

SORPTION OF SELECTED INORGANIC MATERIALS ON RAW AND RETORTED
OIL SHALES

by

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(ABSTRACT)

Shale oil is an attractive, alternative fuel source for a world in which there is an increasing demand for energy. However, it is necessary to assess the environmental impacts of the shale oil industry before widescale production is begun. Diversity of retorting processes, the subsequent variability in waste products and the possible waste management schemes makes assessment of these impacts complicated. Waste treatment and disposal are areas which must be researched thoroughly. To properly evaluate the environmental risks associated with the disposal of processed shales and process wastewaters, an appreciation for the sorption/desorption (S/D) characteristics of oil shales is required.

The overall objective of this research was to evaluate the S/D capacity of four types of shale: Antrim (spent, eastern shale), Anvil (raw, western shale), Oxy 6 and Run 16 (spent, western shales). Batch and continuous-flow, column experiments were performed in which the S/D behavior of five

cations (As, Ca, Cd, Fe, and K) and three anions (F, SO₄, and HCO₃/CO₃) was monitored. The conductivity, redox potential, and pH of the eluent fluids were also determined.

This study showed that retort temperature and porosity of the various shales had a significant effect on their S/D characteristics. Batch elution trials with spent shales produced eluents having a characteristic pH in the range 8.5 to 11.5. In these experiments, the shales retorted at lower temperatures (660°C and 793°C) released higher levels of Ca, K, and SO₄ than did a higher temperature, retorted shale (800 to 1000°C) and raw shale. The shales retorted at lower temperatures also had the highest porosities of the four shales and exhibited a greater capacity for sorption of As and F than did the other shales. Continuous-flow, elution trials showed that most inorganics monitored were flushed from the columns of shale in the first 5 to 8 pore volumes of effluent.

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TABLE OF CONTENTS

SORPTION OF SELECTED INORGANIC MATERIALS ON RAW AND RETORTED OIL SHALE	ii
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ACKNOWLEDGEMENTS	iv
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Chapter

	<u>page</u>
I. INTRODUCTION	1
II. LITERATURE REVIEW	6
Formation of Oil Shale	6
Processing of Oil Shale	9
Retorting Methods	12
Waste Generation	13
Spent Shale.	13
Retort Wastewater	15
Other Wastes Produced	17
Spent Shale Characteristics	19
Shale Leachates	23
Potential Uses for Spent Shale	35
Spent Shale as an Adsorbent for Treating Process Water	35
Co-disposal of Spent Shale with Process Waters	36
Comparison of Batch and Column Leaching Methods Important Considerations for Batch Experiments	37
Established Batch Extraction Procedures	43
Design Factors to Consider for Batch and Column Experiments	46
Batch Experiments	49
Column Experiments	49
Adsorption Processes	51
Fundamentals of Adsorption at the Liquid- Solid Interface	52
Factors Affecting Adsorption from Solution Rate-Limiting Factors of the Adsorption Process	56
Adsorption Isotherms	58
Langmuir and Freundlich Equations	62
Adsorption Isotherms	63
Langmuir and Freundlich Equations	64
III. MATERIALS AND METHODS	69
Batch Experiments	71

Batch Elution Experiment	71
Batch Sorption Experiment	72
Controls for Sorption Experiment	73
Continuous-Flow Column Experiments	74
Column Elution Experiments	76
Column Sorption Experiments with Single Ion Solutions	77
Column Sorption/Desorption with a Combination of Ions	78
IV. RESULTS	80
Physical Properties	80
Batch Elution Studies	82
Batch Sorption Results	91
Column Elution Results	100
Single Ion Column Adsorption/Desorption	116
Sorption/Desorption in a Multi-adsorbate System	127
V. DISCUSSION	144
Application of Results	144
Batch and Column Elution Results	146
Constituents of Leachates from Raw and Retorted Shales	147
Relationship of Retort Temperature and pH of Leachates	150
Fluoride Levels in Leachates	152
Metal Concentrations in Leachates	153
Elution Behavior of Inorganic Materials in Shale Columns	156
Analysis of Sorption Trial Results	157
Batch Sorption Results	158
Discussion of Single- and Multi-adsorbate Trials	164
Desorption Trials	169
Factors Which May Affect Adsorption Capacity	172
Assessment of Batch and Column Experiments	173
VI. SUMMARY AND CONCLUSIONS	175
REFERENCES CITED	178

Appendix

	<u>page</u>
A. EQUILIBRIUM ISOTHERMS FOR BATCH ELUTION TRIALS	188
B. BATCH SORPTION ISOTHERMS	196
C. COLUMN ELUTION TRIALS	207
D. SINGLE-ION DESORPTION TRIALS	235
E. MULTI-ADSORBATE SORPTION/DESORPTION TRIALS	240

LIST OF TABLES

<u>Table</u>	<u>page</u>
1. Elemental Composition of Organic Fraction in Oil Shales	10
2. Major Minerals in Oil Shale	11
3. Retort Water Quality	16
4. Problems Related to Treatment of Retort Waters	18
5. Summary of Some Batch Experiments with Shale Materials	25
6. Summary of Some Column Leaching Experiments with Shale Materials	27
7. Differences in Raw and MIS Spent Shale Leachates from Column Leaching with Distilled Water	30
8. Material Extracted from Spent Shale After 240 Hours of Batch Leaching with Rock Springs Ground Water	31
9. Variation of Conductivity and pH with Number of Pore Volumes of Leachate from each Column	33
10. Batch Experiments Performed for the Evaluation of Solid Wastes	40
11. Column Studies Performed for the Evaluation of Solid Wastes	42
12. Maximum Concentration of Contaminates for Characteristic EP Toxicity	47
13. Various Sorption Studies	53
14. Retort Process for Antrim, Oxy 6 and Run 16 Shales	81
15. Physical Properties of Anvil, Antrim, Oxy 6 and Run 16 Shales	83
16. Summary of Batch Elution Equilibrium Isotherms	85

17.	Summary of Batch Sorption Results	97
18.	Summary of Column Elution Results	106
19.	Summary of Single Ion Column Sorption/Desorption Data	118
20.	Summary of Multi-adsorbate Column Results	128
21.	Concentration Ranges of Various Inorganic Constituents in Batch Eluents from Raw Shales	149
23.	Concentrations of Elements in Batch and Column Eluents Which Approached or Exceeded Standards	154

LIST OF FIGURES

<u>Figure</u>	<u>page</u>
1. Oil Shale deposits of the United States	7
2. Oil Shale Areas in Colorado, Utah and Wyoming	8
3. Elution profile of organic carbon, salts, and pH from Occidental Retort	34
4. Distribution of charge and cation exchange potential of a clay	60
5. Evaluation of Langmuir constants	66
6. Evaluation of Freundlich constants	67
7. Design of the continuous-flow column system.	75
8. Variation in pH of batch eluents from various shales.	86
9. Variation in conductivity of batch eluents from various shales.	88
10. Variation in redox potential of batch eluents from various shales.	89
11. Variation in alkalinity of batch eluents from various shales.	90
12. Variation in arsenic of batch eluents from Oxy and Antrim shales.	92
13. Variation in arsenic of batch eluents from Anvil and Run 16 shales.	93
14. Variation in fluoride of batch eluents from Anvil and Run 16 shales.	94
15. Comparison of As levels remaining in solution during batch sorption and control trials with Oxy shale.	98
16. Arsenic adsorbed as a function of time for three liquid:solid ratios of water to Run 16 shale.	99

17.	Comparison of Cd levels remaining in solution during batch sorption and control trials with Oxy shale.	101
18.	Comparison of F levels remaining in solution during batch sorption and control trials with Anvil shale.	102
19.	Comparison of F levels remaining in solution during batch sorption and control trials with Run 16 shale.	103
20.	Fluoride adsorbed as a function of time for three liquid:solid ratios of water to Antrim spent shale.	104
21.	Variation in pH during column elution of Antrim spent shale.	108
22.	Variation in alkalinity during column elution of Run 16 spent shale.	109
23.	Variation in calcium during column elution of Anvil raw shale.	111
24.	Variation in calcium during column elution of Oxy spent shale.	112
25.	Variation in calcium during column elution of Antrim spent shale.	113
26.	Variation in calcium during column elution of Run 16 spent shale.	114
27.	Variation in fluoride during column elution of Antrim spent shale.	115
28.	Breakthrough curves for arsenic in column adsorption trials with various shales.	120
29.	Breakthrough curves for potassium in column adsorption trials with Anvil and Oxy shales.	122
30.	Breakthrough curves for calcium in column adsorption trials with Anvil and Oxy shales.	123
31.	Desorption of calcium from shale columns previously used in calcium adsorption trials.	124

