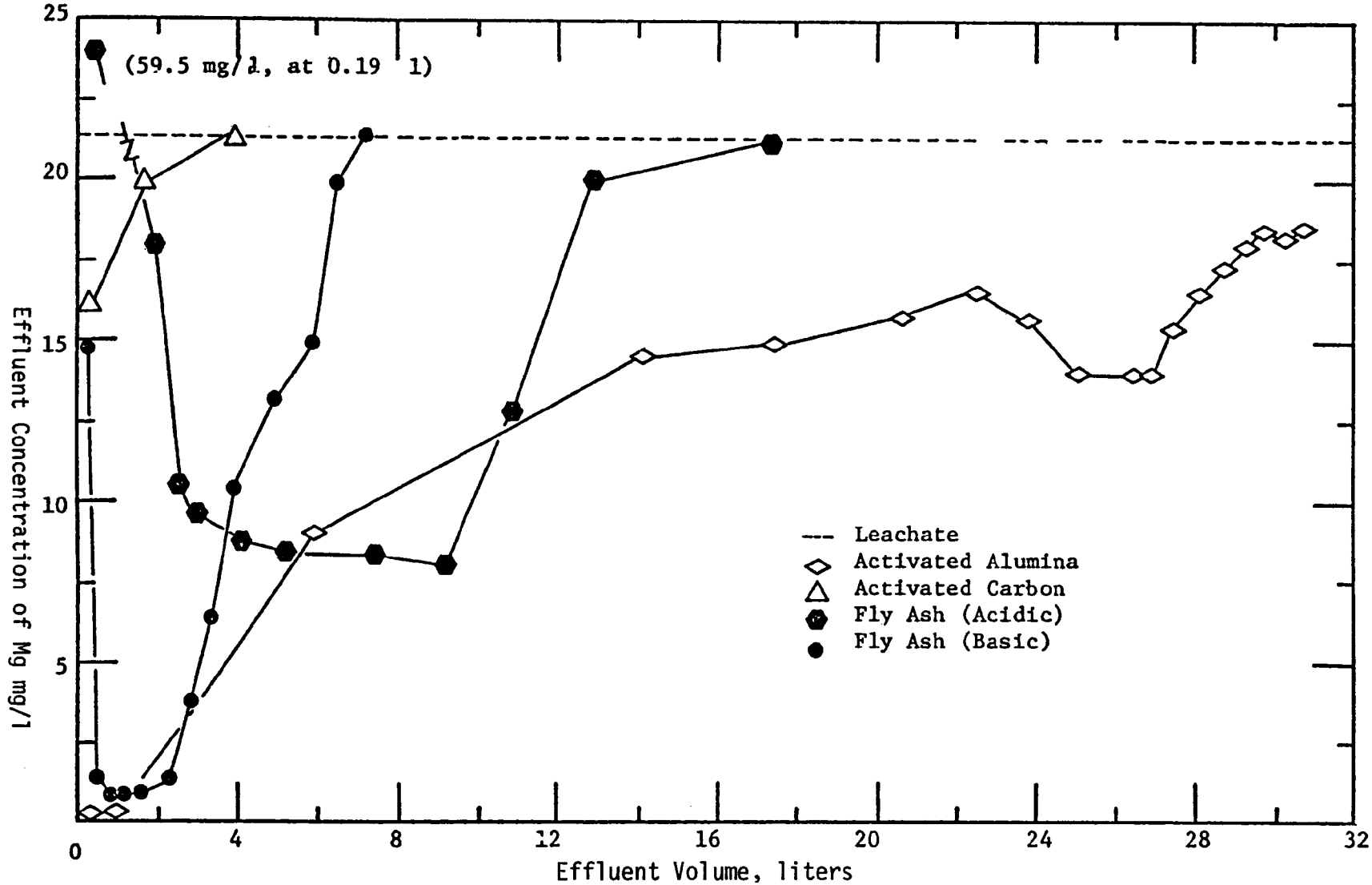

Figure 6. Lysimeter Studies of Magnesium Ion in Calcium Fluoride Sludge Leachate.

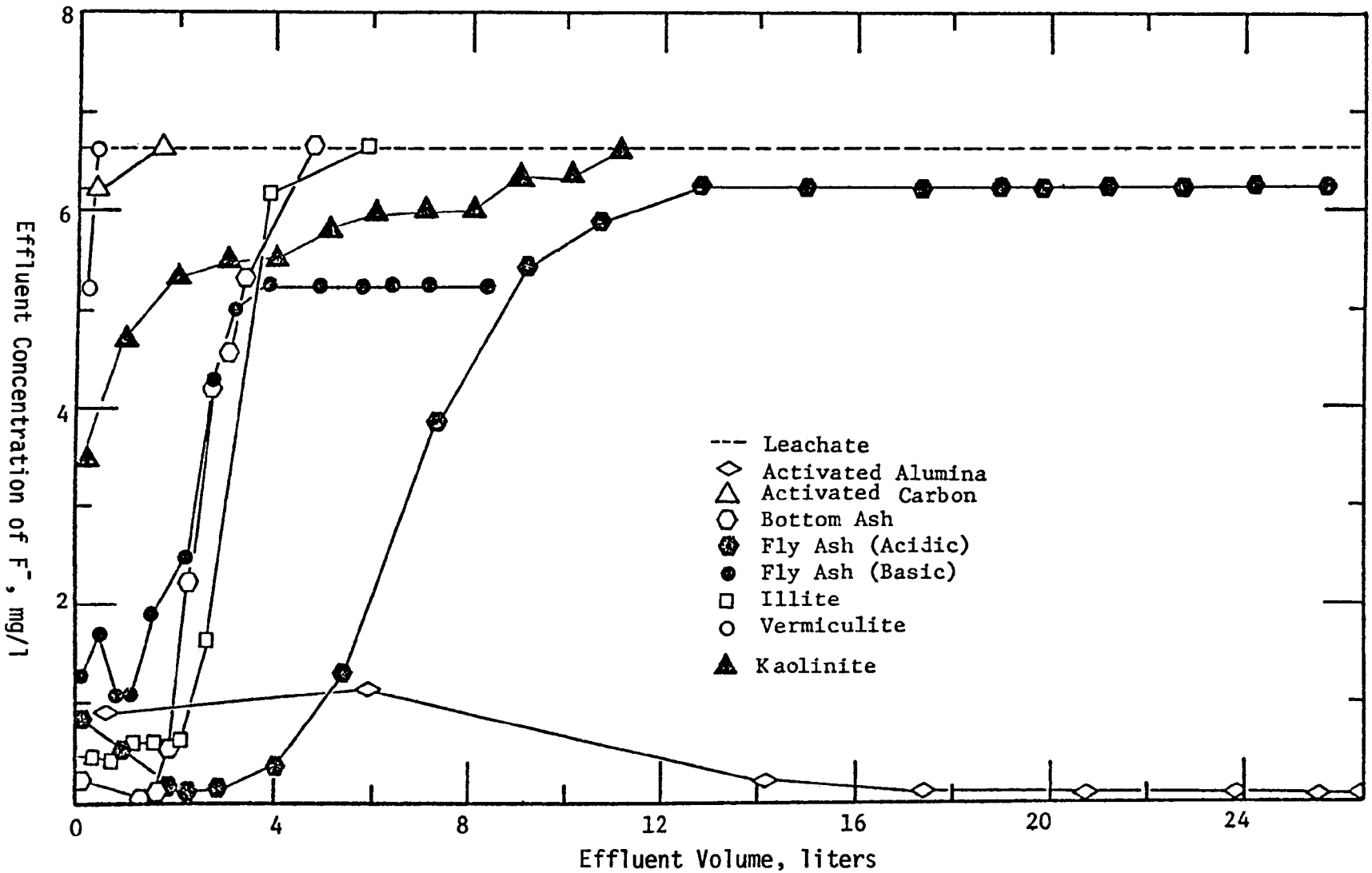

Figure 7. Lysimeter Studies of Fluoride Ion in Calcium Fluoride Sludge Leachate

under static conditions, also appear to be most effective under flowing conditions. However, the basic fly ash and bottom ash, which appear to be more effective than acidic fly ash for fluoride treatment under static conditions, are not as effective under flowing conditions.

The removal of fluoride under flowing conditions appears to be favored by acidic conditions. The acidic fly ash exhibits significantly better removal than either the bottom ash or basic fly ash when acidic conditions are encountered during the initial 4 liters of effluent collected. As the effluent becomes basic, the removal of fluoride by the acidic fly ash decreases (see Figure 7). In the case of the illite-sand mixture and kaolinite-sand mixture, the fluoride is removed until their effluents become basic. At this point, no removal of the fluoride is observed for both sorbents.

Considerable variation was observed in the amount of leachate influent passed through the sorbents before break-through occurred. Activated alumina again appeared to be able to handle large volumes of leachate before fluoride break-through occurred (see Figure 7). Fluoride break-through for the acidic fly ash did not occur until approximately 12 liters of leachate had been passed through this sorbent. The kaolinite exhibited fluoride break-through at 10 liters. Fluoride break-through for the illite-sand mixture and bottom ash occurred at slightly above 4 liters.

Organic Removal--

Bottom ash, acidic and basic fly ashes, vermiculite-sand mixture, illite-sand mixture, kaolinite-sand mixture, activated alumina, and activated carbon were examined for their effectiveness in removing the organics under flowing conditions. The results indicate that acidic fly ash and activated carbon are the most effective sorbents for removing the organics in the calcium fluoride sludge #3 leachate (see Figures 8 and 9). The performance of the activated carbon was as expected since it is widely used for the removal of organics in waste streams. The illite-sand mixture, however, which appears to be the most effective under batch conditions (see Table 4) is not as effective as acidic fly ash under flowing conditions even though account is taken of the fact that the illite lysimeter contains only 20 percent illite. The removal capacity of acidic fly ash for both COD and TOC is 704 and 156 micrograms removed per gram of acidic fly ash used, respectively, as compared with the removal capacity of illite for both COD and TOC of 250 and 80 micrograms removed per gram of illite used, respectively.

Acidic conditions appear to be a factor in the removal of the organics but the acidic fly ash is seen to be less dependent than the illite. Break-through of organics for the illite is observed when its effluent becomes alkaline but the acidic fly ash continues to remove the organics even though its effluent is alkaline (see Figure 8).

The treatment of appreciable volumes of leachate before COD and TOC break-through occurs can better be handled by the activated carbon than acidic fly ash. The COD and TOC break-through for acidic fly ash occurs after 9 liters of calcium fluoride sludge #3 leachate was passed through the sorbent (see Figures 8 and 9). For the case of the activated carbon sorbent, the flow of leachate through this sorbent was stopped after 12 liters had been passed

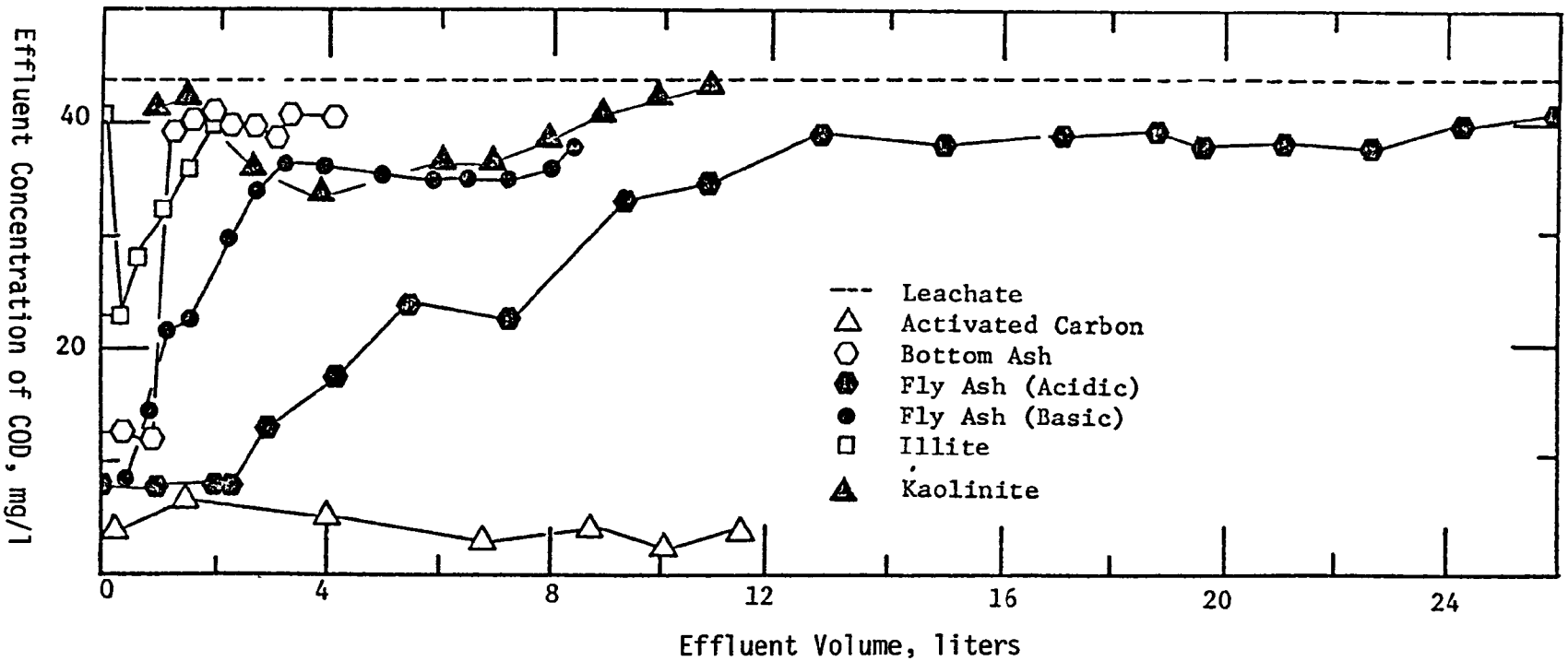

Figure 8. Lysimeter Studies of COD in Calcium Fluoride Sludge Leachate

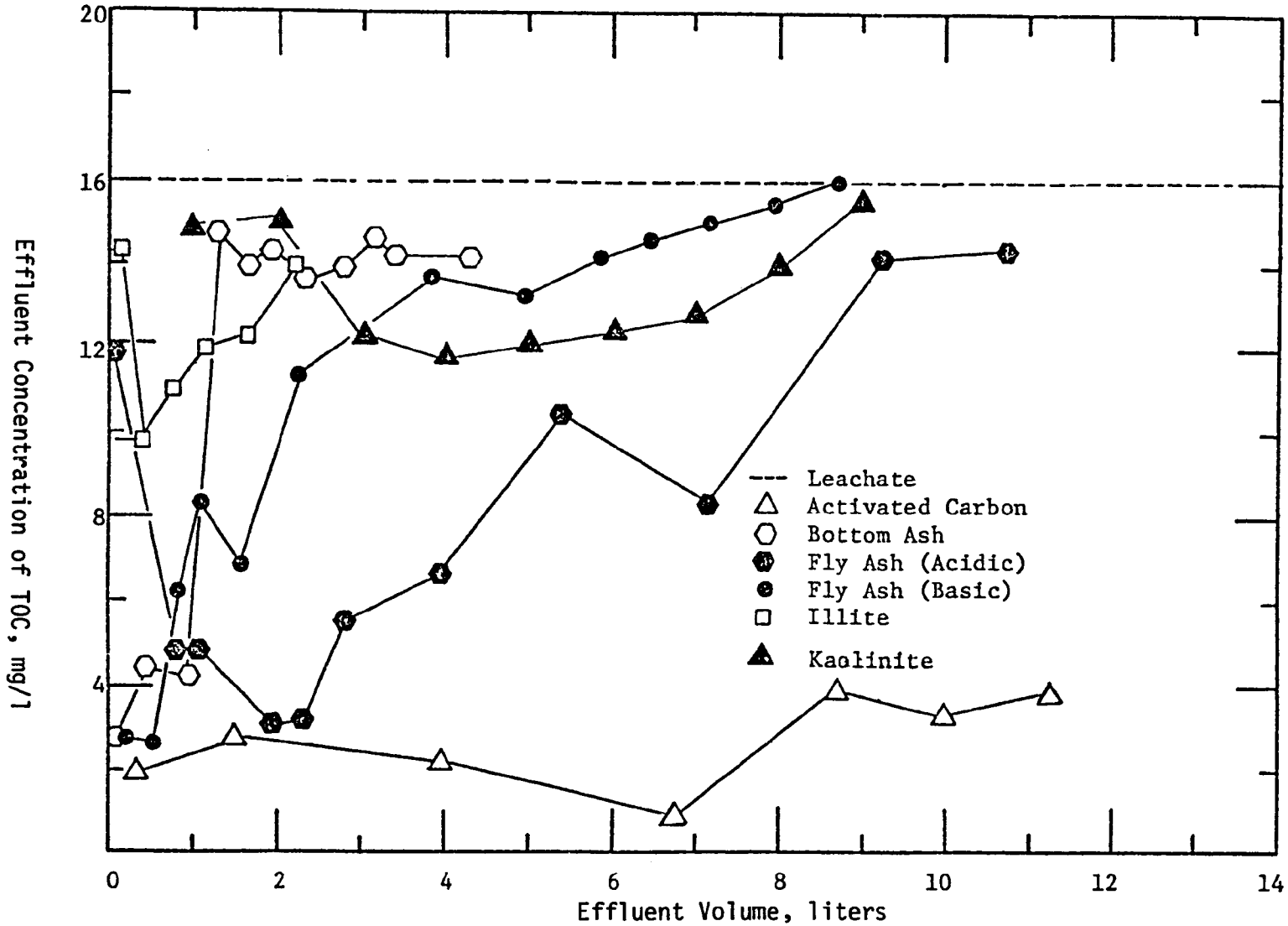

Figure 9. Lysimeter Studies of TOC in Calcium Fluoride Sludge Leachate

through. However, even at this point, effective removal of the organics continued to be observed.