32.	Breakthrough curves for fluoride in column adsorption trials with Anvil and Oxy shales.	125
33.	Breakthrough curves for fluoride in column adsorption trials with Antrim and Run 16 spent shales.	126
34.	Breakthrough curves for arsenic in multi-adsorbate column trials with Antrim spent shale.	129
35.	Breakthrough curves for arsenic in multi-adsorbate column trials with Anvil raw shale.	131
36.	Breakthrough curves for arsenic in multi-adsorbate column trials with Oxy spent shale.	132
37.	Breakthrough curves for fluoride in multi-adsorbate column trials with Anvil raw shale.	134
38.	Breakthrough curves for fluoride in multi-adsorbate column trials with Oxy spent shale.	135
39.	Breakthrough curves for fluoride in multi-adsorbate column trials with Antrim spent shale.	136
40.	Breakthrough curves for fluoride in multi-adsorbate column trials with Run 16 spent shale.	137
41.	Breakthrough curves for calcium in multi-adsorbate column trials with Anvil raw shale.	139
42.	Desorption of calcium from columns of Anvil raw shale which were previously used in multi-adsorbate trials.	140
43.	Breakthrough curves for potassium in multi-adsorbate column trials with Anvil raw shale.	142
44.	Breakthrough curves for potassium in multi-adsorbate column trials with Oxy spent shale.	143
45.	Optimum pH values for metal removal	159
46.	Solubility of metals versus pH	161
47.	Eh-pH diagram of As-H ₂ O system at a _{As} (activity of As) = 10 ⁻³ moles/liter or As = 75 mg/L	162

Chapter I

INTRODUCTION

Since the "energy crisis" of the early seventies, the United States has been striving to develop the nation's natural resources of coal, gas and oil. Along with the increased mining and drilling for coal and oil came the production of synthetic fuels (synfuels); gaseous, liquid, or solid fuel that does not occur naturally. Synfuels can be made from coal, petroleum products, or plant products. Among these are oil shales, one of the largest and least used fossil fuel resources in the United States. Production of shale oil, however, creates many environmental problems that must be resolved before widescale development is begun. This is one of the few times in the history of the United States that an industry is being developed with major concern for the environmental problems it may create.

Two of the major waste problems encountered in shale oil production are, first of all, the disposal of large amounts of spent (or retorted) shale and, secondly, treatment of wastewaters from the retorting processes. It has been estimated that for one gallon of oil, seventy pounds of spent shale will be produced (1). Current disposal methods involve the containment of the shale in

landfills. Process waters contain high levels of organics, suspended solids and total dissolved solids. Treatment costs for this type of wastewater are very high.

During retorting, raw shale is subjected to extremely high temperatures in order to convert the organic material in the shale to crude shale oil. This process greatly changes the shale's mineralogic composition and surface characteristics. When these spent shales come into contact with water, the resulting leachate differs greatly from leachates produced from raw shale. Generally, leachates from spent shales are characterized by a basic pH, high total dissolved solids and potentially toxic organic compounds and inorganic metals.

One of the major concerns regarding the disposal of spent shale in landfills is the hazard posed by leaching of organic and inorganic constituents from the shale if rainwater or groundwater enters the landfill. Therefore, it is essential that the leaching behavior of the shale be known and also the magnitude of the amount of materials released. When this information is obtained, a careful assessment can be made of the possible degree of contamination of groundwater supplies and degradation of surface water quality.

Disposal and reuse alternatives have been suggested in an attempt to reduce the magnitude of the spent shale disposal problem. Shale could be used as an adsorbent in a treatment scheme as is activated carbon. The use of shale to remove some of the pollutants from retort waters in this way would help to reduce costs of treatment. Another suggestion, which is currently under great scrutiny, is to combine the spent shale and process waters in a landfill disposal system. The process water would serve to moisten the shale, preventing dust problems, and the cost of treating process wastewaters would be eliminated. However, under current Resource Conservation and Recovery Act (RCRA) policy, this practice is not permitted. The major concern is that the two separate waste problems might combine to create a more serious problem. Until there is evidence that co-disposal is acceptable, this option cannot be practiced.

Aqueous solutions in most natural systems contain mixtures of many organic and inorganic agents. In a landfill where co-disposal is employed, shale will come into contact with many solutes; some produced by the leaching of constituents from the shale itself and others introduced by the process waters. Hazardous substances may be adsorbed and/or precipitated, thereby reducing the level of concern for potential contamination of surface waters or aquifers.

On the other hand, mixtures of solutes may create adverse conditions for adsorption and possibly cause the release of additional ions from the shale or interact with one another to produce even more hazardous substances.

This leads us to the reasons for this investigation. The batch experiments utilized in this study may be useful for assessing conditions in a situation where spent shale is contained in a landfill with rain, groundwater, and/or process water. The results of column elution experiments might be used to predict how materials associated with shale in an in situ retort or landfill might behave as rain, groundwater, and/or process pass through the body of shale. The continuous-flow columns will also provide for evaluation of the sorption capacity of particular shales for inorganics of interest.

The objectives of this study were to:

1. Determine the background levels of soluble, leachable inorganics substances, such as arsenic, calcium, cadmium, fluoride, iron, potassium, carbonate, and bicarbonate present in spent and raw shale, and the time required for an equilibrium state to be reached between the shale and distilled water;
2. Assess the ability of various shales to act as an adsorbent for various inorganic ions;

3. Compare batch and column experimental procedures for the assessment of adsorption capacity and extent of elution.

Chapter II

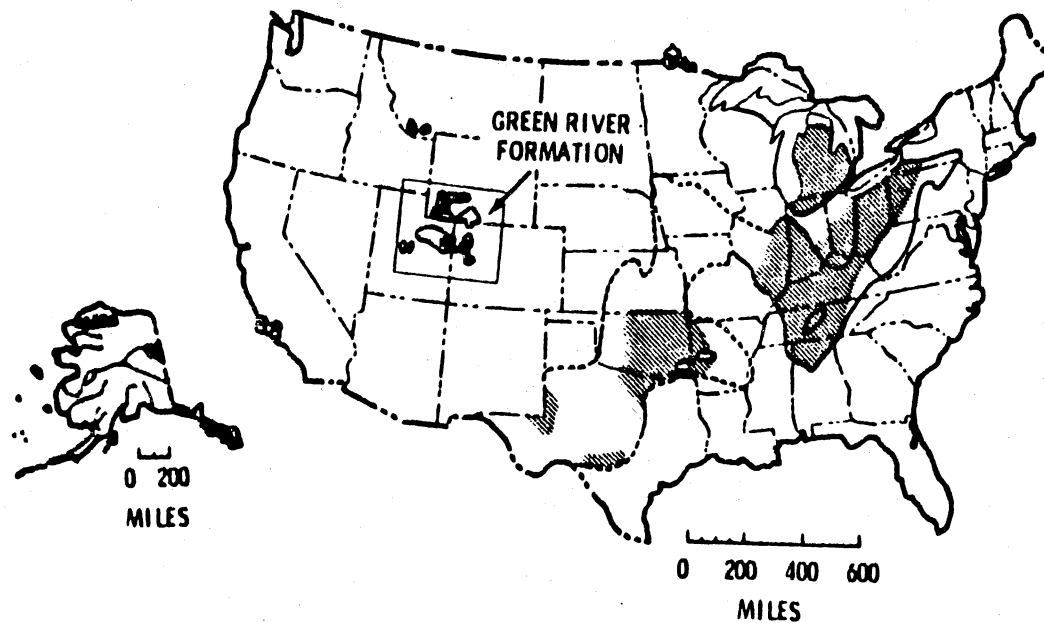
LITERATURE REVIEW

FORMATION OF OIL SHALE

Oil shales originated from sediments containing debris from living organisms that were deposited in stagnant or stratified bodies of water during the Tertiary Age. As deposition continued, sediments were isolated from the atmosphere and the water basin was filled in with organic materials. After millions of years, the organic matter was converted to kerogen.

Two-thirds of the oil shale deposits of the world are in the United States as shown in Figure 1 (2,3). Most of these are in the Green River formation of Colorado, Utah and Wyoming (Figure 2) (4). There is an estimated 600 billion barrels of potential oil here in deposits at least three meters thick (5). With an average of 0.6 barrel per ton of shale, it is estimated that there are over 80 billion barrels of recoverable shale oil in this formation (5).

Oil shales are also known as marlstones and consist not only of kerogen, but also dolomite, feldspars, quartz, illite and smaller amounts of albitite, calcite and pyrite. The organic fraction of the shale is only 14 per cent, while the inorganic fraction comprises 86 per cent. Table 1







- | | |
|--|---|
| <p> TERTIARY DEPOSITS
 GREEN RIVER FORMATION IN
 COLORADO, UTAH, AND WYOMING;
 MONTEREY FORMATION, CALIFORNIA;
 MIDDLE TERTIARY DEPOSITS IN
 MONTANA. BLACK AREAS ARE
 KNOWN HIGH-GRADE DEPOSITS.</p> <p> MESOZOIC DEPOSITS
 MARINE SHALE IN ALASKA</p> | <p> PERMIAN DEPOSITS
 PHOSPHORIA FORMATION,
 MONTANA</p> <p> DEVONIAN AND MISSISSIPPIAN
 DEPOSITS (RESOURCE ESTIMATES
 INCLUDED FOR HACHURED AREAS
 ONLY). BOUNDARY DASHED
 WHERE CONCEALED OR WHERE
 LOCATION IS UNCERTAIN.</p> |
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Figure 1. Oil shale deposits of the United States (3).