Permeability Results--

The use of refined and natural sorbents for the removal of specific constituents in the leachate of industrial sludge depends on the removal capacity of the sorbent for a constituent in the leachate. The sorbent should also exhibit suitable permeabilities to handle hydraulic loadings without ponding occurring at the bed surface. A series of constant head permeability tests were performed on activated alumina, activated carbon, bottom ash, basic fly ash, the illite-sand mixture (20 percent illite 80 percent Ottawa sand), and vermiculite-sand mixture (20 percent vermiculite, 80 percent Ottawa sand) using the calcium fluoride sludge #3 leachate in order to determine the permeability characteristics of these sorbents. Here the coefficient of permeability versus leachate volume was determined for each sorbent until breakthrough of organics from the illite-sand mixture occurred at about 5 liters (see Figures 8 and 9).

The results indicate that the coefficient of permeability remains essentially constant with effluent volume for the sorbents tested, with the exception of activated alumina and kaolinite (see Figure 10). The coefficient of permeability for the activated alumina is reduced from an initial value of 7.7×10^{-4} cm per sec. to 2.1×10^{-5} cm per sec. at the completion of the test (see Table 12). This amounts to approximately one-fortieth of its initial value but then appears to level off after break-through of contaminants has occurred. Apparently, the removal of constituents from the leachate by these sorbents results in a reduction in pore volume through which the leachate flows. This does not appear to be the case for the other sorbents where the coefficient of permeability remains fairly constant as the constituents are removed from the leachate. Thus, although activated alumina is effective in removing the cations from the calcium fluoride sludge #3 leachate under flowing conditions (see Table 4), its presence in a bed for treatment of leachate from calcium fluoride sludge over a period of time may lead to ponding due to the marked reduction in its coefficient of permeability.

Summary of Results

In general, a comparison of the results of the batch tests with those obtained with the lysimeter using the same calcium fluoride sludge #3 leachate indicates that significantly greater removal capacities for given constituent are obtained under flowing conditions than under static conditions (see Table 4). For example, the fluoride sorbent capacity obtained for illite under non-flowing conditions was 79.9 micrograms of fluoride removed per gram of illite used as compared to 205 micrograms of fluoride removed under flowing conditions. Also, in some cases, where the static test results showed no sorbent capacity the lysimeter tests showed significant removals. The sorbent capacity of acidic fly ash for magnesium under non-flowing conditions was zero. Under flowing conditions, 250 micrograms of magnesium was removed per gram of acidic fly ash used (see Table 4).

In some cases, the removal of calcium, copper, and magnesium by sorbents

such as illite-sand mixtures and acidic fly ash appears favored by an increase in pH to alkaline conditions. As the pH of their effluent is increased, the cations that are leached from these sorbents at lower pH are removed at the higher pH. In other cases alkaline conditions do not appear to favor the removal of copper and magnesium by the basic fly ash, or calcium by the vermiculite-sand mixture. Greater removals are achieved by these sorbents under flowing conditions, even though the effluent collected from the lysimeters and from the static test are both alkaline. The reasons for the latter observations are not known at this time. However, it is presumed that the selectivity of specific sorbents for the removal of a constituent is influenced by other constituents in the leachate. In the static tests, the more competitive constituents could bind to the sorbent first and thus reduce the available binding sites to the less competitive constituents. However, under flowing conditions, the more competitive constituents may be primarily removed in the top of the column. The less competitive ions may bind to the sorbents further down the columns as a result of decrease in the concentration of the more competitive constituents in the top of the column. The combined effects of pH, ion exchange capacity and sorption capacity on the interaction between the contaminants in the leachate and the sorbents are the areas that need further study.

Metal Finishing Sludge #3 Leachate

The effectiveness of acidic and basic fly ashes, vermiculite, illite, kaolinite, activated alumina, and activated carbon for removing calcium, copper, magnesium, nickel, fluoride, and organics in the metal finishing sludge #3 leachate, was examined under flowing conditions. The above constituents were selected because their concentrations in the leachate were at levels that could be measured using the atomic absorption spectrophotometer or specific ion probes. In addition, the pH, before and after the leachate passed through the sorbents, was monitored to determine if pH has an effect on the sorbent's ability to remove a specific constituent.

The results of this study are shown in Figures 11 to 18. The dotted lines in each of these figures represent the concentration of the constituent present in the metal finishing sludge #3 leachate prior to treatment with a sorbent.

The pH of the effluent leachate samples collected from the lysimeter containing the different sorbents again approaches (with the exception of activated alumina and kaolinite) upon the addition of leachate, the pH of the influent leachate (see Figure 11). It is presumed that if additional volumes of leachate were added to the activated alumina and kaolinite, the pH of their effluents would also approach that of the leachate. The collection of leachate from the activated alumina was stopped after 10 liters because its permeability became excessively low (see Figure 20). The kaolinite was not taken beyond 10 liters because break-through of calcium occurred at this point (see Figure 12). After 4 liters of leachate was added to the sorbents, the pH of the effluent metal finishing sludge leachate approached that of the influent. Sixteen liters of leachate was required to reach this point for the fluoride sludge leachate, however. The stronger alkalinity of the metal finishing sludge #3 leachate (pH = 8.2) may be the reason for this

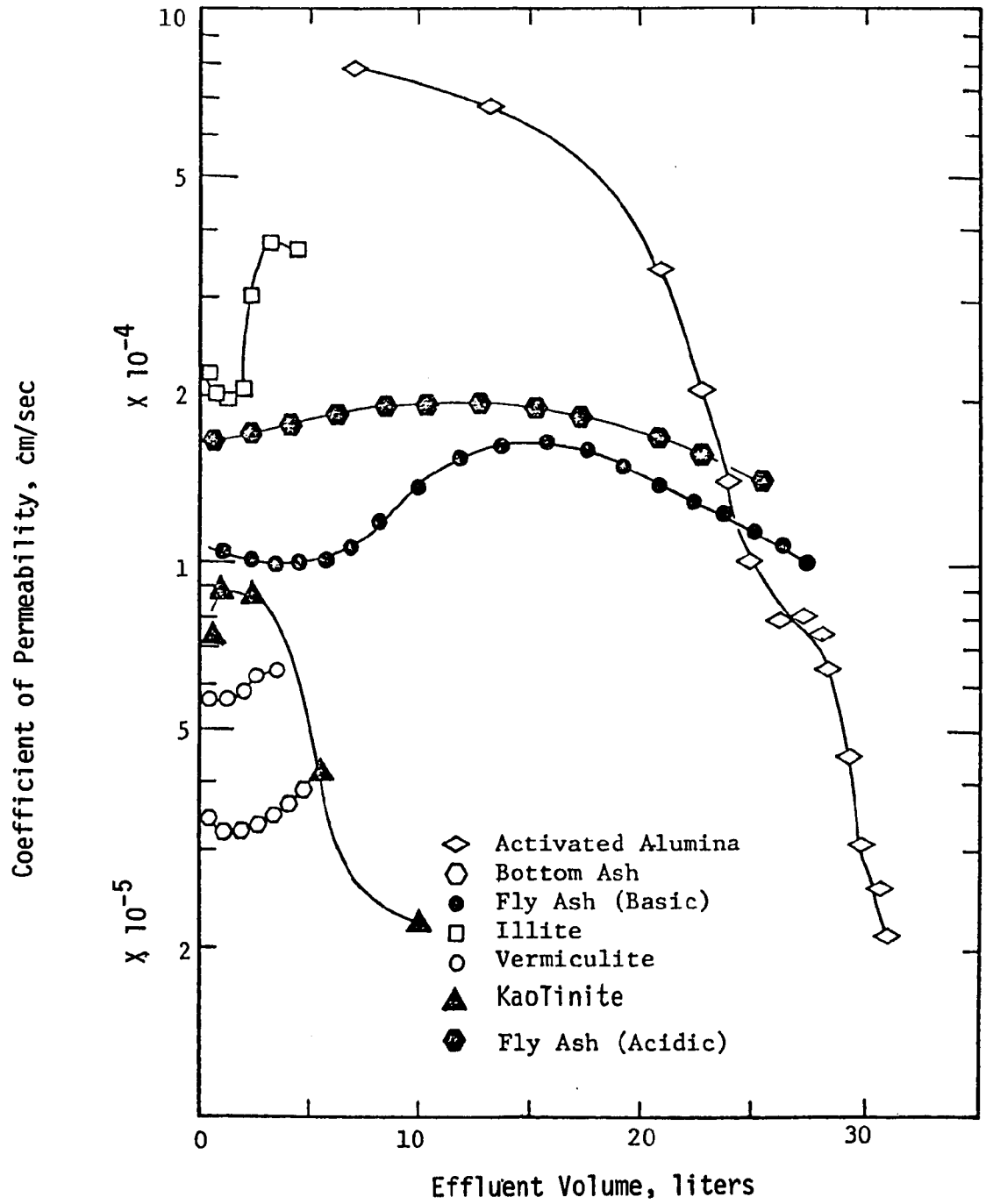

Figure 10. Permeability Studies of Sorbent Materials with Calcium Fluoride Sludge Leachate

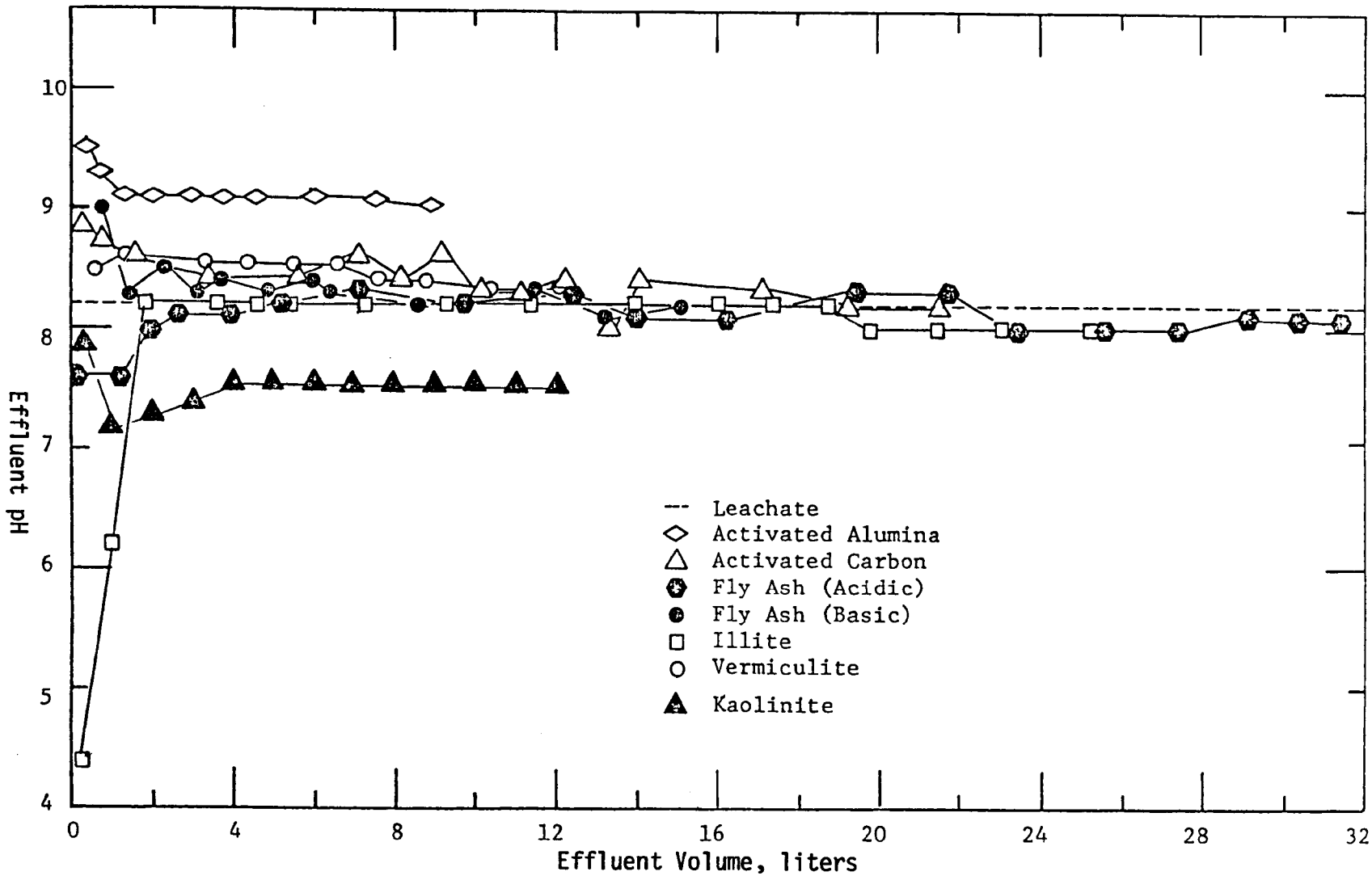

Figure 11. Lysimeter Studies of pH in Metal Finishing Sludge Leachate

behavior. As a result, the pH of the effluent in all cases becomes alkaline after a little less than 2 liters has passed through the sorbents.

Calcium Removal-

The removal of calcium from the metal finishing sludge #3 leachate by the sorbents, under flowing conditions, is represented in Figure 12. Here, the illite-sand mixture, vermiculite-sand mixture, kaolinite-sand mixture, and activated alumina were shown to be effective sorbents for the removal of calcium. The sorbent capacity exhibited by each of these sorbents is 1828, 1280, 930, and 737 micrograms of calcium removed per gram of sorbent used, respectively (see Table 8). The sorbent capacity obtained for the activated alumina is lower than the clay-sand mixtures even though it appears more effective (see Figure 12). Calculation of this sorbent capacity is based on only 10 liters of leachate being passed through this sorbent, as compared with 22 liters and 14 liters of leachate passed through the illite and vermiculite, respectively. The flow of leachate through the activated alumina essentially stopped after 10 liters had been passed through this sorbent.