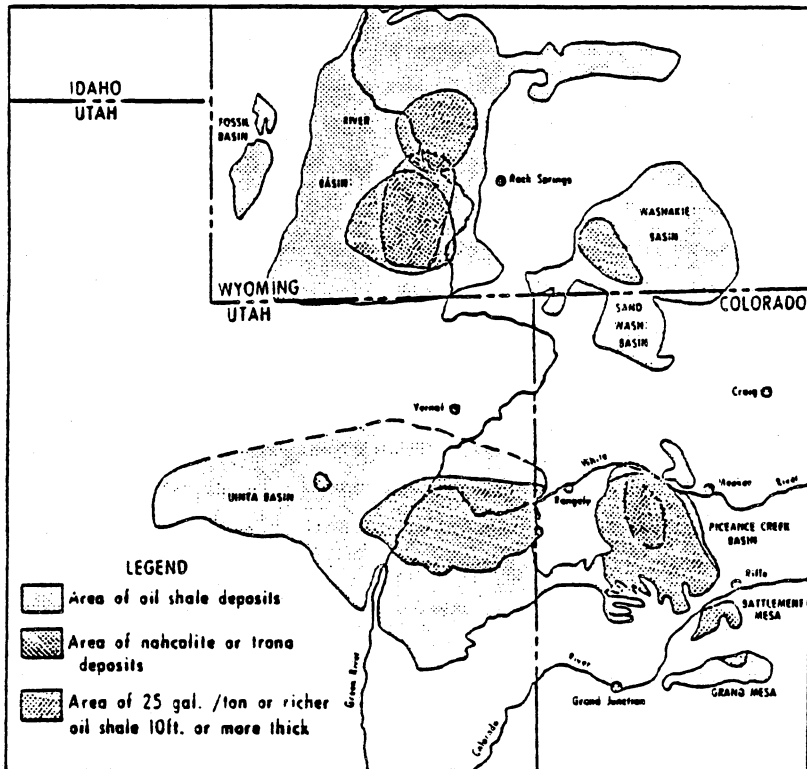


Figure 2. Oil shale areas of Utah, Colorado, and Wyoming (4).

presents the elemental composition of the organic fraction of oil shale which is 90 per cent kerogen and 10 per cent bitumen (6). Kerogen is a heteroatomic polymer of molecular weight greater than 3,000. It is insoluble in most organic solvents and has a 3-dimensional structure with subunits linked with sulfur and oxygen. Kerogen is thermally unstable at temperatures of 250°C and greater (6). Shale that contains 30 per cent by volume organic matter yields 25 gallons of oil per ton of shale (7).

A summary of the major elements found in raw shale are presented in Table 2 (8). Raw shale contains trace elements that may be of environmental concern. Knowledge of the concentrations and form of these elements is important, for during retorting, such elements can be partitioned into various phases; gases, particulates, wastewaters, or solid waste (9).

PROCESSING OF OIL SHALE

Processing of oil shales is known as retorting, a method by which the kerogen-containing, crushed shale is heated to temperatures ranging from 400 to 1200°C with the subsequent release of vapors and gases which cool and are collected as syncrude.

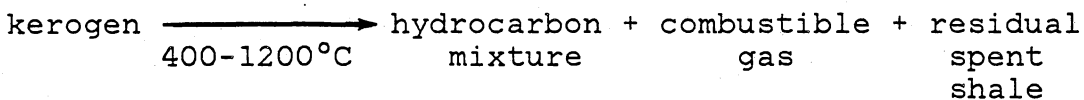


TABLE 1

ELEMENTAL COMPOSITION OF ORGANIC FRACTION IN OIL SHALES¹ (6)

carbon	81
hydrogen	10
oxygen	6
nitrogen	2
sulfur	1

1. All values in per cent

TABLE 2
 MAJOR MINERALS IN OIL SHALE (8)

Dominant

Quartz	SiO_2
Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Calcite	CaCO_3
Albite	$\text{NaAlSi}_3\text{O}_8$

Locally Abundant

K-Feldspar	KAlSi_3O_8
Dawsonite	$\text{NaAl}(\text{OH})_2\text{CO}_3$
Analcime	$\text{NaAlSi}_2\text{O}_6\text{H}_2\text{O}$
Nahcolite	NaHCO_3
Illite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
Pyrite	FeS_2
Siderite	FeCO_3

The hydrocarbon mixture is an impure synthetic crude oil that can be treated and refined like petroleum into various products. Approximately 90 per cent of the organic matter leaves as oil vapor, noncondensable gases and water. Ten per cent of the carbon acts as fuel for energy production in combustion (7).

Retorting Methods

There are basically three retort methods for processing oil shales: 1) surface retorting of mined shale; 2) underground or in situ retorting without mining; and, 3) modified in situ (MIS) retorting in which part of the shale is first removed by mining. The surface retorting processes can be further subdivided into the following methods (10).

1. Direct Retorting: uses combustion of part of the carbonaceous material in the shale as a heat source.
2. Indirect Retorting: uses an external heat source such as heat carrier solids.

In situ methods involve heating of the shale while it is still underground. The shale must be fragmented first by blasting, but large pillars are left in place for support of the overburden. In situ methods can be vertical, in which the combustion front (heating zone) travels downward through the shale bed along with vapors and gases and the converted

kerogen (2). The horizontal method is simply a horizontal movement of the combustion zone and is best used for thin beds of shale.

Modified in situ processes entail the removal of from 15 to 25 per cent of the shale to create a void space for in situ retorting. This percentage of shale is retorted on the surface while the rest is left under ground to be retorted in situ.

WASTE GENERATION

Retorting of oil shale produces several waste types that must be dealt with through treatment processes or proper disposal. If the oil shale industry is to be developed on a large scale, it is necessary to investigate waste generation with regard to volume, treatment options and the degree of hazard these wastes may impose on the environment.

Spent Shale.

The most significant waste with respect to volume is the retorted (spent) shale. It is estimated that a 500,000 barrel/day plant may produce one million tons of spent shale per day (1).

The high temperatures encountered during retorting greatly alter the chemical and physical characteristics of the shale. The oxygen concentration and particle size of the raw shale are also important parameters which have a major effect on the properties of the spent shale (10). As will be seen from the results of this study, different technologies of retorting shale have a great impact on the final properties of the spent shale. These properties are the result of such retorting parameters as particle size of the feed shale, carbon and mineral content of the feed, retorting rate, composition of the recycle gas and the temperature utilized in retorting.

During surface retorting of shale, the mass of the shale will decrease 12 to 15 per cent, however, the volume may increase up to 30 per cent of the original volume due to mining, crushing and heating (11). The surface disposal of this shale is obviously a problem of great magnitude.

Modified in situ retorting leaves most of the shale in place and only a small percentage must be disposed of on the surface. This fact enhances the desirability of this type of shale processing. However, retort abandonment may cause many environmental problems such as aquifer disruption, leaching of the shale by groundwater and rainwater, surface subsidence and contamination of surface waters (12). The

many problems of spent shale disposal and possible technologies and solutions have been discussed in detail (6,10,11 - 13).

Retort Wastewater.

There are several different types of wastewaters that can be generated during oil shale processing. Surface retorting produces far less wastewater than does in situ retorting. In situ

processing of shale may produce water in many ways (14):

1. Water produced as a byproduct of combustion of organic matter.
2. Water produced by dehydration of oil shale minerals.
3. Native groundwater.
4. Water that forms due to the introduction of steam into the formation.

Retort water is the initial aqueous effluent that is recovered with the oil and is generally the most heavily polluted waste stream. Table 3 lists the concentrations of conventional pollutants in surface and in situ retort waters (15).

Retort waters contain a high concentration of organic matter which is indicated in the BOD and COD values. However, from 10 to 30 per cent of the BOD and COD is due to

TABLE 3
RETORT WATER QUALITY (15)

Constituents	Utah <u>in situ</u> ¹	Simulated <u>in situ</u> ²	Surface Retort
TOC, mg/l	2,000	2,000	42,000
BOD, mg/l	3,000	3,000	40,000
COD, mg/l	8,000	8,000	153,000
Conductivity, μ hos/cm	17,000	>20,000	>20,000
Suspended Solids, 103°C	1,400	120	-
Total Alkalinity, mg/l as CaCO ₃	19,000	80,500	-

1. Shale retorted underground
2. Simulated underground retorting in experimental retorts on the surface

the presence of thiosulfate (15). The suspended solids in these waste streams is difficult to remove by sedimentation. Treatment of retort waters is also complicated by high ammonia levels and toxic elements that must be removed before biological treatment. Table 4 lists some major problems encountered in treatment of retort waters (15).