It should be noted that both acidic and basic fly ashes exhibit leaching at leachate volumes below 2 liters (see Figure 12). After this, the calcium is removed. The concentration of calcium in initial effluent fractions collected from the fly ash lysimeters is greater than that obtained when the acidic and basic fly ashes were mixed with water under static conditions (see Table 7). The volumes of effluent collected from the acidic and basic fly ash lysimeters is equivalent to leachate to sorbent ratios of 1.2 to 1 and 0.6 to 1, respectively. This is significantly lower than the water to sorbent ratio of 2.5 to 1 used in the static studies to achieve maximum leachate concentrations as indicated by conductance measurements. Apparently, the larger ratio did not provide a saturated concentration of leachable calcium since the concentrations of calcium in the initial effluent fraction collected from the lysimeters is greater than that obtained in the background of sorbent materials determinations under static conditions.

Considerable variations are observed in the concentrations of calcium present in the initial fractions of effluent collected from the lysimeters (see Figure 12). This is presumed to be due to the different amounts of calcium that may be leached from the sorbents as is apparent from the data for background of sorbent materials obtained under static conditions (see Table 7).

Greater sorbent capacities were obtained under flowing conditions than under static conditions (see Table 8). In fact, no sorbent capacities were obtained for the acidic and basic fly ashes and illite under static conditions, but significant removals were obtained under flowing conditions.

The reason for this is not clear at this time. The pH does not appear to be a factor, as was indicated earlier for the calcium fluoride sludge leachate lysimeter results, since the initial fractions of effluent collected from the acidic and basic fly ash lysimeters exhibit alkaline pH.

The illite-sand mixture appears capable of handling the greatest volume of leachate before break-through of calcium occurs (see Figure 12). Activated

TABLE 12 : 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

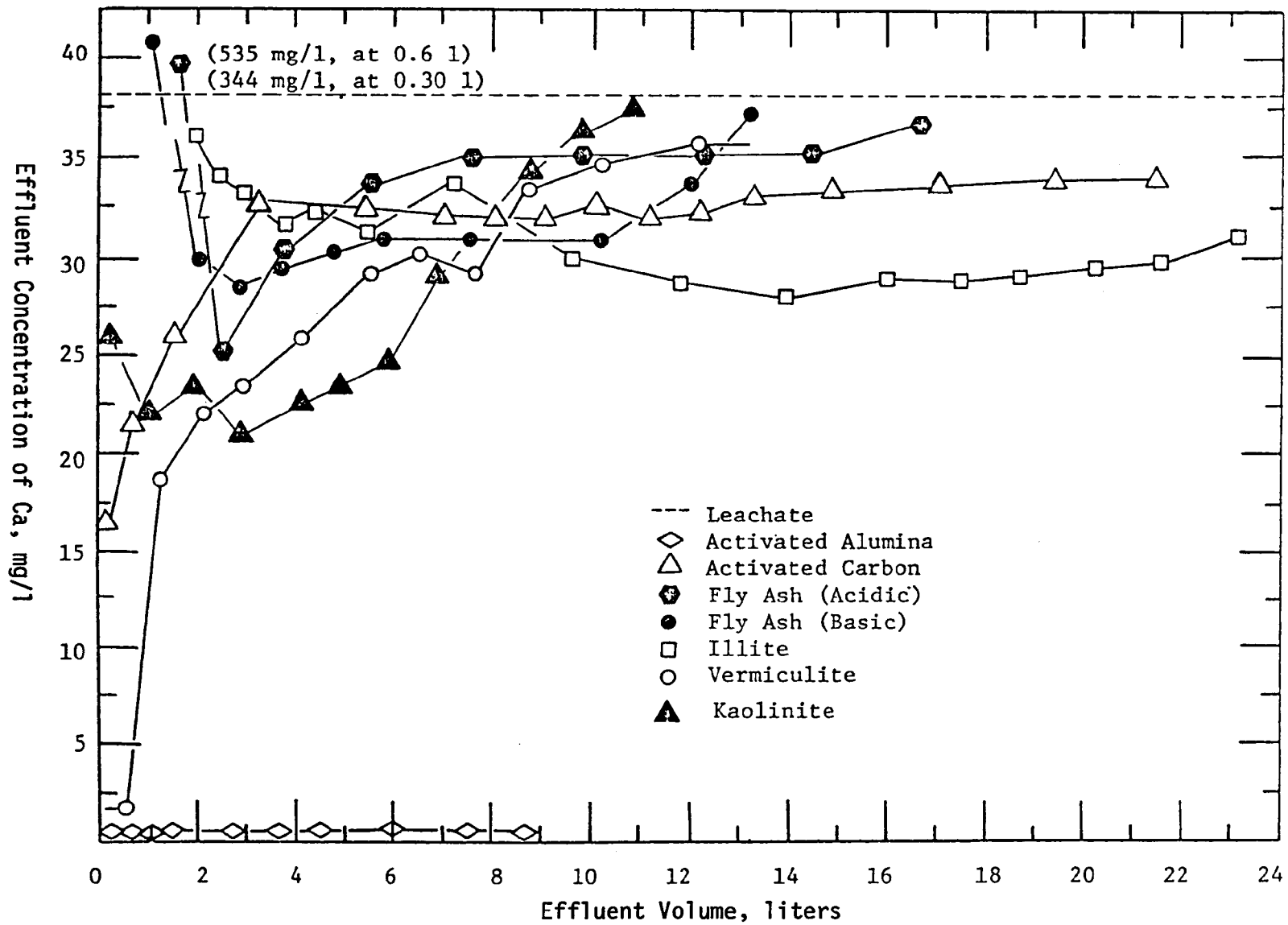

Figure 12. Lysimeter Studies of Calcium Ion in Metal Finishing Sludge Leachate

alumina would probably handle the greatest volume of leachate prior to break-through if the samples of effluent leachate could be collected beyond the 10 liters of leachate that were passed through the activated alumina. This could not be shown because the flow through this sorbent virtually stopped after 10 liters had been passed through the sorbent.

Copper Removal--

The removal of copper from the metal finishing sludge #3 leachate can be achieved by the acidic fly ash, the illite-sand mixture, the vermiculite-sand mixture, and activated carbon (see Figure 13). Although acidic fly ash appears to be more effective for removing the copper than the illite and vermiculite-sand mixtures, it must be remembered that the amount of vermiculite and illite used in these tests is only 20 percent by weight of the acidic fly ash used. If this is taken into account, the illite and vermiculite are then found to exhibit sorbent capacities of 57.5 and 20.5 micrograms of copper removed per gram of sorbent used, as compared with 16.5 micrograms of copper removed per gram of the acidic fly ash (see Table 8).

No leaching of copper from the acidic fly ash is observed. The fact that the pH of the effluent leachate from this sorbent is never acidic may be the reason. When the effluent leachate is acidic, as was encountered with the illite at volumes below 1 liter, copper is leached out of illite (see Figure 13).

An analysis of the sorbent capacity exhibited by the illite for copper shows a significant removal capacity for copper under flowing conditions but none under static conditions (see Table 8). Apparently, the fact that the pH of the illite effluent was significantly acidic in the static studies resulted in leaching rather than removal of the copper.

Activated carbon appears to be able to treat copper in the largest volume of metal finishing sludge #3 leachate (see Figure 13). Acidic fly ash and the illite-sand mixture appear to be next for treating large volumes of this leachate.

Magnesium Removal--

The activated alumina, acidic fly ash, and illite-sand mixture appear to be the most effective sorbents for the removal of magnesium and for handling the largest volumes of the metal finishing sludge #3 leachate before break-through occurs (see Figure 14). The sorbent capacities for each of these sorbents were 495, 488, and 1840 micrograms of magnesium removed per gram of sorbent used, respectively (see Table 8).

No leachable magnesium was observed with the acidic fly ash, as was encountered with fluoride leachate. This may be due to the fact that the pH of acidic fly ash, even in the initial effluent fractions collected, remains above 7.

Nickel Removal--

Activated carbon, acidic fly ash and activated alumina appear to be the most effective in removing the nickel in the metal finishing sludge #3 lea-

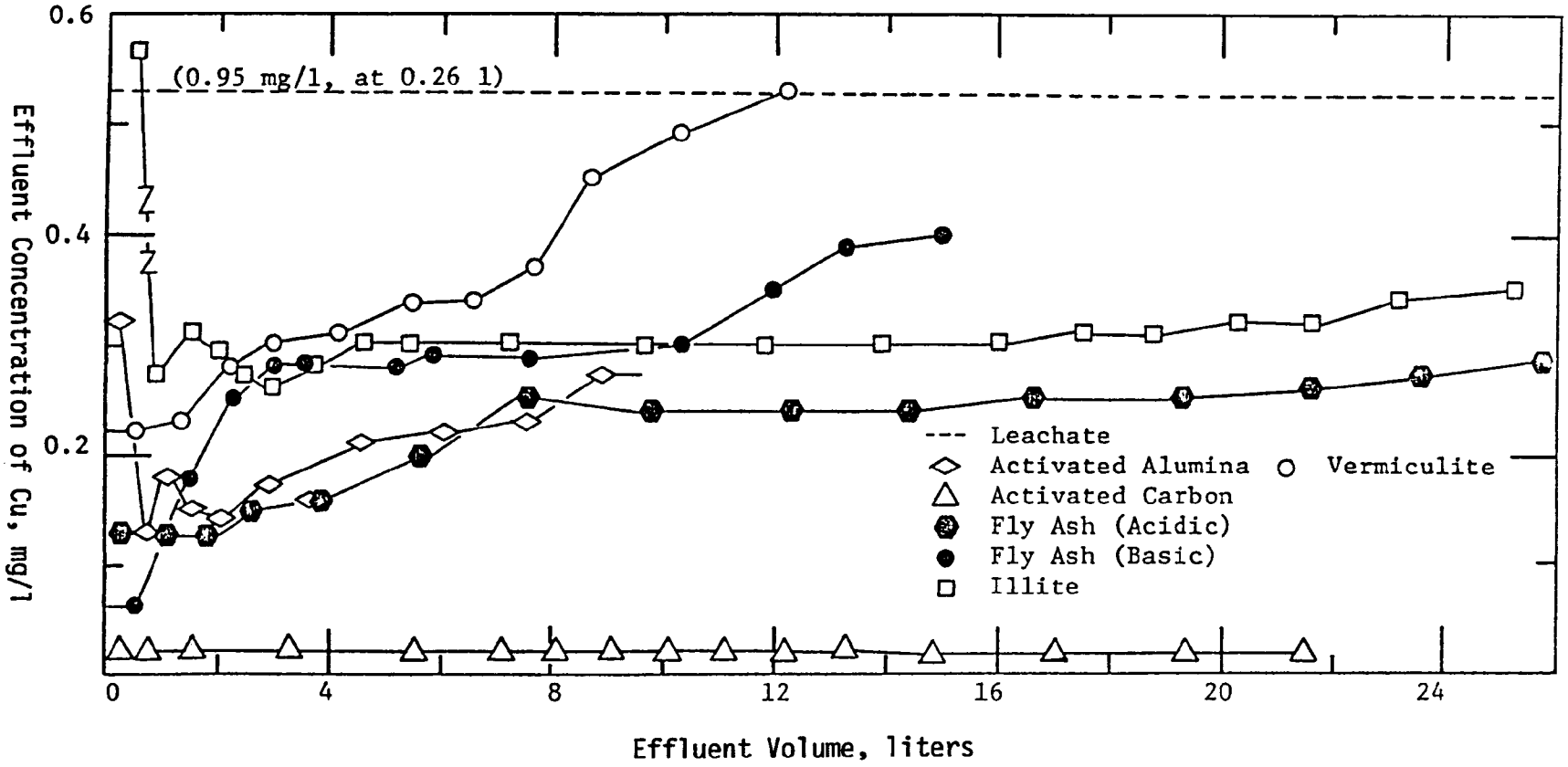

Figure 13. Lysimeter Studies of Copper Ion in Metal Finishing Sludge Leachate.

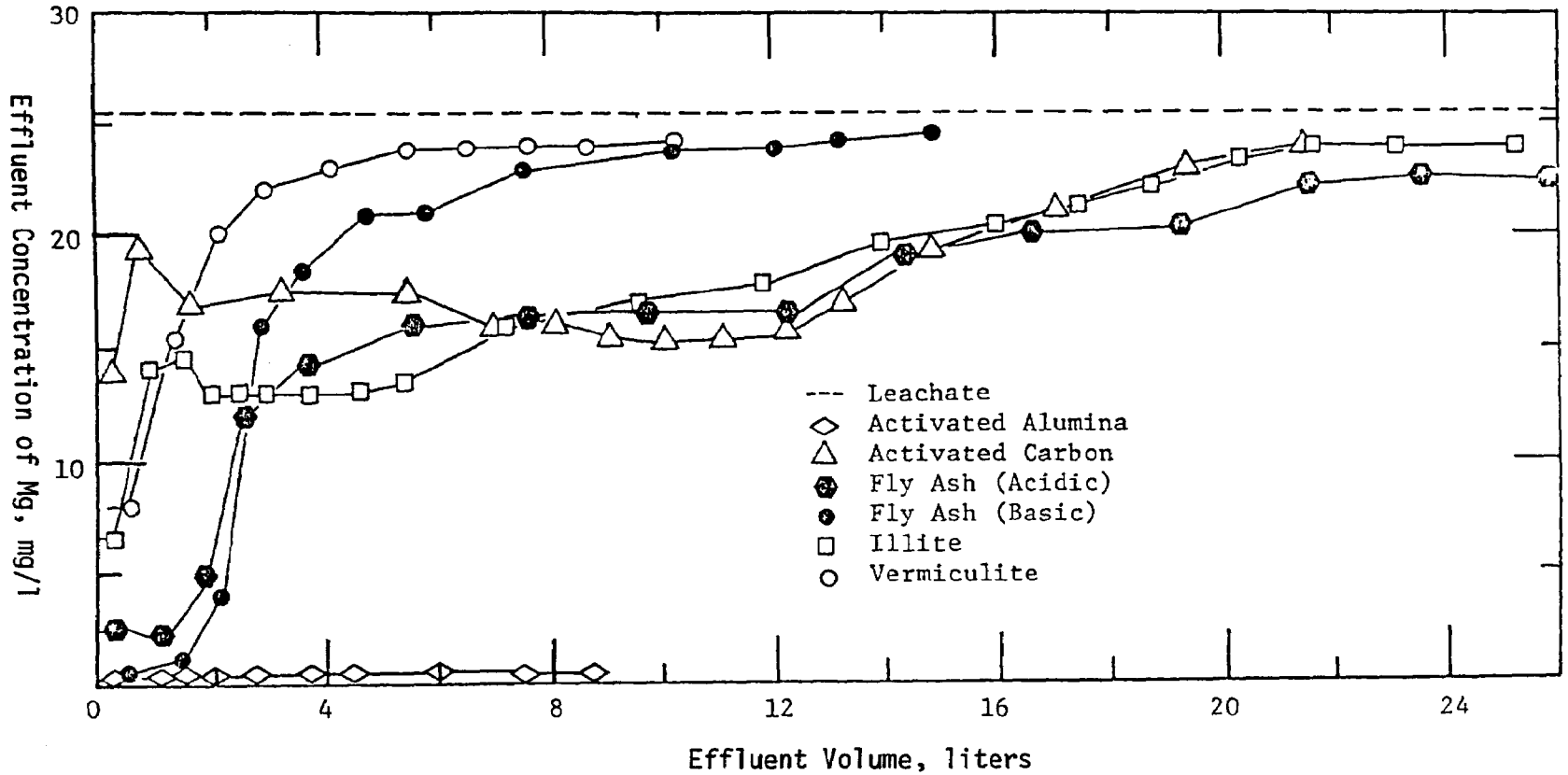

Figure 14. Lysimeter Studies of Magnesium Ion in Metal Finishing Sludge Leachate

chate (see Figure 15). However, if account is taken of the fact that the illite-sand mixture contains only 20 percent by weight of the activated carbon and acidic fly ash used, then illite is the most effective. The sorbent capacities for illite, activated carbon, acidic fly ash and activated alumina are 7.3, 7.2, 4.9, and 2.5 micrograms of nickel removed per gram of sorbent used (see Table 8). These sorbents are also capable of handling the largest volume of leachate before break-through of the nickel occurs. Break-through for the illite-sand mixture occurs at 24 liters whereas, with acidic fly ash or activated carbon, break-through of the nickel did not occur even after 24 liters of metal finishing leachate had passed through these sorbents (see Figure 15).

Fluoride Removal--

Significant removal of fluoride in the metal finishing sludge #3 leachate appears to be difficult. Neither the illite-sand mixture, kaolinite-sand mixture nor activated alumina (which were effective for removing fluoride from the calcium fluoride leachate) seems suitable for treating the fluoride in this leachate (see Figure 16). The removal capacities for the illite and activated alumina are only 2.7, 3.6, and 11.4 micrograms of fluoride removed per gram of sorbent used, respectively (see Table 8) as compared to 205, 183, and 348 micrograms of fluoride removed per gram of sorbent used for the fluoride sludge leachate (see Table 4).

Apparently, the basic conditions encountered in the effluents from the lysimeters due to the addition of the alkaline metal finishing sludge leachate minimizes the removal of the fluoride. In the illite lysimeter, fluoride is removed where acidic conditions were encountered. Above 1 liter, where alkaline pH was measured, break-through of the fluoride from the illite lysimeter is observed (see Figure 16).

Organic Removal--

The activated carbon, acidic fly ash, and the illite-sand mixture appeared to be the most effective sorbents for the removal of organics (see Figures 17 and 18).

The COD sorbent capacity exhibited by these sorbents are 1476, 1228, and 3060 micrograms of COD removed per gram of sorbent used, respectively (see Table 8). The TOC removal capacities are approximately one-third of that obtained with the COD measurements. A comparison of the sorbent capacities for the illite-sand mixture and activated carbon reveal that the clay-sand mixture is more effective than the activated carbon in removing the organics from this leachate. These results are significant because an inexpensive sorbent has been identified for treating the organics in the metal finishing sludge leachate that shows as much promise as the activated carbon. The activated carbon is generally recognized as being an excellent sorbent for the removal of organics in waste streams.

The sorbent capacity exhibited by these sorbents for the organics in the metal finishing sludge #3 leachate is much higher than that obtained in the removal of organics from the fluoride sludge leachate. Apparently, the acidic conditions which favored the removal of organics from the calcium fluoride sludge leachate are not required for the removal of organics from the metal finishing sludge leachate. In all cases, with the exception of the initial

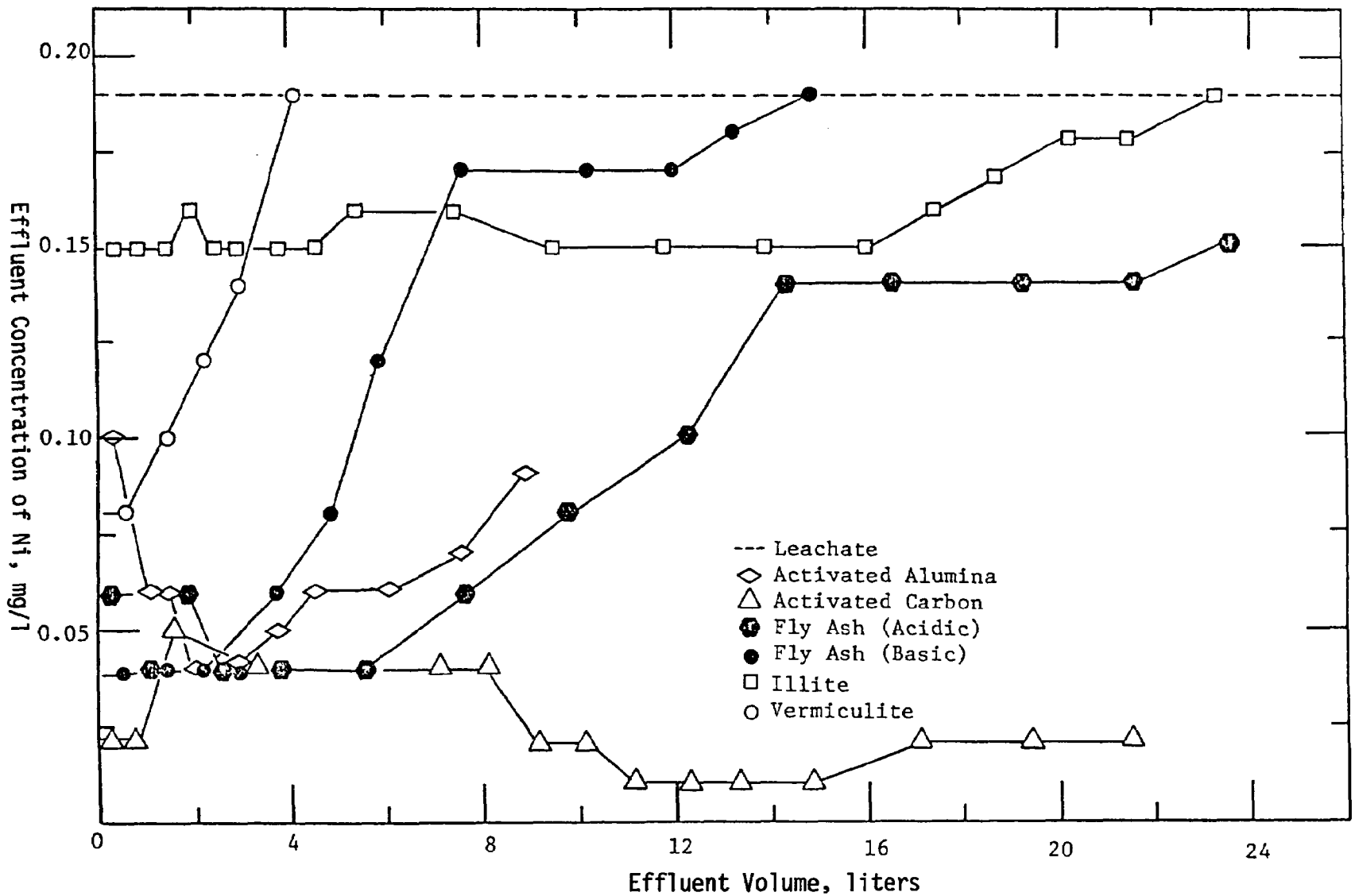

Figure 15. Lysimeter Studies of Nickel Ion in Metal Finishing Sludge Leachate.

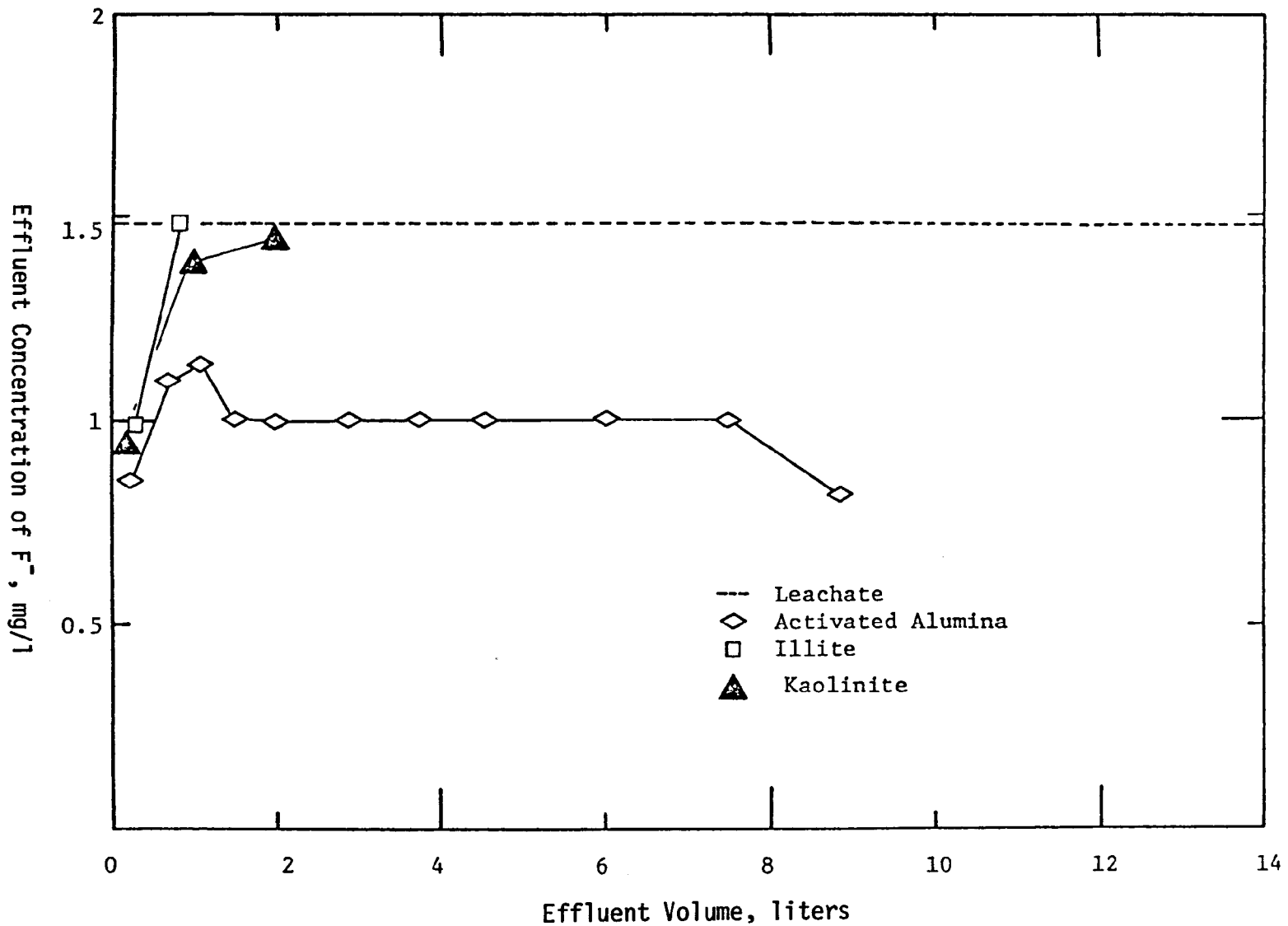

Figure 16. Lysimeter Studies of Fluoride Ion in Metal Finishing Sludge Leachate.

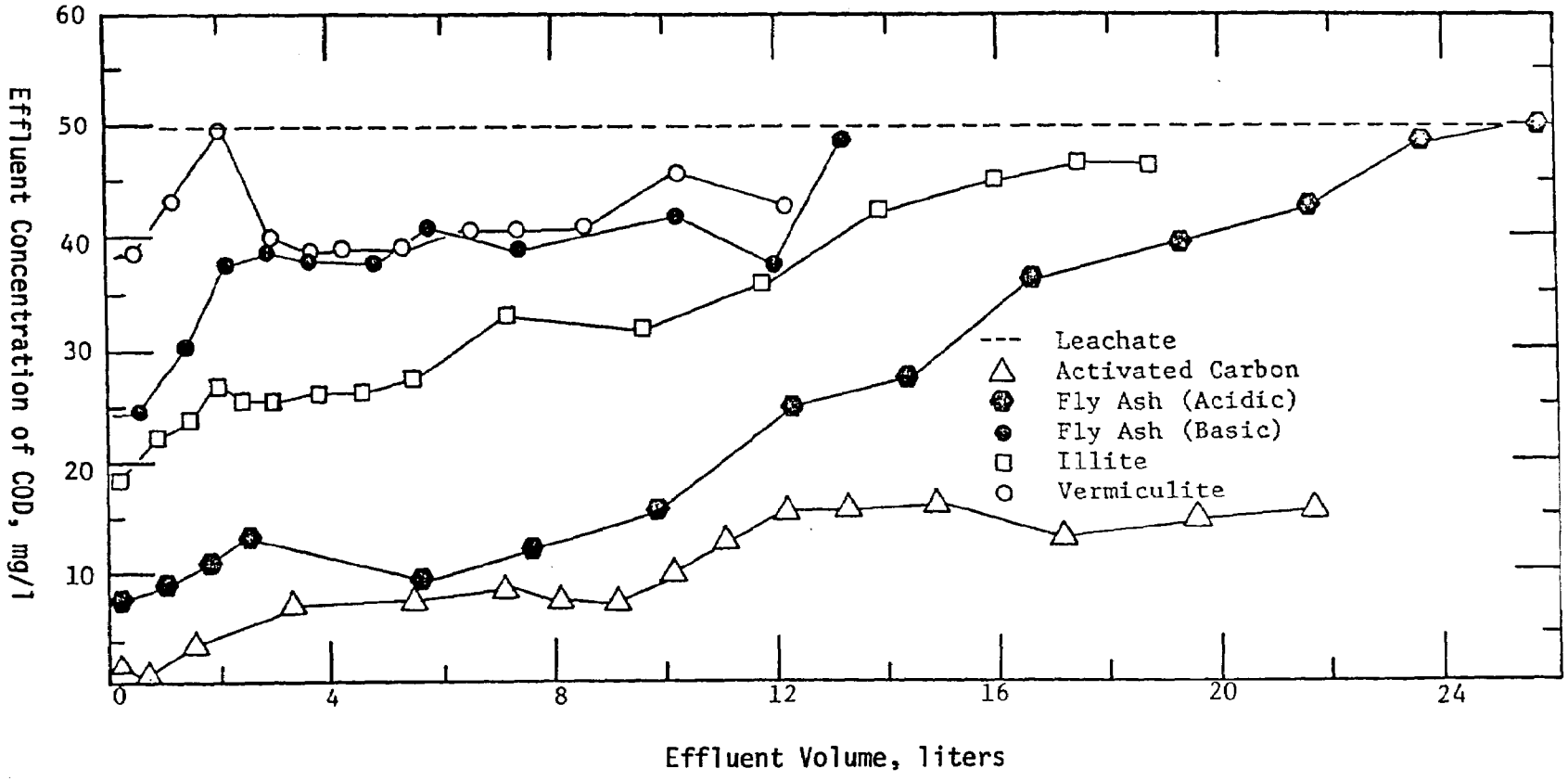

Figure 17. Lysimeter Studies of COD in Metal Finishing Sludge Leachate.