Other Wastes Produced

Offgases are released into the atmosphere from above ground retorts and air pollution control equipment such as scrubbers produce sludge that must be disposed of properly. These gases, NH_3 , NO_x , SO_x , F, As and Hg, if released in high concentrations could, contribute significantly to air pollution problems (2,6). Deposition of these toxic elements on soil and in water can create lethal conditions for soil and aquatic organisms.

Crude shale oil may be refined to some extent on or near the retort site before being set to final refining. Prerefinery wastewaters from shale oil are similiar to those produced in petroleum refineries. TOSCO II prerefining processes produced the following wastes: spent, heavy-metal catalysts (Zn, Co, Mo, Fe, Cr, Cu), diatomaceous earth, caustic wash solutions, coke, deactivated carbon and extracted arsenic (6).

TABLE 4

Problems Related to Treatment of Retort Waters (15)

-
1. Stable suspension of organic matter which resists chemical coagulation and may interfere with subsequent treatment processes.
 2. High ammonia concentrations which must be reduced to permit biological treatment and meet discharge or reuse standards.
 3. High BOD concentrations which may require costly biological treatment processes for removal.
 4. High levels of refractory organics which may require costly adsorption processes for removal.
 5. High salinity which limits reuse and requires costly desalination processes if the water is to be discharged to surface streams or used for agricultural purposes.
 6. Presence of toxicants, such as arsenic, which may interfere with biological treatment and produce hazardous sludges, requiring expensive disposal methods.
-

SPENT SHALE CHARACTERISTICS

As mentioned earlier, the retorting process greatly alters the chemical and physical characteristics of the shale. Decomposition and dehydration of minerals are the major reactions that occur when temperatures begin to reach 500°C (16). The extent of these reactions is dependent upon the retorting temperature, gas atmosphere, heating rate and duration, the mineral composition of the raw shale and other parameters.

In situ retorted shales undergo more extreme conditions than do surface retorted shales because there is less heat lost to the surroundings. Surface retorts generally reach temperatures around 700°C while in situ retorts can experience extremes of 1200°C (17).

Kerogen conversion occurs at approximately 400°C, after which carbonate decomposition begins at temperatures above 500°C. This reaction results in the formation of metallic oxides which are hydrated to form strongly alkaline hydroxides (16). At this temperature, dawsonite, nahcolite, and shortite decompose to yield sodium carbonate, carbon dioxide and water.

Slightly higher temperatures, 650 to 750°C, cause the decomposition of calcite and dolomite and the subsequent formation of periclase (MgO) and lime (CaO) at approximately

800°C (18). Kuo et al. (19) reported that periclase and lime are consumed almost immediately resulting in the formation of insoluble mineral forms. It is suspected that the lime reacts with quartz and periclase to form insoluble silicates such as akermanite and diopside.

When retort temperatures reach 1000°C and greater, thermally induced solid-state reactions take place, forming minerals that have been identified previously as products of contact metamorphous (20). Smith et al. (17) found that samples began to sinter at 1000°C and fuse at 1200°C. At these high temperatures, minerals have increased mobility and interact with each other to form igneous and/or metamorphic minerals. Sintering increases the compressive strength of the spent shale subsequently reducing the possibility of subsidence.

The environmental significance of high temperature reactions is that the products are insoluble, chemically inert and when leached with water, exhibit a slightly basic pH and little buffering capacity (17). Kuo et al. (19) found that the leaching of shales formed under these temperatures was similar to that of raw shale. Extreme temperatures occurring for a long duration period are necessary for these reactions to occur, such as in MIS retorting.

Investigations have discussed in detail the high temperature reactions that occur in MIS retorting and minimize the undesirable aspects of spent shale leaching, such as increased inorganic concentrations and elevated pH (17 - 19). Kuo et al. (19) suggested that temperatures low enough to avoid decomposition of carbonate mineral or high enough to cause silication be used to reduce the leaching problems of spent shale. Parker et al. (16) found that a higher degree of leached materials occurs in shales retorted at 600 to 800°C.

Authors have also found that the introduction of steam into in situ retorts enhances the decomposition of dolomite and calcite and their subsequent silication (18,19). The use of a carbon dioxide atmosphere inhibited these reactions. Peterson and Wagner (18) pointed out that postburn activities such as injection of recycle gas and cooling water can have an effect on the spent shale characteristics.

Although high temperature retorting definitely presents many advantages, Peterson and Wagner (18) have indicated the possibility of an increased mobility of trace elements under these conditions that pose environmental hazards if released into the environment. The mobility of these elements are affected by:

1. decomposition reactions
2. reactions of original minerals
3. ability of newly formed minerals to incorporate these elements in their structures
4. oxidation/reduction nature of the atmosphere in the retort
5. solution chemistry

Peterson and Wagner's (18) study indicated that arsenic, boron, fluoride, molybdenum and vanadium are mobilized from spent shales containing akermanite-gehlenite as the major silicate phase. These elements seem to be less mobile in the diopside silicate phase. They suggested that either weathering of the akermanite or the retorting conditions leading to its formation were responsible for the increased mobility. It is possible that diopside is capable of accommodating the elements in its crystal structure (20). However, it is not certain that these explanations are the true cause of the observed behavior; it may be the result of changes in the raw shale constituents.

SHALE LEACHATES

There has been extensive investigation into the quality of leachates derived from spent and raw shales (8,11,12,16 - 19,21 - 27). Some have used field lysimeters to study MIS leachates (24,25). Others have leached simulated in situ spent shale; shale that was processed in experimental retorts which simulate in situ conditions (18,19,27). Most of the work has been done in batch and column leaching experiments in the laboratory (8,16,21,22). A few have examined the effects of leachates on soils (26,28). Tables 5 and 6 summarize some of the batch and column experiments performed to assess the effect of shale materials on leachate quality.

Fox (29) provided an excellent summary of the literature concerning the water quality of leachates from in situ shale retorts and surface disposal piles. Many aspects are covered such as the mechanics of leaching, leachate transport and leaching of organics and inorganics.

Leachate quality is of tremendous importance due to the large volumes of spent shale that will be disposed of underground and in landfills or surface disposal piles. Forces such as erosion, runoff and percolation of rainwater through spent shale may cause severe contamination of ground and surface waters (11). It has been estimated that exposed

retorted shale in the Piceance Basin could contribute 70 kilograms (kg) of salt and seven metric tons/hectar of suspended material to surface waters each year (34).

Fox (29) concluded that contamination of groundwater would take possibly centuries due to the low flow velocities in aquifers but also pointed out that potential long term effects to the salinity of the Colorado River system and ground water aquifers are serious issues that must be investigated.

Spent shale contains in addition to soluble salts and trace elements, potentially toxic or carcinogenic organic substances that may be released in leachates. Amy and Thomas (30) concluded that there exists a high potential for contamination of groundwaters by organic materials leached from in situ shale. They found that high levels of organic carbon were leached from spent shale that had been produced by inert gas trials and combustion trials using recycle gas as part of the input gas.

TABLE 5

SUMMARY OF SOME BATCH EXPERIMENTS WITH SHALE MATERIALS

Reference	L:S ¹	Leaching Medium	Solid	(Wt.)	Agitation	Time
Amy and Thomas (30)	1:1	DI ²	Spent Shale	50 g	none	1 to 10 days
Amy et al. (27)	4:1 to 1:1.7	Grd. H ₂ O DI	Spent Shale	50 g	none	30 days
Denver ³ Research Institute (23)	20:1	Acetate acid solution	Spent Shale	100 g	shaker	24 hours
Esmali and Runnells (31)	2.5:1	leachate	Weathered bedrock	20 g	wrist-action shaker	24 hours
Fox and Jackson (1)	1:1	Process water	Spent Shale	50 g	shaker	5 days
Fransway and Wagnet (24)	1:1	DI	Spent Shale	50 g + 1 g	mix twice	24 hours

TABLE 5 (cont.)

SUMMARY OF SOME BATCH EXPERIMENTS WITH SHALE MATERIALS

References	L:S ¹	Leaching Medium	Solid	(Wt.)	Agitation	Time
Jackson and Jackson (32)	4:1 ⁴ 20:1 ³	DI Process water Acetate acid solution	Spent Shale	350 g 100 g	shaker	24 hours
Kuo <i>et al.</i> (19)	7:1 to 75:1	DI	Spent Shale	n.r. ⁵	stir	Until no further changes
Parker <i>et al.</i> (16)	n.a. ⁶	Grd. water	Slab of Spent Shale	n.a.	stir	30 days
Peterson and Wagner (18)	5:1	DI	Raw and Spent Shale	n.r.	none	2 days
Stollenwerk and Runnells (33)	2.5:1	DI	Raw and Spent Shale	10 g	shaker	127 days

1. liquid:solid
2. distilled water

3. EPA Extraction Procedure Test
4. ASTM Method D3987

5. not reported
6. not applicable

TABLE 6

SUMMARY OF SELECT COLUMN-LEACHING EXPERIMENTS WITH SHALE MATERIALS

Reference	Column Dimensions	Solid	(Wt.)	Leaching Medium	Flow Direction	Flow Rate	Leaching Pd. (Vol. or time)
Amy and Thomas (30)	n.r. ¹ glass	spent shale	50 g	DI ²	recirculated	1 ml/min, 3 ml/min	10 days
Batelle-Pacific Laboratory (22)	0.7 x 15 (cm) glass	spent shale	4 g to 7.7 g	DI	down	intermittent	1.1 column volumes
Esmali and Runnells (31)	n.r. plastic	weathered bedrock	n.r.	DI leachate	down	constant head	2.4 pore volumes
Fox and Jackson (1)	1" diameter glass	spent shale	250 g	process water	upflow	5 ml/min	160 ml
Glaze and Runnells (26)	5.5 x 1 (cm) plastic	soil	n.r.	leachate	down	constant 0-2 cm head	70 pore vol; 1 pore vol per 5 days
Kuo <i>et al.</i> (19)	7.5 cm x 1.2 m glass	spent shale	n.r.	DI	down	constant head; intermittent	50 pore volumes

TABLE 6 (cont.)

SUMMARY OF SELECT COLUMN-LEACHING EXPERIMENTS WITH SHALE MATERIALS

Reference	Column Dimensions	Solid	(Wt.)	Leaching Medium	Flow Direction	Flow Rate	Leaching Pd. (Vol. or time)
Leenhardt and Stuber (28)	10 x 120 (cm) glass	soil	n.r.	DI, simulated and actual process water	down	constant head	44 liters
Ramirez <u>et al.</u> (21)	1.0 x 36 (in) plexiglass	raw and spent shale	n.r.	DI tracer solution	upflow	4.71 to 21.10 ml/hr	up to 853 in.
Stollenwerk and Runnells (33)	2.8 x 30 (cm) glass	raw and spent shale	200 g	DI	down	constant 0-2 cm head	18 pore volumes
Stollenwerk and Runnells (8)	2.8 x 30 (cm) glass	raw and spent shale	200 g	DI	down	Equilibrated, then leached; intermittent flow	12 pore volumes
University of Colorado (22)	1.5 x 15 (cm) glass	spent shale	n.r.	DI	upflow	n.r.	5 column volumes

1. not reported

2. distilled water

As discussed in the previous section, retorting parameters have a great impact on the quality of leachates. Lower temperature retorts (600-800°C) produce a spent shale that contains many soluble minerals which contribute to high TDS and pH values in leachates (16 - 19). Table 7 lists the concentrations of various elements found in the leachate of raw and spent shales (18). These data illustrates the difference between trace elements released from spent shale consisting of mostly akermanite or diopside. Recall that in the previous section of this chapter, Peterson and Wagner (18) suggested that spent shale containing mostly akermanite is more likely to leach potentially harmful trace elements. According to them, some of the factors that affect leachate quality are:

1. extent of occurrence of minerals in shale
2. amount of each element available in the shale
3. forces that control desorption from the solid to liquid phase
4. reactions that take place in the bulk solution as the leachate moves towards equilibrium

Table 8 lists the concentrations of various elements found in leachates of high and low temperature retorted shales that had undergone batch leaching with ground water (16).

TABLE 7

Differences in Raw and MIS Spent Shale Leachates from Column Leaching with Distilled Water¹ (18)

	raw shale leachate	spent shale ² (akermanite)	spent shale ³ (diopside)
pH	9.5	10.3	9.8
Cond. ⁴	740	1120	995
As	0.6	0.026	0.016
B	10.7	6.55	1.19
Ca	2.06	4.51	46.1
F	6.0	12.0	5.4
Mo	1.1	0.814	0.64
V	0.5	1.90	0.23

1. mg/l except where indicated
2. spent shale containing mostly akermanite (7776' elevation)
3. spent shale containing mostly diopside (7750' elevation)
4. conductivity in micromhos/cm

TABLE 8

Material Extracted from Spent Shale After 240 Hours of Batch Leaching with Rock Springs Ground Water (16)

Element	Ground Water	Low Temp. ¹	High Temp. ²
Ca	6.3	0.21	9.75
Cu	Trace	0.21	0.38
CO ₃	3300	3100	1213
Fe	0.77	0.60	0.44
K	38.5	39.8	59.0
Li	0.19	0.32	1.62
Mg	11.8	12.0	3.0
Na	5065	4340	4225
pH	9.3	9.4	9.9
Zn	0.19	0.08	0.07

1. Spent shale from a low temperature retort process
2. Spent shale from a high temperature retort process

In a summary of preliminary leaching results from Occidental Retort 3E, a modified in situ retort, three different laboratories investigated leachate quality of this spent shale through batch and column leaching experiments (22). Column leaching results from the Univ. of Colorado indicated that most of the dissolved salts were rinsed out of the column of shale after two pore volumes of distilled water had passed through. Table 9 presents the pH and conductivity values measured in the first five pore volumes of leachate. The rapid rinseout reflected in the conductivity values is most likely due to higher temperature silicates in the MIS retorted shale.

Batelle-Pacific NW laboratory (22) used a slightly different column leaching procedure, but, their results paralleled the Univ. of Colorado's with respect to the rapid rinseout of soluble inorganics (Figure 3). In a column leaching study conducted by Utah State Univ., the concentration of most parameters measured were reduced to less than 10 per cent of the original values after 0.1 to 1 pore volumes of water been leached (23).

This rapid flushing behavior of soluble shale constituents from retorted shale is a very attractive characteristic when considering safe environmental disposal of shale. For example, Thode et al. (35) designed a

TABLE 9

Variation of Conductivity and pH with Number of Pore Volumes of Leachate from each Column (22)

Core number	Depth (ft)	pH				
		Pore Volume Number				
		1	2	3	4	5
1	442-445	8.6	9.8	9.9	9.7	9.5
3 + 4	457-463	7.8	8.3	-	8.5	-
14 + 15	483-484.5	8.8	8.5	8.6	9.0	9.4
17 + 18	500-515	9.0	8.8	-	9.2	-
		Conductivity (micromhos/cm)				
		Pore Volume Number				
		1	2	3	4	5
1	442-445	3340	1090	460	440	410
3 + 4	457-463	6100	830	490	430	-
14 + 15	483-484.5	9940	3190	2310	1010	320
17 + 18	500-515	12170	3580	730	640	-

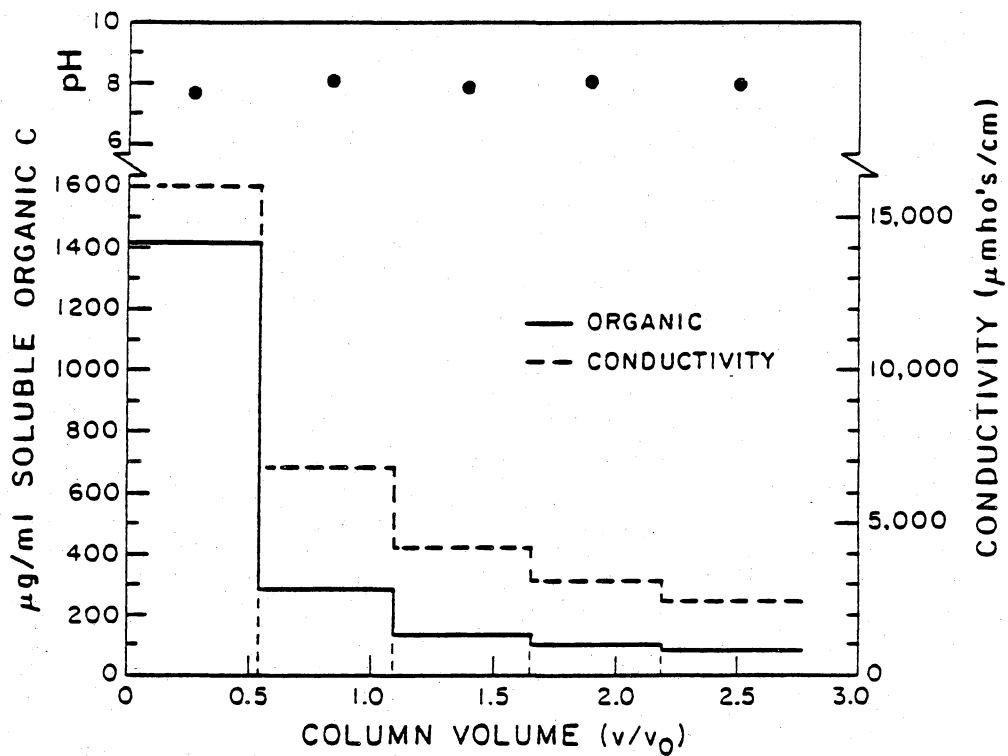


Figure 3. Elution profile of organic carbon, salts, and pH from Occidental Retort (22).

multistage leaching of a MIS retort which would force leach a retort, with fresh water carrying away most of the soluble materials, particularly trace elements, to a surface treatment or disposal facility. This process would leave behind a retort which would be considered much "safer" environmentally with regard to possible aquifer contamination.