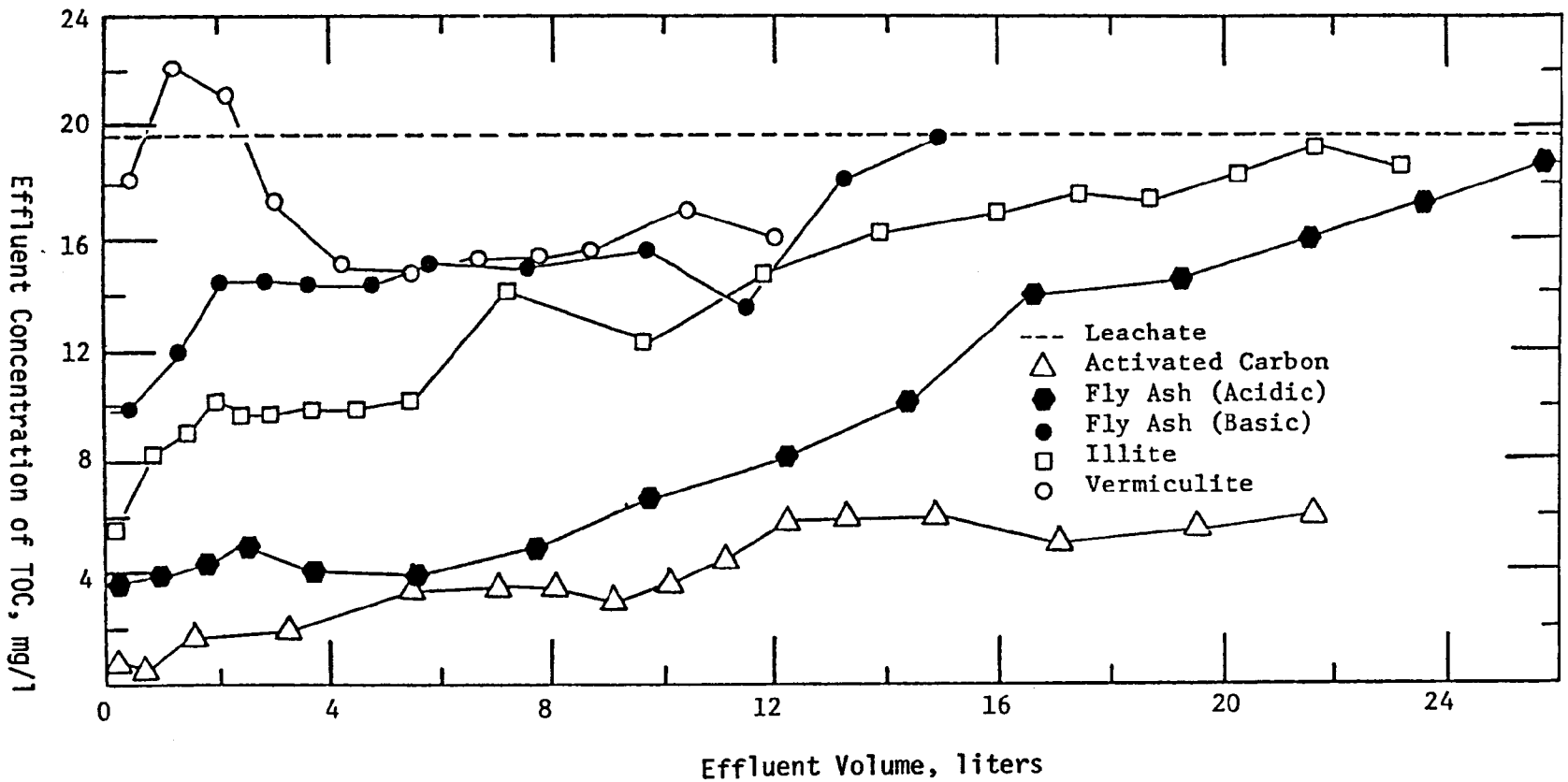

Figure 18. Lysimeter Studies of TOC in Metal Finishing Sludge Leachate.

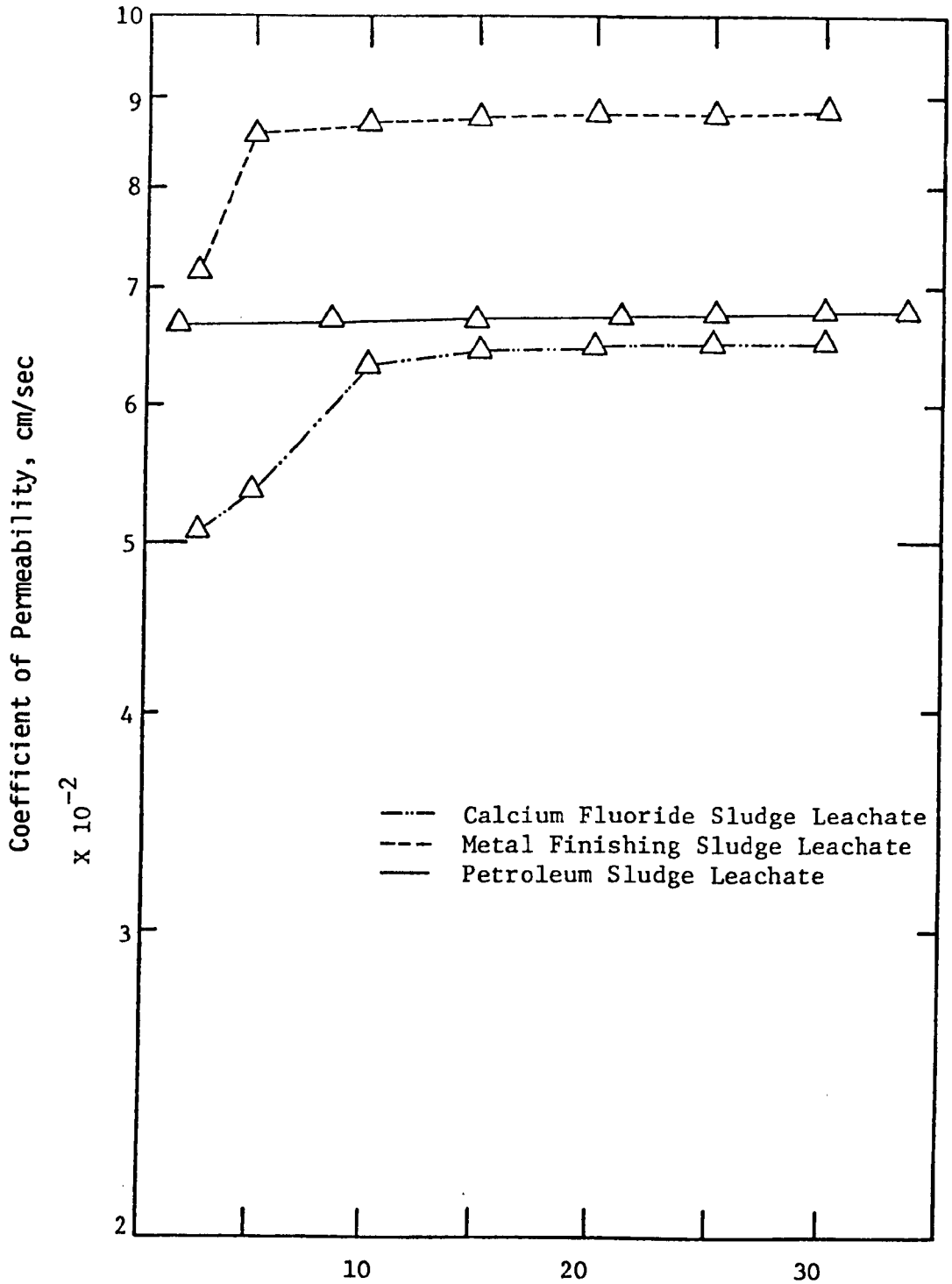

Figure 19. Permeability Studies of Activated Carbon.

fraction collected from the illite lysimeters, the pH of the effluent from the lysimeters is basic (see Figure 11). In fact, the break-through of organics did not occur for the illite when its effluent became basic as occurred with illite in the removal of organics from the calcium fluoride sludge leachate.

Permeability Results--

In addition to the sorbent capacities exhibited by activated alumina, activated carbon, acidic and basic fly ashes, illite-sand mixture, and vermiculite-sand mixture, for the various constituents in the metal finishing sludge #3 leachate, variations in the permeability exhibited by these sorbents as the leachate passes through were also examined. All the sorbents examined, with the exception of activated carbon (see Figure 19) exhibited a decrease in the coefficient of permeability. The results again show - as was the case with the calcium fluoride sludge #3 leachate - that the activated alumina exhibits the greatest reduction in the coefficient of permeability upon the addition of influent (see Figure 20). This decrease was approximately a hundred times greater than the decrease encountered with the fluoride leachate (see Table 12). In addition, the coefficient of permeability for the basic fly ash and the vermiculite-sand mixture showed significant decreases. This decrease was approximately an order of magnitude greater than that observed with the fluoride leachate.

Summary of Results

In view of the above results, the effective treatment of calcium, copper, magnesium, nickel, and the organics can be best handled by the use of the illite-sand mixture, vermiculite-sand mixture, and kaolinite-sand mixture in a layered system. The vermiculite-sand mixture, although not so effective as the illite, could be used to remove the calcium because the lysimeter results for the illite suggest the possibility of leaching of calcium from this sorbent during the period when the effluent from the illite is acidic (see Figure 12). Kaolinite is effective for the fluoride removal. However, the reduction in the permeability of vermiculite and permeability of kaolinite must be considered in the design of a bed to minimize the possibility of ponding at the surface.

Activated alumina, which is effective for removing the majority of the constituents in the metal finishing leachate, does not appear suitable for the treatment of this leachate. The marked decrease in the coefficient of permeability exhibited by this sorbent could result in the formation of an impermeable barrier.

Petroleum Sludge Leachate from an A.P.I. Gravity Separator

The effectiveness of activated alumina, activated carbon, bottom ash, acidic and basic fly ashes, illite and vermiculite for the removal of calcium, copper, magnesium, zinc, fluoride, cyanide, and the organics was investigated under flowing conditions. These constituents were selected because they were at concentration levels in the leachate that could be readily measured with the atomic absorption spectrometer and specific ion probes. In addition, the pH of the leachate, before and after it was treated with the sorbents, was also monitored to study the effect that pH may have on the removal of the various

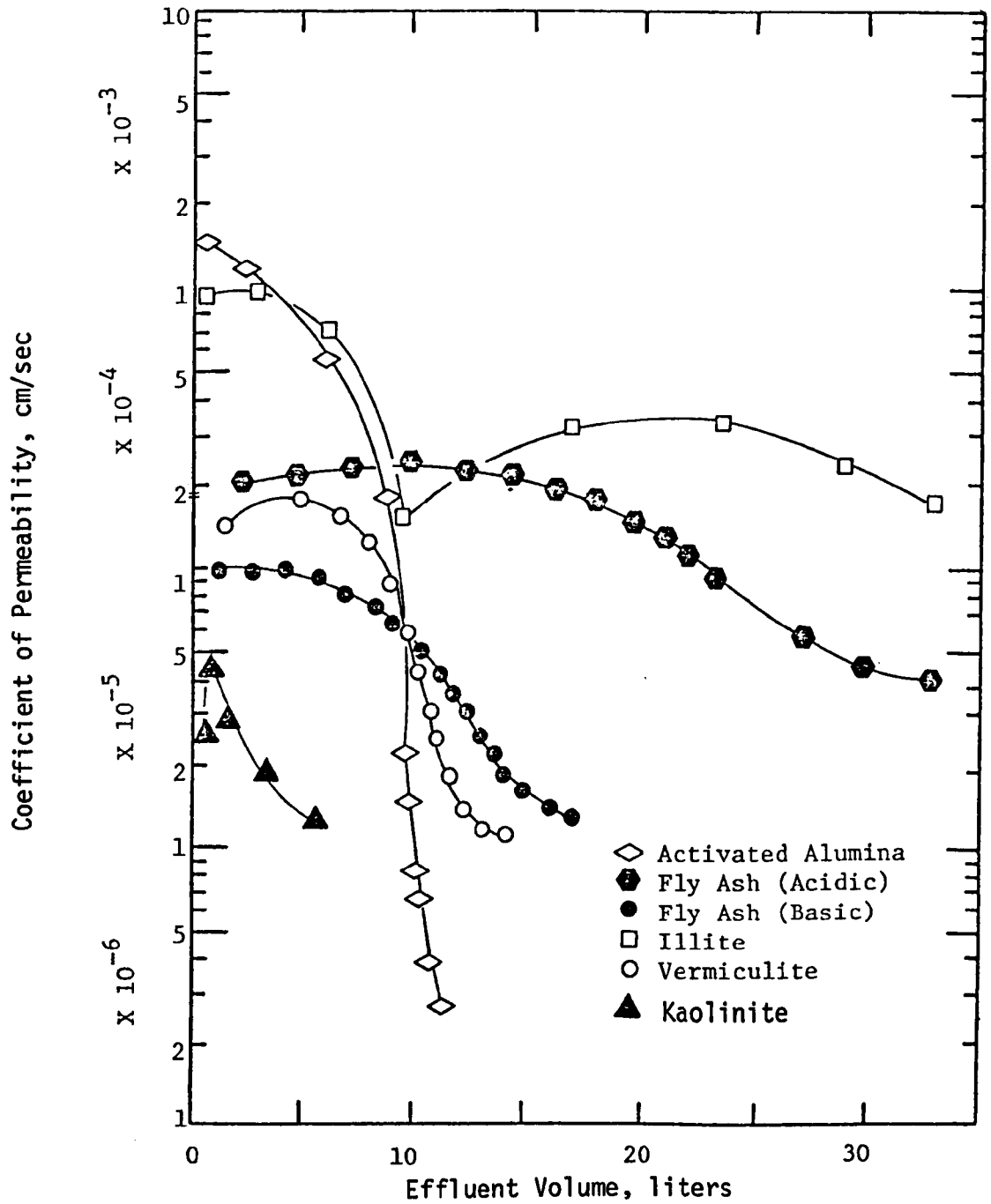

Figure 20. Permeability Studies of Sorbent Materials with Metal Finishing Sludge Leachate.

constituents by these sorbents. The results of these studies are shown in Figures 21 to 29.

The monitoring of pH in the effluent leachate collected from the lysimeter containing the different sorbents again showed that the pH of the initial effluent samples was similar to that exhibited by each sorbent, but soon approached that of the leachate (see Figure 21). In fact, the pH of each of the sorbents became acidic after 6 liters of leachate was passed through.

An examination of the changes in pH of the illite and acidic fly ash, which both exhibit acidic conditions initially, revealed different behavior. The effluent from the illite remained acidic, as would be expected since the leachate added to it is acidic, but the acidic fly ash became alkaline and then acidic again (see Figure 21). The reason for this latter observation is not understood at this time.

Lysimeter effluent samples of activated alumina and bottom ash were not collected and analyzed beyond a volume of 2 liters because of the marked reduction in permeability exhibited by both of these sorbents (see Figure 28).

Calcium Removal--

The removal of calcium in the petroleum sludge leachate by activated alumina, activated carbon, illite-sand mixture, kaolinite-sand mixture, vermiculite-sand mixture, and bottom ash is shown in Figure 22. Here it may be seen that both the illite-sand mixture and vermiculite-sand mixture are most effective for removing calcium, followed by activated carbon and kaolinite-sand mixture. Their sorbent capacities are 1110, 1010, 160 and 74 micrograms of calcium removed per gram of sorbent used, respectively (see Table 11). The initial effluent fraction collected from the illite lysimeter indicates that calcium is being leached from this sorbent. However, as leachate is continually added to this lysimeter, the calcium begins to be removed.

The reason for the calcium being leached initially and then removed upon further addition of leachate is not clear at this time. The alkaline conditions which favored the removal of calcium in the calcium fluoride sludge leachate and metal finishing sludge leachate by the illite do not appear essential for the removal of calcium in the petroleum sludge leachate by the illite. Acidic conditions were encountered in the effluent from the illite until break-through of the calcium occurred at 9 liters (see Figure 22).

The activated alumina would probably exhibit a greater sorbent capacity for calcium than the illite-sand mixture as seen from the lysimeter result (see Figure 22) if additional effluent could be collected from this lysimeter. However, such low flows were encountered through this sorbent after 2 liters of leachate passed through, that the time required for collection of significant volumes of effluent could not be justified within the scope of this investigation.

The vermiculite-sand mixture, although not as effective as the illite-sand mixture in removing the calcium, should be used in combination with the illite-sand mixture in a layered system. The illite exhibits leaching of calcium in the initial fractions of effluent collected from the lysimeter.

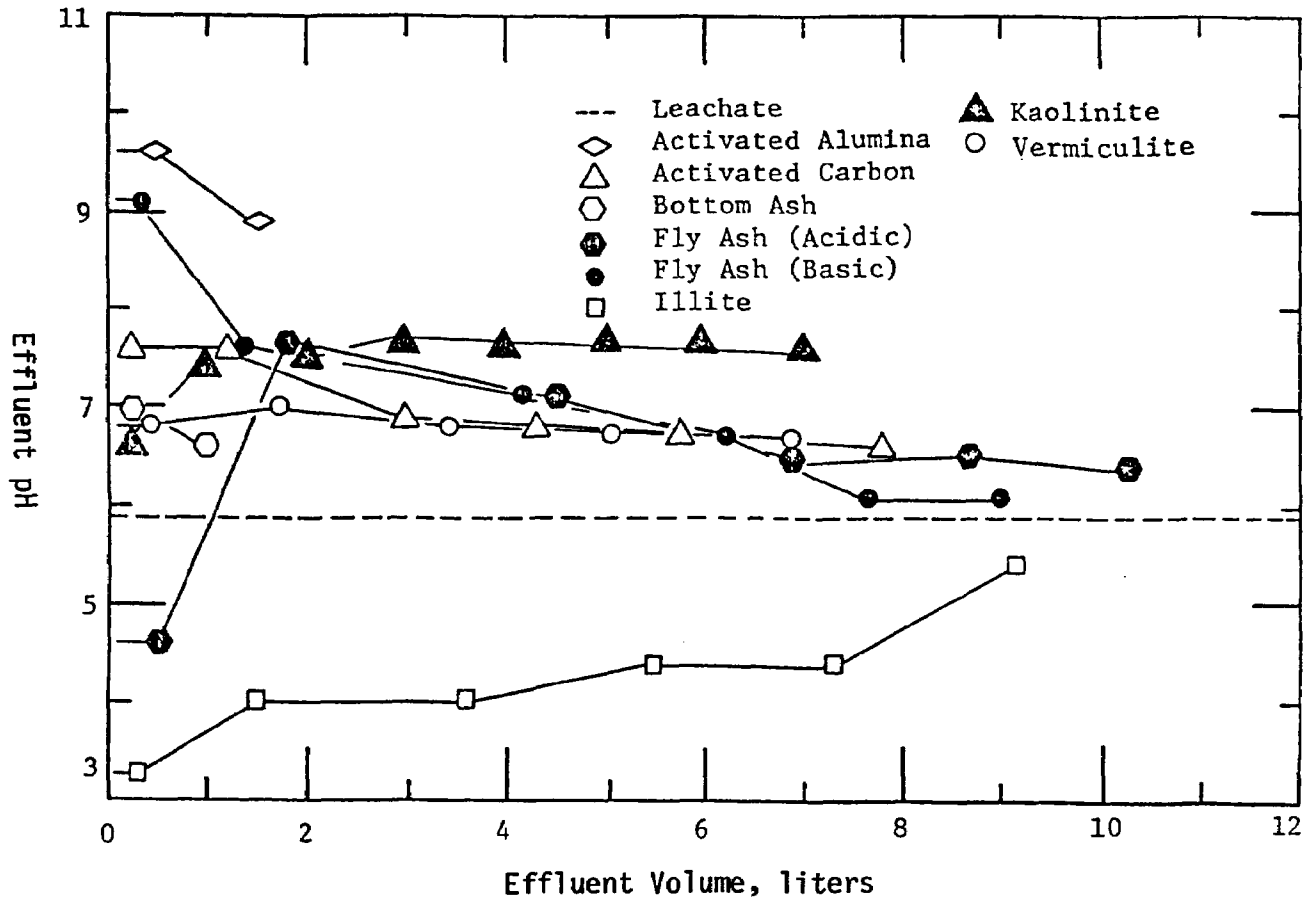

Figure 21. Lysimeter Studies of pH in Petroleum Sludge Leachate.

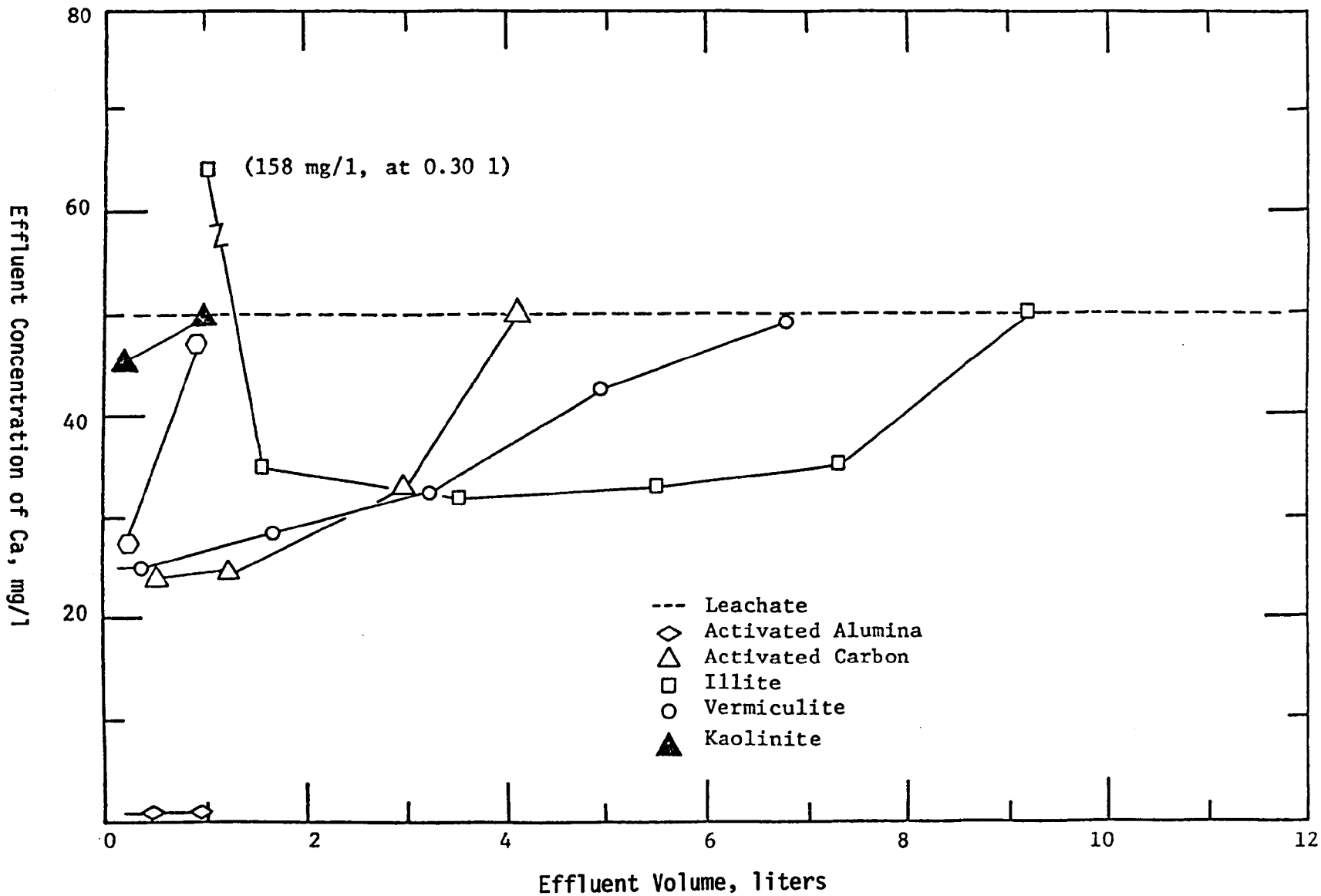

Figure 22. Lysimeter Studies of Calcium Ion in Petroleum Sludge Leachate.

Thus, the vermiculite-sand mixture could remove this initial leachable calcium and reduce its concentration in the effluent.

Copper Removal--

Activated alumina, activated carbon, bottom ash, acidic and basic fly ashes, illite and vermiculite were investigated for removal of the copper in the petroleum sludge leachate. The most effective sorbents under flowing conditions were observed to be acidic and basic fly ashes followed by vermiculite-sand mixture, activated alumina, and bottom ash. The sorbent capacities were 2.7, 2.5, 1.6, 0.39 and 0.04 micrograms of copper used per gram of sorbent used, respectively (see Table 11). Break-through of copper for the acidic and basic fly ashes is not apparent even after these sorbents were treated with 9 liters of leachate (see Figure 23). The acidic fly ash again appeared to leach copper until the effluent leachate became alkaline. The copper began to be removed by this sorbent when slightly less than 2 liters of leachate had been passed through this sorbent.

No removal of copper is observed with the illite. In fact, copper is leached from this sorbent until 10 liters of effluent have been collected. Alkaline conditions were not encountered in the effluent. The effluent remained acidic for all the fractions collected (see Figure 21). Significant variations are observed in the copper concentrations present in the initial fractions of effluent collected from the lysimeters. These variations are presumed to be the result of the different amounts of copper that are leached from the sorbent into the effluent. Illite exhibited the greatest amount of copper leaching in the static studies (see Table 10). In the lysimeter studies, it also exhibited the greatest amount of leaching. The initial 0.6 liters of illite effluent collected contains 1.4 mg/l of copper.

The basic fly ash, although not as effective as the acidic fly ash in the removal of copper, should be used in combination in a layered system with acidic fly ash to remove the leachable copper from the acidic fly ash. The copper is leached from the acidic fly ash until its effluent becomes alkaline.

Magnesium Removal--

The basic fly ash and the kaolinite-sand mixture appear to be the most effective, followed by illite-sand mixture, activated alumina, and vermiculite-sand mixture for removing the magnesium ion according to the lysimeter results (see Figure 24). Break-through of the magnesium occurs after 4 liters of leachate is added to the basic fly ash and after 5 liters of leachate have been added to the kaolinite. However, the kaolinite-sand mixture exhibited a significantly greater sorbent capacity than the basic fly ash. There were 753 and 140 micrograms of magnesium removed per gram of sorbent used, respectively. The larger sorbent capacity for the kaolinite resulted from the fact that the amount of kaolinite used in the lysimeter was only 20 percent of that used for the basic fly ash. The sorbent capacities for the illite-sand mixture, activated alumina, and vermiculite-sand mixture were 180, 107, and 90 micrograms of magnesium removed per gram of sorbent used, respectively.

The acidic fly ash was observed to exhibit significant leaching of magnesium in the initial 4 liters of effluent collected from the lysimeter. The maximum concentration of magnesium that was encountered was 49.5 mg/l in

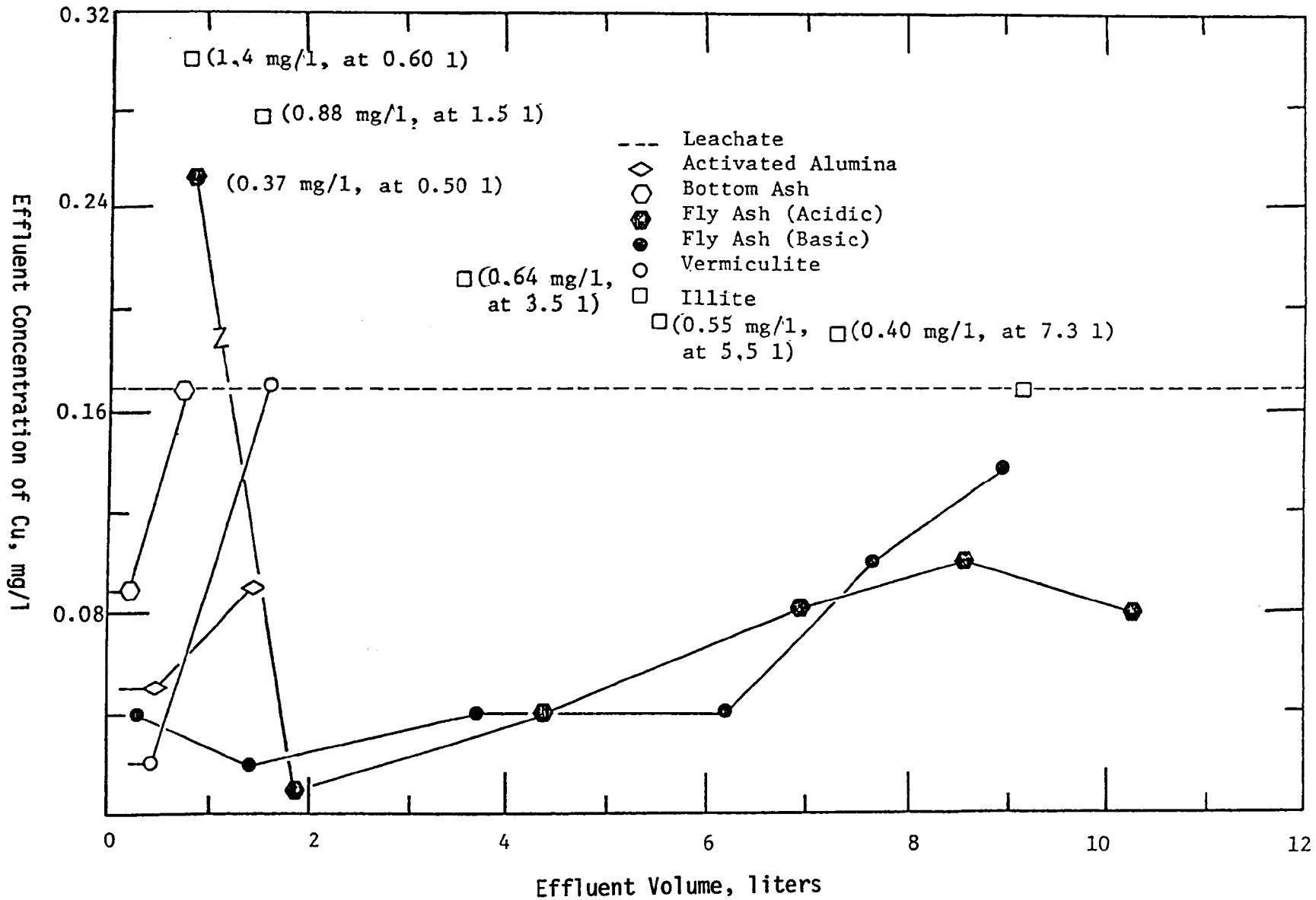

Figure 23. Lysimeter Studies of Copper Ion in Petroleum Sludge Leachate.

the column effluent collected at 1.9 liters (see Figure 24). Changes in pH of the effluent to more alkaline conditions do not appear to inhibit this leaching. This leaching appeared in the effluents that exhibited acidic pH and those that exhibited alkaline pH. The reason for this is not clear at this time. The effect of changes in pH on specific ion exchange and adsorption interactions between the contaminants in the leachate and these sorbents is an area of study that may provide the answer to above results.

Zinc Removal--

The removal of zinc from the petroleum sludge leachate under flowing conditions can be achieved with the use of acidic and basic fly ashes, followed by the vermiculite-sand mixture, activated carbon, activated alumina and bottom ash (see Figure 25). However, if account is taken that the vermiculite used is only 20 percent of the fly ash used, then vermiculite appears to be the most effective sorbent for zinc removal based upon the sorbent capacities. The sorbent capacities exhibited by vermiculite, acidic and basic fly ashes, and activated carbon, activated alumina and bottom ash are 6.4, 2.0, 2.0, 1.3, 0.43, and 0.23 micrograms of zinc removed per gram of sorbent used, respectively (see Table 11).

The acidic fly ash exhibited leaching of the zinc when its lysimeter effluent is acidic but began to remove the zinc once this effluent became alkaline. The alkaline condition occurred after slightly greater than 1 liter of leachate has been added to this sorbent (see Figure 21).

Both the illite-sand mixture and kaolinite-sand mixture exhibited leaching of the zinc until 9 and 6 liters of leachate were added to the illite and kaolinite lysimeters, respectively. After the addition of these volumes, the concentration of zinc in the effluents coincided with the concentration of zinc in the influent and no removal of zinc was observed (see Figure 25).

The effluent from illite column exhibited only acidic conditions. The lack of pH change in the lysimeter effluent may be responsible. Where there was a pH change from acidic to basic effluent, such as for the acidic fly ash, leaching of zinc from the acidic fly ash was inhibited.

Fluoride Removal--

The activated alumina, activated carbon, acidic and basic fly ashes, illite, kaolinite, and vermiculite were examined for their effectiveness in removing fluoride from the petroleum sludge leachate. The results indicated that the illite-sand mixture, acidic and basic fly ashes are the most effective sorbents studied, followed by kaolinite-sand mixture, activated alumina, and activated carbon, for removing fluoride. No removal of the fluoride by the vermiculite-sand mixture was observed. The concentrations of fluoride in the lysimeter effluent were the same as in the influent (see Figure 26).

The sorbent capacities exhibited by the illite-sand mixture, acidic fly ash, basic fly ash, kaolinite-sand mixture, activated alumina and activated carbon for fluoride removal are 12.1, 9.9, 7.2, 4.3, 3.4 and 1.3 micrograms of fluoride removed per gram of sorbent used , respectively (see Table 11).