POTENTIAL USES FOR SPENT SHALE

It is evident from the previous discussions that the proper disposal of spent shale is an issue of tremendous importance. There has been some investigation into alternatives for the potential use of shale as a treatment process itself.

Spent Shale as an Adsorbent for Treating Process Water

It has been suggested that spent shale be utilized as an adsorbent in a retort water treatment system. Fox and Jackson (1) have investigated two applications of spent shale; one in which process water from a retort is piped to an adjacent retort and circulated through it, resulting in a reduction of contaminants in the retort water. However, this proposal contradicts studies which investigated means of reducing pollutants in MIS retorts (35). Their second

suggestion involves the use of spent shale as an adsorbent in packed columns, as activated carbon is used in wastewater treatment systems (1). After a series of batch and column experiments, they found that spent shales from different retorting process had varying degrees of adsorptive capacity. The batch experiments indicated that some spent shales are effective in removing 99 per cent of dissolved inorganic carbon (DIC) from the retort water. Shales which exhibited effective organic removal had the poorest DIC removal.

Column results from Fox and Jackson's (1) investigation indicated that spent shale is not a satisfactory method for removal of gross levels of organic carbon, however, they found that treatment with shale reduced the odor and color of the process waters very effectively. This is most likely because the organic compounds that contributed to the problem were removed.

Co-disposal of Spent Shale with Process Waters

Jackson and Jackson (32) discussed the advantages and disadvantages of co-disposal of process waters and spent shale. Process water could be used to moisten shale before disposal (to eliminate dust), reducing the amount of makeup water required for processing and disposing of the shale.

The most obvious advantage of co-disposal is that it eliminates the cost involved in the treatment of retort waters. However, as mentioned earlier in this chapter, process waters contain significant concentrations of organics and inorganics that have a definite potential for creating problems with this disposal method. The mixing of retort waters with spent shale may cause previously immobile elements in the spent shale to mobilize, increasing the hazards presented by the leaching of this waste into the environment (32).

The results of the former study indicated that the wetting of spent shale with process water did not contribute to release of sulfate, chloride, total organic carbon and ammonia nitrogen in leachates as compared to the levels released after wetting with distilled water. The retorting process and hence the physical and chemical characteristics of the spent shale appear to control the concentrations of contaminants in the leachate.

COMPARISON OF BATCH AND COLUMN LEACHING METHODS

One of the goals of this research was to compare the advantages and disadvantages of batch and column leaching experiments in the interests of developing a method that would act as a standard, rapid and reproducible evaluation

procedure for a particular solid waste. Leaching experiments are generally used to classify a solid waste and/or to assess the potential hazards associated with leachate quality.

Solid waste leaching studies (or extraction experiments) are useful for evaluating the compatibility of different waste types that may be disposed of together, for assessing the degree of leachate control needed at a site and for predicting the aggressiveness of the leachate generated in a landfill (36). Characteristics which determine the aggressiveness of a leachate are: pH, buffering capacity, redox potential, complexation capacity and ionic strength (37). While producing a synthetic municipal leachate, Stanford et al. (38) defined the aggressiveness of a leachate as its ability to extract chemical constituents from a solid waste.

Cote and Constable (37) advised that when conducting an experiment for classification of a solid waste, a standard methodology should be used to allow for comparison and reproducibility among different laboratories. However, when designing an experiment to predict leachate quality that is generated under field conditions, it is best to simulate the site conditions as closely as possible.

Batch experiments have several advantages not found in column experiments. They generally require a shorter time period than column leaching and are more reproducible and less trouble to set up. However, they are not as representative of field conditions as are column studies. Column leaching experiments are difficult to reproduce because of problems such as channelling, non-uniform packing, clogging and in extended leaching trials, biological growth (37). Tables 10 and 11 present some of the details of various leaching studies performed on different types of solid wastes. Tables 5 and 6 also display the results of batch and column experiments for evaluation of solid shale materials.

TABLE 10

BATCH EXPERIMENTS PERFORMED FOR THE EVALUATION OF SOLID WASTES

References	L:S ¹	Leaching Medium	Solid	(Wt.)	Agitation	Time
Boyle <u>et al.</u> (38)	2:1 ¹	Acetic acid soln., DI ³	Solid Foundry Wastes	100 g	Shaker	24 hours
Cote and Constable (36)	20:1 10:1 4:1	Acetic acid soln., synthetic leachate, DI	Industrial sludges	n.r. ⁴	Nine different Methods	0 to 48 hours
Cote and Constable (39)	20:1 4:1	Acetic acid soln., synthetic leachate, DI	Bottom and fly ashes, mine tailings	n.r.	Rotating tumbler	24 hours
Glordano <u>et al.</u> (40)	16:1	Acetic acid soln.	Fly ash residue	10 g	Horizontal shaker	24 hours
Harris and Silberman (41)	100:1	Chelating soln. in Tris buffer	Coal, fly ash	1 g	Shaker 1 hour filter, add new soln., continue procedure	7 days

TABLE 10 (cont.)

BATCH EXPERIMENTS PERFORMED FOR THE EVALUATION OF SOLID WASTES

Reference	L:S ¹	Leaching Medium	Solid	(Wt.)	Agitation	Time
Jackson et al. (35)	10:1	DI	Fly ash, Organic and Inorganic sludges	100 g	Tumbled on rotary extractor	4 sequential extractions of 18 hrs each
Maskacinec and Brown (42)	20:1 ²	DI, citrate buffer, acetic acid soln. DI with resin	Municipal, paper mill and industrial sludges	100 g	Rotary extractor stirring	24 hours
Saunders <u>et al.</u> (43)	20:1 ²	Acetic acid soln.	Metal- finishing sludge	100 g	Shaker	24 hours

1. Liquid:Solid

2. EPA Extraction Procedure

3. Distilled water

4. Not reported

TABLE 11

COLUMN STUDIES PERFORMED FOR THE EVALUATION OF SOLID WASTE

Reference	Column Dimensions	Solid	(Wt.)	Leaching Medium	Flow Direction	Flow Rate	Leaching Pd. (volume or time)
Darcel (44)	3.5 cm diam. plexiglass	baghouse dust, mine tailings, inorganic sludges	100 g	DI ¹ acetate acid solution	down	12.5 ml/m	72 hours
Dudas (45)	6.9 cm diam. plastic	fly ash	250 g	DI	down	governed by hydraulic conductivity	2 years
Glordano <i>et al.</i> (40)	15 x 60 cm plastic	fly ash, soil	400 g	DI	down	intermittent	2 weeks
Jackson <i>et al.</i> (35)	5 x 60 cm glass	fly ash, inorganic and organic sludges	100 g	DI	down	0.93 mg/min.	four 1 L fractions per 48 hrs
Maskarinec and Brown (42)	2.5 x 45 cm glass	municipal paper mill and industrial sludges	100 g	DI	upflow	n.r. ²	2 liters
Stevens <i>et al.</i> (46)	15 x 150 cm	pesticide contaminated wastes	fill column	DI	down	2.5 mm/day	28 months

1. distilled water

2. not reported

Jackson et al. (36) designed a study to compare batch and column leaching methods with respect to concentrations of constituents in the leachate and experimental variation. The column experiments were designed to reduce leaching time by use of an increased flow rate. Sand was added to the waste to reduce the chance of clogging and channelling. These adjustments were made to increase the desirability of using column methods, which better simulate real leaching conditions.

Leaching profiles from the batch and column results were significantly different from 12 to 16 of the elements analyzed. These differences were attributed to the degree of air exposure and the amount of agitation during the batch experiment. Jackson et al. (36) also found that the batch results were less variable, enhancing the prospects for its development into a standard leaching procedure for classification of hazardous wastes.

Important Considerations for Batch Experiments

Cote and Constable (37) conducted a study which evaluated several different parameter options available when setting up a batch leaching experiment. They discussed the following five conditions that should be carefully considered while designing a batch study.

1. Agitation: It is important to consider the degree of contact between the leaching medium and the solid waste. Ideally the particles should be in complete contact with the leachate. The agitation should be sufficient to prevent stratification without deterioration of the physical structure of the solid.
2. Leaching Medium: The leaching medium chosen for the batch tests should simulate conditions that are likely to occur with disposal of the solid waste. For example, a solid waste that is landfilled by itself will encounter mostly rainwater that has percolated through the soil. The bottom layers will in turn come into contact with leachate generated by the waste above. The leaching media used in batch experiments should simulate these leachates. It can be seen, however, that in some cases, such as co-disposal with many waste types, that it would be difficult to produce a synthetic leachate that will represent all conditions encountered in the actual waste pile.
3. Liquid-to-Solid Ratio: A suitable liquid-to-solid ratio for the container to be agitated should provide enough sample for analysis and concentrations that are above detection limits. Before comparing results

between labs, caution should be taken when interpreting the liquid-to-solid ratio because the liquid portion may be considered part of the waste, part of the leaching media, or independent of both. The manner in which the ratio is interpreted can have a significant effect on the results of the study, such as in the case where the waste contains a large percentage of liquid (a municipal sludge).