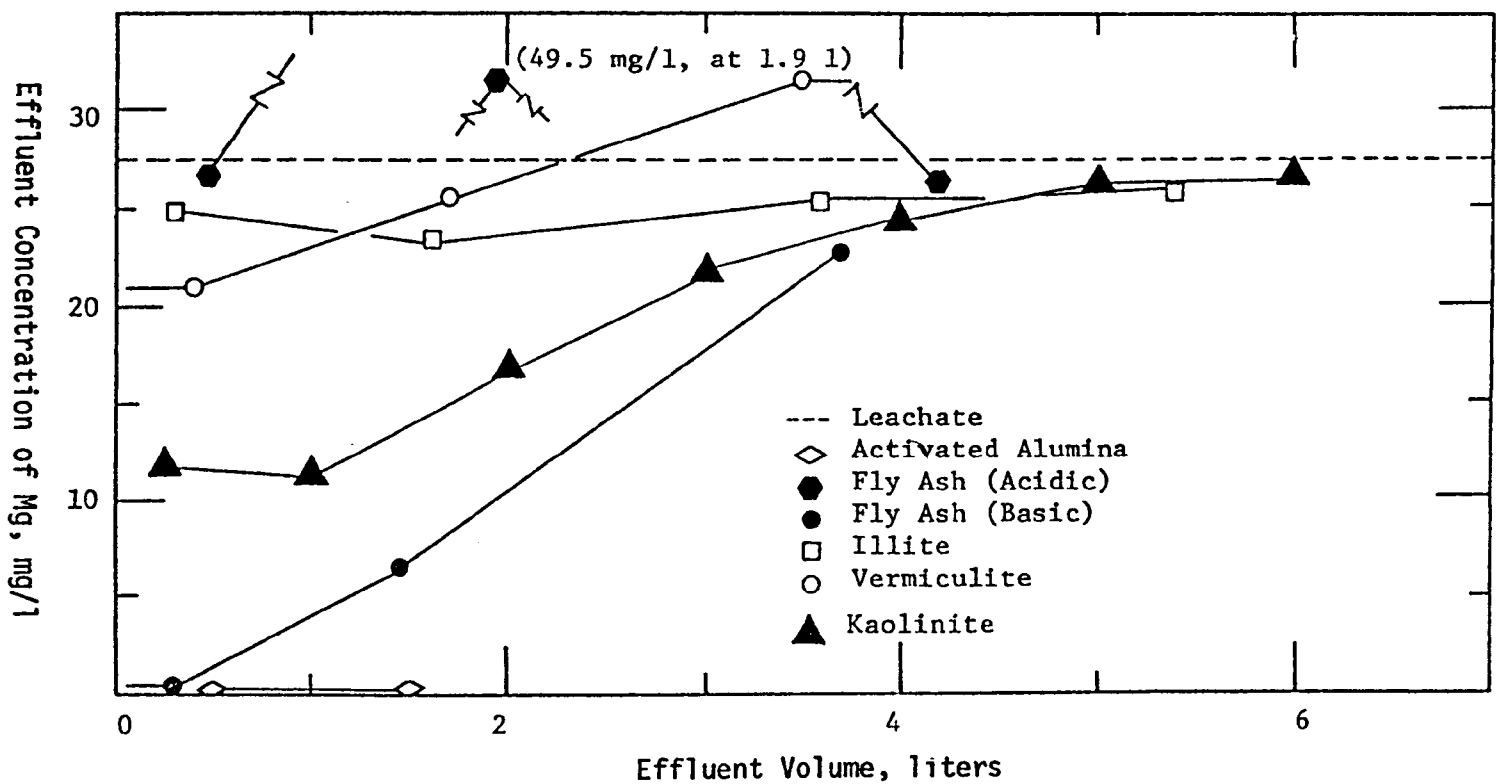

Figure 24. Lysimeter Studies of Magnesium Ion in Petroleum Sludge Leachate.

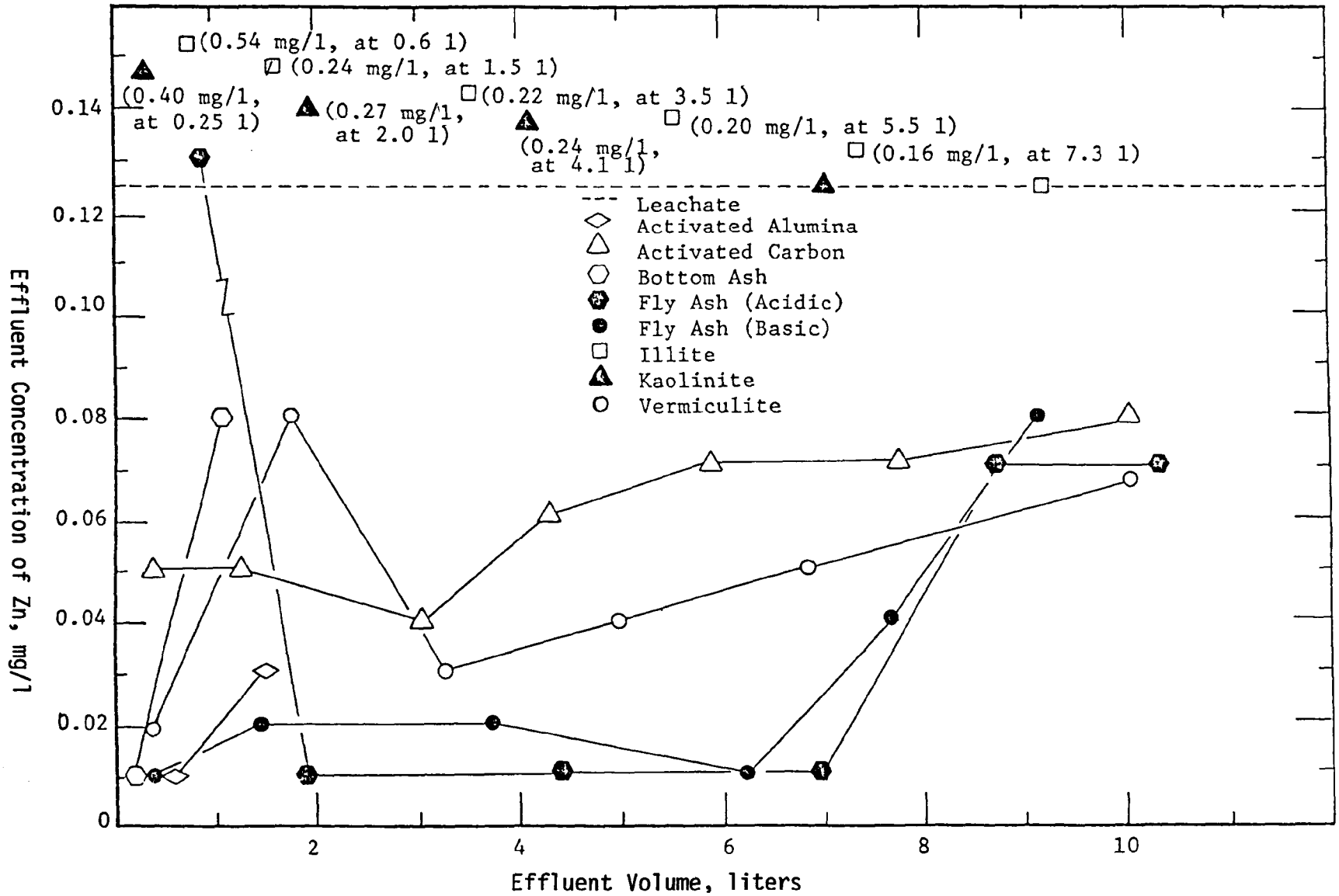

Figure 25. Lysimeter Studies of Zinc Ion in Petroleum Sludge Leachate.

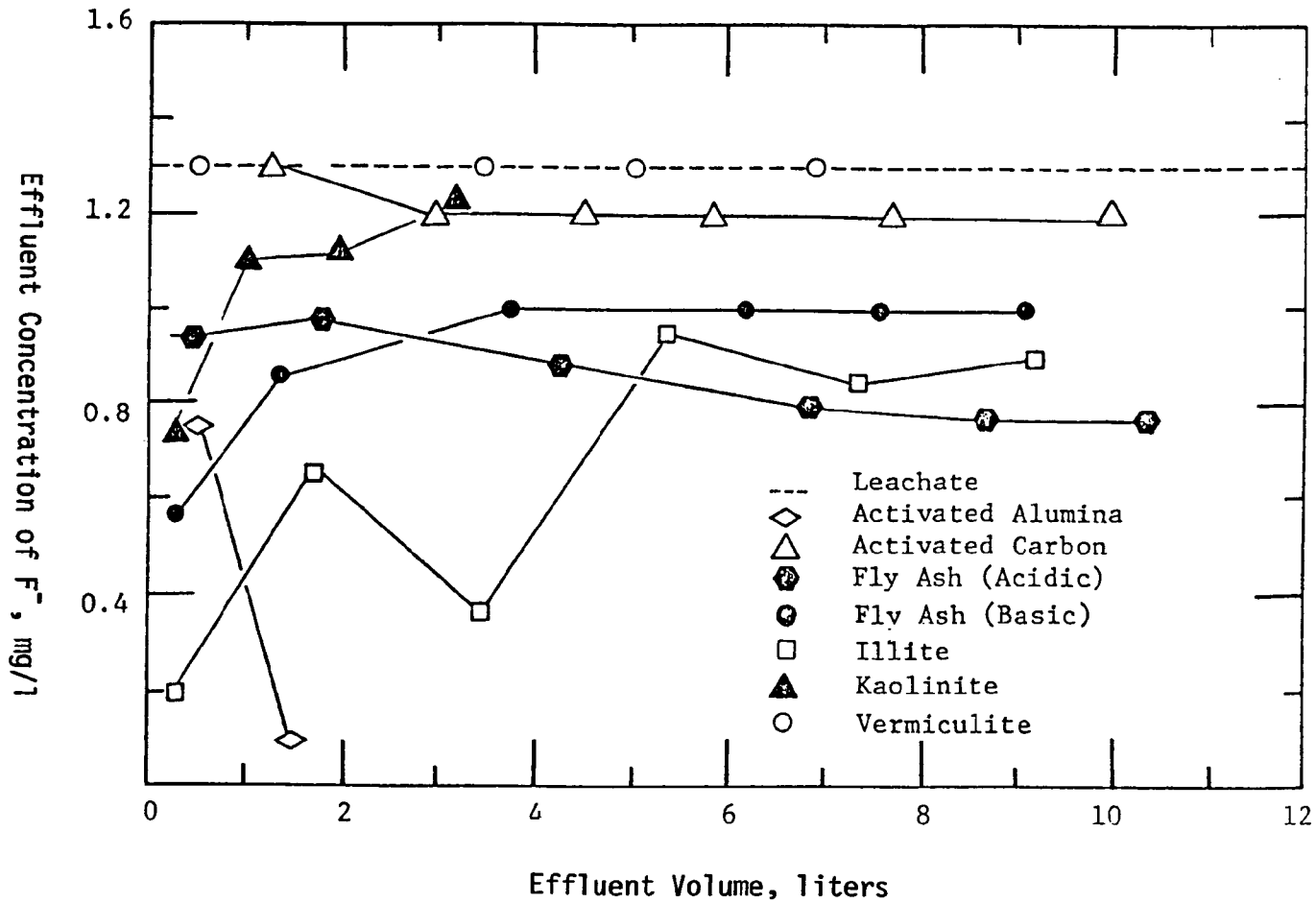

Figure 26. Lysimeter Studies of Fluoride Ion in Petroleum Sludge Leachate.

Cyanide Removal--

The activated alumina, activated carbon, acidic and basic fly ashes, bottom ash, illite-sand mixture, kaolinite-sand mixture, and vermiculite-sand mixture were investigated to determine their effectiveness in removing cyanide from petroleum sludge leachate. The results indicated that all the sorbents, with the exception of activated alumina and bottom ash, exhibited removals of the cyanide (see Figure 27). Their sorbent capacities were 2.9, 3.3, 3.3, 15.5, 4.2, and 13.3 micrograms of cyanide removed per gram of sorbent used, respectively (see Table 11). The illite-sand mixture followed by the vermiculite-sand mixture appeared to be the most effective based upon a comparison of the sorbent capacities. No removal of cyanide was obtained using either bottom ash or activated alumina.

Organic Removal--

The activated alumina, activated carbon, bottom ash, basic and acidic fly ashes, illite-sand mixture, kaolinite-sand mixture, and vermiculite-sand mixture were examined to determine their effectiveness in removing organics from the petroleum sludge leachate, under flowing conditions. The results indicate that all these sorbents exhibit some removal of the organics (see Figures 28 and 29). A comparison of the sorbent capacities indicate that the vermiculite-sand mixture is the most effective in removal of COD and TOC, followed by the illite-sand mixture, basic and acidic fly ashes, activated carbon, activated alumina, and bottom ash in decreasing order (see Table 11).

It should be noted from the sorbent capacities that the vermiculite-sand mixture is significantly more effective than the activated carbon in removing the organics from this leachate for the 10 liters of leachate added to these lysimeters. This finding is significant in that activated carbon is considered to be an effective sorbent for the removal of organics from waste streams.

Permeability Results--

The type of leachate being treated by a sorbent has a significant effect on the permeability of the sorbent, with the exception of activated carbon. The initial magnitude of the coefficient of permeability exhibited by the activated carbon was not influenced by the leachate (see Figure 19). Also, it did not change significantly upon the addition of leachate. On the other hand, the activated alumina decreased markedly upon the addition of the leachate (see Figure 30). The coefficient of permeability for bottom ash also exhibited a parallel behavior.

The coefficient of permeability for acidic and basic fly ashes, illite-sand mixture and vermiculite-sand mixture in general exhibited far less variation upon the addition of the petroleum sludge leachate than either the activated alumina or bottom ash. The coefficient of permeability for the kaolinite initially was much lower than the above sorbents. However, it exhibited less of a decrease upon the addition of leachate than either the bottom ash or activated alumina.