4. Length of Leaching Period: After a review of the literature, Cote and Constable (37) admit that not one leaching period is the most favorable for all solid wastes; however, they do feel that it is not necessary to continue leaching for days. In most cases 24 hours or less is sufficient for contaminants to reach equilibrium.
5. Particle Size: The surface area of particles in a waste may influence the kinetics of release, but should not affect equilibrium concentration. Permeability, agitation and time of leaching will determine how significant this effect may be. Generally, there are two ways to approach particle size choice. One is to reduce it to a particular size that will enhance reproducibility or to simulate the size found in field conditions.

Established Batch Extraction Procedures

The EPA Extraction Procedure Toxicity Test was developed to define the concentration levels of toxic contaminants in a potentially hazardous waste. A solid waste is hazardous if it has any of the characteristics of ignitability, corrosivity, reactivity and EP toxicity as defined by the EPA (48). The EP toxicity test procedure is a batch experiment which employs strict pH control (5.0 ± 0.2 units) with 0.5 N acetic acid. The solid waste is placed in a container with 16 times its weight of distilled water and agitated for 24 hours with monitoring and adjustment of the pH during this time. The extract is prepared for analysis of the contaminants seen in Table 12 which also lists the maximum allowable concentration limits.

Cote and Constable (40) developed a batch leaching procedure which they call the Wastewater Technology Center Leaching Test (WTC). This method was designed to bridge the gap between standard leach test and field conditions. Three leaching mediums were employed; distilled water, acetic acid solution and a synthetic municipal leachate.

The results of this study indicated that the concentration of the contaminants in the leachate were largely affected by the final pH of the leachate. The synthetic leachate seemed to enhance the release of

TABLE 12

Maximum Concentration of Contaminates for Characteristic EP Toxicity (48)

EPA Hazardous Waste Number	Contaminant	Maximum Concentration (mg/l)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin	0.02
D013	Lindane	0.4
D014	Methoxychlor	10.0
D015	Toxaphene	0.5
D016	2,4-D	10.0
D017	2,4,5-TP Silvex	1.0

constituents on a greater scale than the acetic acid leaching medium. It was also concluded that an acidic extraction solution causes the final pH to be a function of the pH of the waste and the amount of acid available to react with it. These are important considerations when assessing the hazards of disposing of an acidic waste in landfill.

Jackson and Jackson (32) used two standard methods to leach spent shales that had been pre-moistened with process water or distilled water, the ASTM Method D3987 (49) and the EP Toxicity Test (48). The purpose of their study was to compare the differences in the concentrations of constituents released during leaching of shale that had been moistened with process water (co-disposal) as opposed to moistening with distilled water, the ideal case. It was felt that for the purposes of the investigation, the EP test did not allow for evaluation of the effects of co-disposal with process water upon leachate quality. However, the ASTM test which specifies the use of distilled water, provided a useful means of investigating leachate quality.

DESIGN FACTORS TO CONSIDER FOR BATCH AND COLUMN EXPERIMENTS

The experimental design of batch and continuous-flow, sorption/desorption studies can vary widely. However, there are several variables which are important to consider in each situation. Included among these variables are: porosity, liquid-to-solid ratio, flow rate, contact time, solid density, bulk density, particle size, homogeneity, moisture content, composition and structure of the sorbent, etc. These factors provide the investigator with some insight for selection of the best set of design parameters and interpretation of results. The previous section discussed the advantages and disadvantages of batch and column methods and several of the variables that must be considered in these experiments. This section will discuss several of the variables important to this study.

Batch Experiments

A wide variety of batch-type experiments have been performed for the analysis of shale leachates (Tables 5 and 10). In most of these experiments a liquid-to-solid ratio (L:S) ranging from 1:1 to 75:1 was used. The most common L:S ratios ranged from 1:1 to 20:1. The ASTM and EPA Extraction procedures specify that 4:1 and 20:1 ratios, respectively, be employed. For the batch elution trials of

this study, a 33:1 ratio was selected. At a L:S ratio of 33:1 each of the agents of interest in this work were readily detected. Lower ratios would be useful in a situation where leachable contaminants are present at very low levels.

Several L:S ratios are generally used in sorption studies. to develop isotherms. The L:S ratios selected depend largely on adsorbent capacity and degree of affinity for the sorbate. Ratios of 33:1, 20:1 and 10:1 were used in the batch sorption trials of this study.

Elution and sorption periods generally range from 0 to 48 hours; however, many experiments are continued for five to seven days. This extended period, seven days, was chosen for this study, to provide a longer time period for equilibrium conditions to be attained.

Batch experiments are usually performed in vessels small enough to be easily agitated such as 250 mL Erlenmeyer flasks, one liter bottles, etc. In this study, 250 mL Erlenmeyer flasks were used and proved to be a convenient, suitable reaction vessel. The type of vessel selected generally depends on the agitating mechanism available, amount of fluid needed for analysis, number of sampling periods and so on.

Column Experiments

Tables 6 and 11 present the design features of several column studies performed with shale and other solid wastes. Glass columns were preferred over plastic types unless fluoride or boron were involved in the experiments. Column diameters ranged from 0.7 to 150 cm; column lengths, 1.0 cm to 1.2 meters. The most commonly used dimensions were 2.6 cm (\approx one inch) in diameter and 30 to 60 cm (1 to 2 feet) long. The dimensions of columns used in this study were 2.6 cm by 30 cm.

Generally, the mass of solid waste used in studies is approximately 100 to 200 g (Tables 6 and 11). Problems such as channelling and clogging must often be dealt with. The mass of shale selected for the column trials of this study was 100 g.

In many leaching studies intermittent gravity flow is used to simulate rainfall. A constant head on columns operating in a downflow mode is also commonly used. Continuous-flow columns are used in order to quickly quantify the amount of material that will elute from the solid waste. Columns were operated as upflow reactors in this study to avoid channelling problems and insure complete wetting of the shale.

ADSORPTION PROCESSES

One of the main goals of this study was to determine the behavior of certain inorganic ions at the liquid-solid interface of shales which had undergone different methods of retorting. To comprehend the nature of this interaction, it is necessary to have an understanding of adsorption processes.

Adsorption from aqueous solutions is a process used widely in many areas of science and technology such as for organics removal in water purification systems, for the decoloration of petroleum fractions and crude sugar syrups, in the clarification of beverages and for recovery of valuable ions from process solutions (50). Table 13 presents a variety of sorption studies which utilized both batch and column methods for analysis of sorption behavior or various solutes on several types of adsorbents. The following section is devoted to a general explanation of the adsorption phenomenon at liquid-solid interfaces.

TABLE 13 VARIOUS ADSORPTION STUDIES

Reference	Description of study	Adsorbent Surface	Type of Experiment
Benjamin (50)	Effects of heavy metals on sorption of $\text{CrO}_4 + \text{SeO}_4$ (multiadsorbate system)	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (amorphous)	Batch (2 hours)
Benjamin and Leckie (51)	Adsorption of Cd, Zn and Pb on amorphous iron oxyhydroxide as a function of pH, and ion and adsorbent concentration.	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (amorphous)	Batch (4 hours)
Benjamin and Leckie (52)	Effects of complexation by Cl , $\text{SO}_4 + \text{S}_2\text{O}_3$ adsorption of Cd onto oxide surfaces.	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (am) SiO_2 FeOOH Al_2O_3	Batch (4 hours)
Bowman <u>et al.</u> (53)	Sorption/Desorption of nickel and the effects of solution composition.	Soil	Batch (24 hours)
Cavallaro and McBride (54)	Complexation and adsorption of Cu and Cd; competition with Ca.	Soil	Batch (24 hours)
Costa and Rodrigues (55)	Equilibrium and adsorption study of phenol sorption.	Resins, activated carbon	Batch
Forbes <u>et al.</u> (56)	Specific adsorption of Cd, Co, Cu, Pb, and Zn, influence of surface clays, ion size and adsorption density.	Soil	Batch (24 hours)

TABLE 13 VARIOUS ADSORPTION STUDIES (cont.)