Summary of Results

The basic fly ash, the vermiculite-sand mixture and the kaolinite-sand mixture appear to be the most effective sorbent combination for treating the

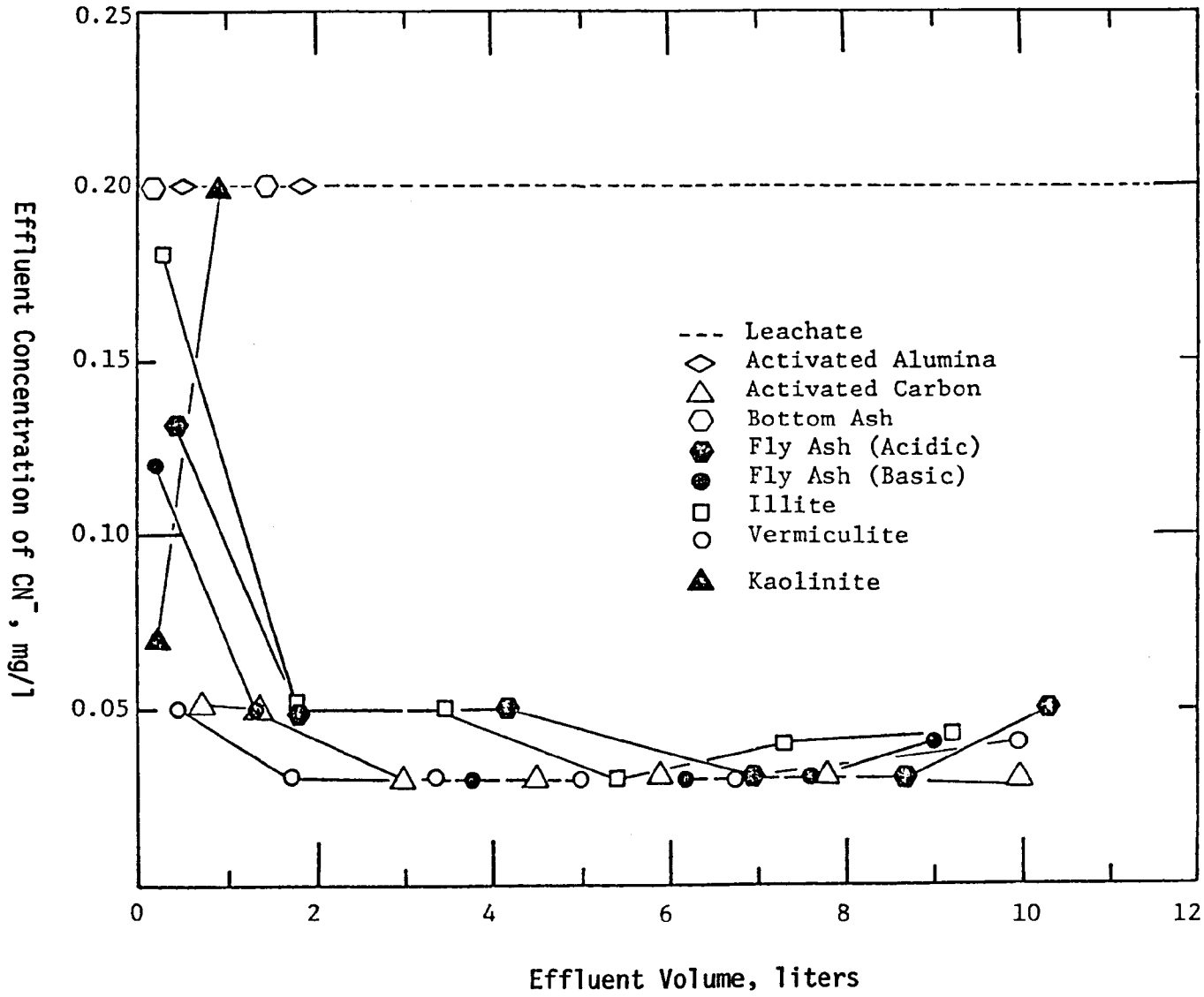

Figure 27. Lysimeter Studies of Cyanide Ion in Petroleum Sludge Leachate.

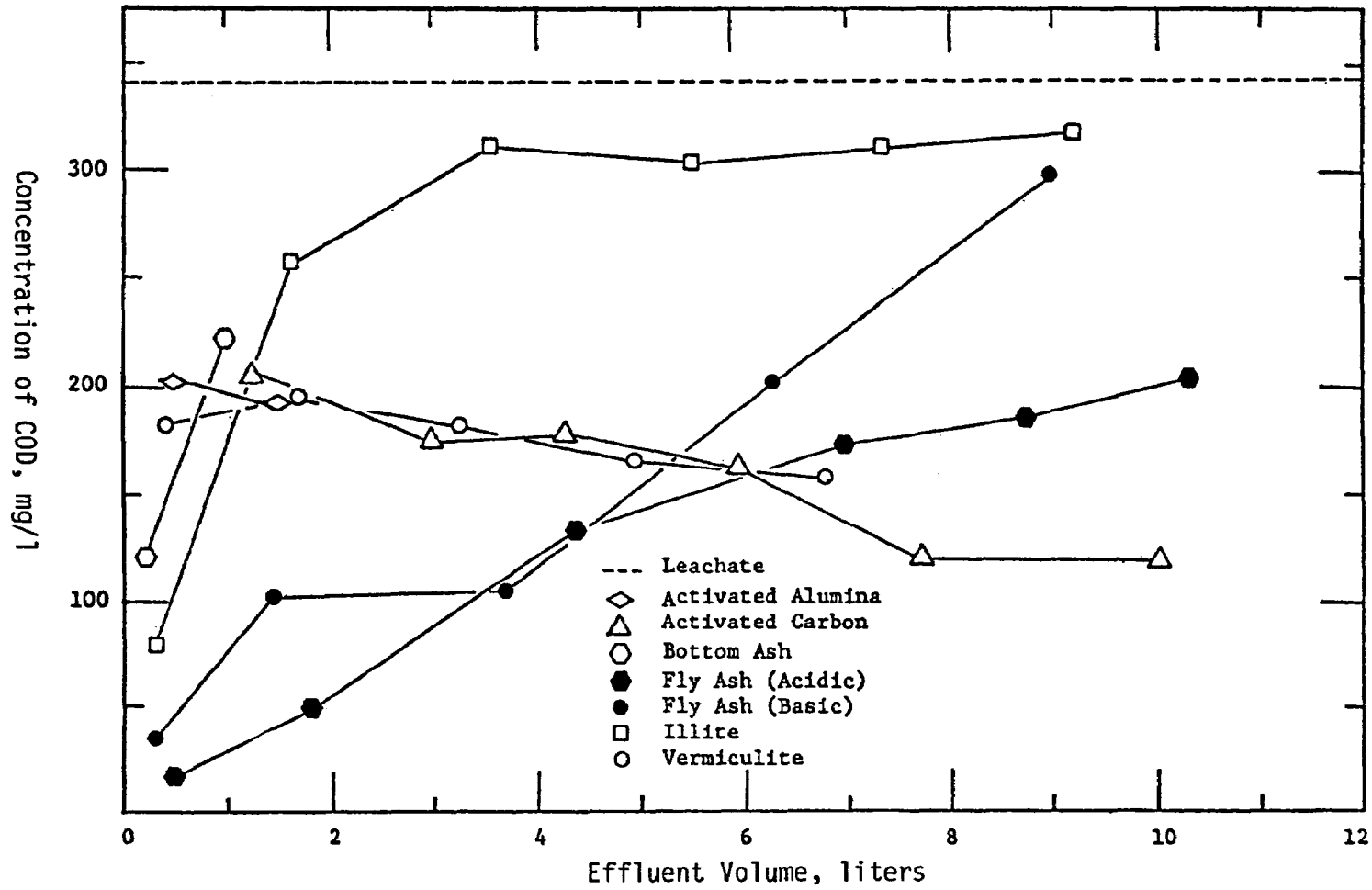

Figure 28. Lysimeter Studies of COD in Petroleum Sludge Leachate.

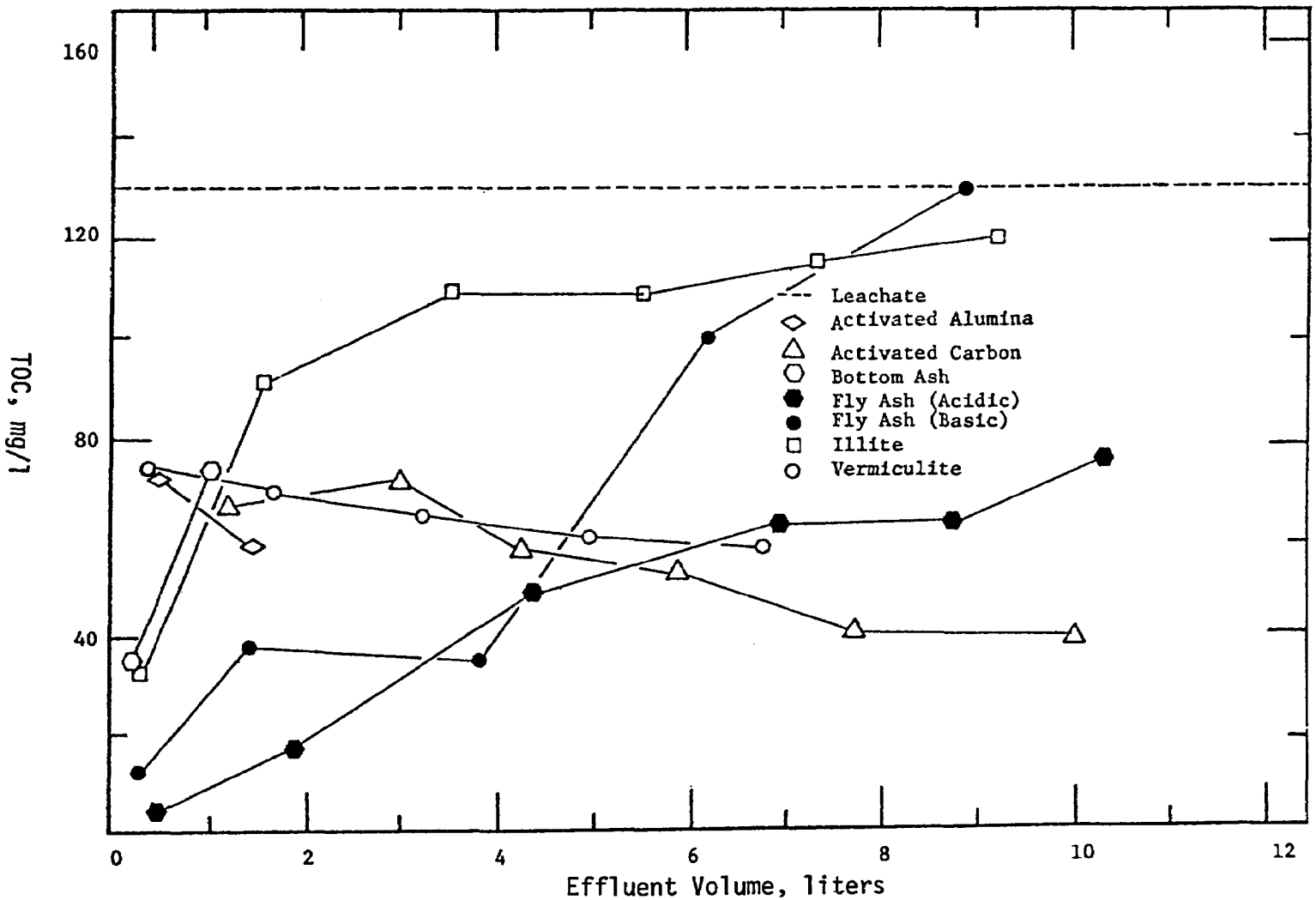

Figure 29. Lysimeter Studies of TOC in Petroleum Sludge Leachate.

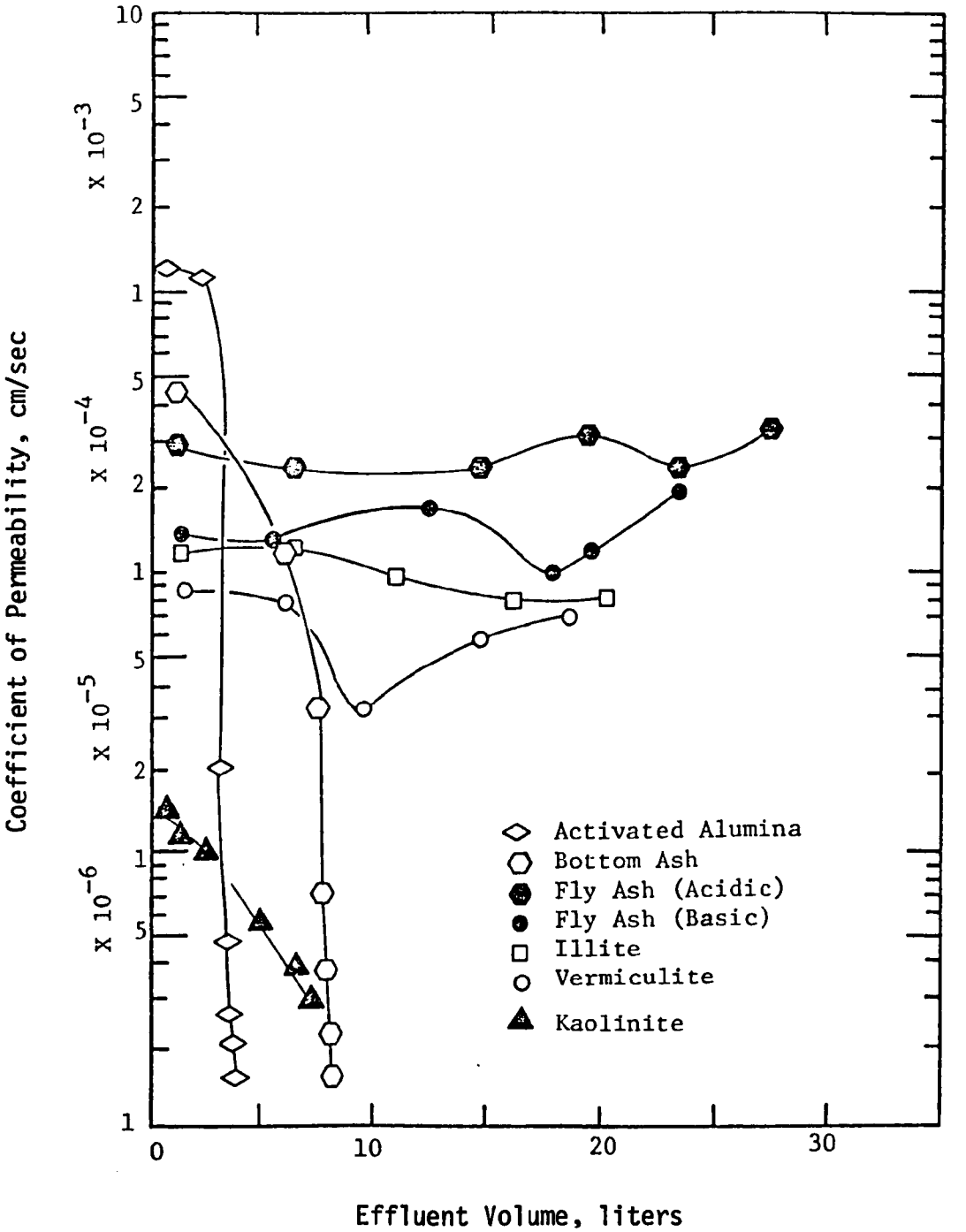

Figure 30. Permeability Studies of Sorbent Materials with Petroleum Sludge Leachate.

petroleum sludge leachate. The basic fly ash would be used for removing the copper and fluoride, the vermiculite-sand mixture for the calcium, zinc, cyanide and the organics and the kaolinite-sand mixture for removing the magnesium ion.

The kaolinite-sand mixture is significantly more effective than the other sorbents for removing the magnesium ion based upon a comparison of the sorbent capacities. Hence, it is included in the above combination even though it exhibited leaching of zinc ion. The presence of a significant amount of vermiculite-sand mixture in a layered system could minimize this problem.

Although illite was found to be the most effective for the removal of calcium, fluoride and cyanide based upon a comparison of the sorbent capacities, the illite does not show promise because it exhibited leaching of copper and zinc in over half of the effluent fractions collected from the lysimeter. Similarily, the acidic fly ash was found to be the most effective for the removal of the copper and the next most effective for fluoride, but it was not selected because in over two-thirds of the effluent fractions that were analyzed for magnesium, the acidic fly ash showed leaching of this ion.

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16. ABSTRACT

This report covers the initial laboratory studies carried out to identify the most promising sorbents that may be used to significantly reduce the concentration of measurable contaminant in calcium fluoride sludge leachate, metal finishing sludge leachate and petroleum sludge leachate. Laboratory evaluations were made of bottom ash, acidic and basic fly ashes, vermiculite, illite, activated carbon, kaolinite, natural zeolite, activated alumina, and cullite for the removal of contaminants in the leachate and liquid portion of these three industrial sludges.

Batch and lysimeter studies were carried out to evaluate the static and dynamic sorbent capacity for the constituents present in the leachate. Permeability exhibited by these sorbents when contacted with an industrial sludge leachate was also studied. The pH, conductivity, chemical oxygen demand (COD), total organic carbon (TOC), cationic and anionic species in the leachate before and after contact with the sorbent materials and the coefficient of permeability were determined.

Considerable variations in composition and concentration of leachate constituents were shown. Batch and lysimeter studies revealed that no single sorbent could be used to reduce the concentration of the constituents found in the leachate of a specific sludge; rather, combinations of two or more sorbents could be used.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Leaching Pollution Waste treatment Linings Sorbents	Solid waste management Industrial sludges	13B

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