Reference	Description of study	Adsorbent Surface	Type of Experiment
<u>Giusti et al.</u> (57)	Adsorption of 1, 2 and 4 component systems of petrochemicals.	Activated carbon	Batch isotherms, continuous-flow columns
<u>Hasain et al.</u> (58)	Sorption of SO ₂ on shale related at different temperatures.	Spent shale	Packed beds
<u>Hertzenburg and Sherry</u> (59)	Adsorption of Pb and Cd	Zeolite	Batch (3 days)
<u>Kawabata and Morigaki</u> (60)	Adsorption of DBS (surfactant)	Resins	Batch, column
<u>Lai et al.</u> (61)	Adsorption of Na, Mg, and Ca; influence of cation concentration.	Soil	Column
<u>Levi-Minzi et al.</u> (62)	Cd adsorption from dilute solutions	Soil	Batch (24 hours)
<u>Loch et al.</u> (63)	Behavior of heavy metals on a synthetic leachate on soil.	Sand and clay mixtures	Column
<u>Mathews</u> (64)	Developed adsorption model that takes into account particle size.	Coal, Activated carbon	Batch (6 days)
<u>Matoske and Klusman</u> (65)	Exposed soil samples to Hg ⁰ or HgO in field and lab environments	Soil	Expose sample to controlled or natural atmosphere

TABLE 13 VARIOUS ADSORPTION STUDIES (cont.)

Reference	Description of study	Adsorbent Surface	Type of Experiment
Means <u>et al.</u> (66)	Sorption of PAH compounds	Soil and sediment samples	Batch equil., sorption isotherms (24 hours)
Miragaya (67)	Specific sorption of trace amounts of cadmium	Soil	Column
Pandey and Chaudhi (68)	Sorption of inorganic Hg on activated carbon and coal that had been treated various ways.	Coal, activated carbon	Batch column
Rao <u>et al.</u> (69)	Study of kinetics of adsorption of Cd and Pb at low concentrations.	Resin	Batch
Rouston and Li (70)	Sorption of collidine	Soil and spent shale	Batch (24 hours)
Soon (71)	Solubility and sorption of Cd in soil pretreated with sewage sludge.	Soil	Batch (48 hours)
Weber and Morris (72)	Kinetics of removal of biochemically resistant organisms from water	Activated carbon	Batch column
Weber and Morris (73)	2-component adsorption systems	Activated carbon	Batch
Weber and Morris (74)	Adsorption of common organic pollutants; adsorption capacity of carbon.	Activated carbon	Batch (1 to 4 weeks)

Fundamentals of Adsorption at the Liquid-Solid Interface

Adsorption is a surface phenomenon that occurs as a result of forces in the phase or surface boundaries at the interface of two phases such as liquid-solid, liquid-liquid, gas-liquid, or gas-solid. A typical adsorbent material has a high degree of porosity or permeability, hence a large surface area which provides many sites for adsorption. In many instances the adsorbate has a fixed capacity for exchange of one solute for another, such as in ion exchange.

Adsorption systems consist of three, major components:

- 1) the adsorbent or material that is the adsorbing phase; 2) the adsorbate (or solute), the material being adsorbed; and,
- 3) the solvent which contains the solute (76). The adsorption process involves the building of a monolayer of adsorbate attached to the adsorbent at the liquid-solid interface causing a decrease in free energy of the system (77). The system therefore becomes more ordered and the enthalpy change is negative. Thermodynamic investigation of adsorption systems gives insight into the strength of the binding that is taking place at the interface and hence the type of adsorption that is occurring.

There are generally three types of adsorption: 1) exchange adsorption, 2) physical adsorption and 3) chemisorption (76). Exchange adsorption involves the

concentration of ions (the solute) at the liquid-solid interface as a result of electrostatic attraction to charged sites on the adsorbent. In a simple adsorption system in which there are two potential ionic adsorbates in similar concentration, the ion having the strongest charge will be preferred over the other ion. If the two solutes have similar charges, molecular size is the next important parameter; the smaller ion can get closer to potential adsorptive sites (76).

Physical adsorption is caused by van der Waal's forces which are electrostatic attractions between molecules or atoms caused by fluctuations in their electron distributions. When dipoles are produced by these fluctuations, the result is an attraction between molecules of the adsorbate and adsorbent (76). Physical adsorption is indicated by a low heat of adsorption (≤ 10 kcal/mole) and is often observed for solutes consisting of neutral molecules (77). The molecules are not strictly bound in place and are free to "wander" in the monolayer (76). Physical adsorption often takes place at low temperatures.

Chemisorption is a type of adsorption in which the molecules of the adsorbate (the solute) undergo chemical reactions with the adsorbent forming a strong localized bond. There is no freedom of movement within the interface.

A high heat of adsorption is an indication of this type of adsorption, the values approaching those measured in chemical reactions (77). Chemisorption occurs mostly at high temperatures and can also occur at low adsorbate concentrations.

Most adsorption occurs as a combination of three processes just discussed. It is often difficult to tell which type of adsorption is most dominant in a system because the forces that influence the different adsorption processes can interact.

Another type of adsorption, which Weber (76) called "specific adsorption", is often involved in the adsorption of organic molecules. This type of adsorption involves the interaction of structural components of the molecule with the adsorbent and can exhibit a wide range of adsorption energies, some similar to physical adsorption, others to chemisorption.

Factors Affecting Adsorption from Solution

Adsorption at the liquid-solid interface is primarily caused by the lyophobic (solvent-disliking) tendency of the solute for that solvent and/or a strong attraction of the solute for the adsorbent (76). The intensity of adsorption of a solute is closely tied to its solubility. The

solubility of the solute can be considered as a measure of the leaving tendency of a solute in a solvent (77).

There are many other factors that affect adsorption processes. Physical and chemical characteristics of the adsorbent, the nature of the binding sites on its surface, the actual surface area (area/unit mass) and polarity of the adsorbent (and solute) are important factors that must be considered when investigating an adsorption system. Tinsley (77) discussed the following properties of soil, the most significant adsorptive surface in the natural environment, which have an important impact on adsorption.

1. Mineral Fraction: The extent of the mineral fraction will of course vary among soil types. Layer silicates and metal hydroxides, which form clay minerals, constitute this fraction. The structure of the clay minerals allows for a negative charge, creating the ion exchange capabilities seen in Figure 4.
2. Organic Fraction: The three major organic components of soils are divided into three categories, humin, humic acid and fulvic acid. These hydrophobic organic materials provide an exchange surface and very high cation exchange capacity.

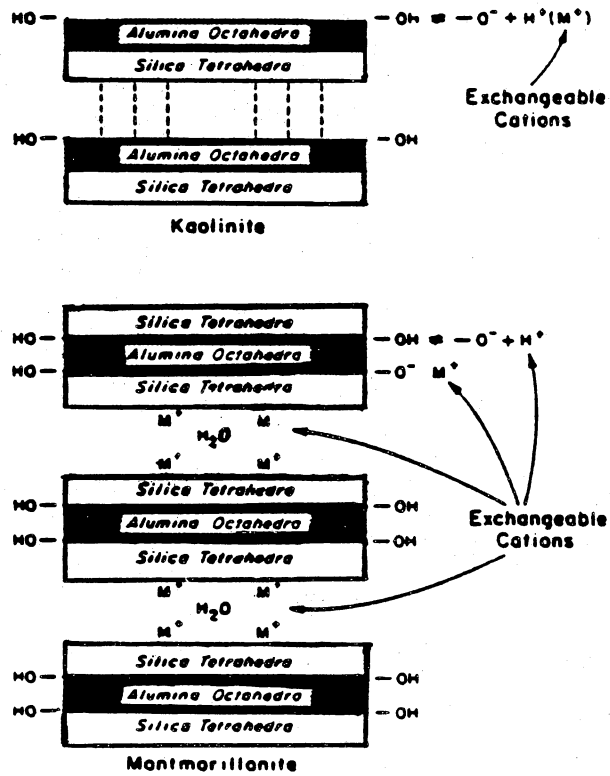


Figure 4. Distribution of charge and cation exchange potential of a clay (77).

3. Hydrophobic Bonding: Hydrophobic organics in water tend to be adsorbed into a more hydrophobic region whereas hydrophilic substances will be less likely to leave solution (76,77). This behavior is thermodynamically favored because water molecules form an ordered configuration around the hydrocarbon, which represents a decrease in the entropy. If the hydrocarbon has the opportunity to interact with a hydrophobic or nonpolar region the water will revert to its less ordered structure (higher entropy level).
4. Ligand Exchange: An adsorbent molecule can, if it is a stronger chelating agent, replace one or more ligands.
5. Dipole-Dipole Interactions: An adsorbent may form bonds with large organic molecules that have dipole moments, when the distribution of charge favors attraction between the two.
6. Hydrogen Bonding: Hydrogen bonding can occur where the adsorbent Y, has some basicity and the adsorbate, XH, has a degree of polarity; $XH \cdots Y$. Strong hydrogen bonding systems involve highly electronegative components; for example, $OH \cdots O$ and $OH \cdots N$, which are common in both mineral and organic systems.

The oil shale surface is very complex and has a large surface area available for adsorption, a variety of binding sites, possibilities for hydrophobic interactions, simple ion exchange and all of the other factors previously described. All of these characteristics combine to make it very difficult to analyze the interaction of sorbates with oil shale.

Rate-Limiting Factors of the Adsorption Process

There are three consecutive steps involved in the adsorption of a solute onto an adsorbent. The first, known as film diffusion, is the transport of the solute through a surface film to the outer surface of the adsorbent (76). This is followed by the diffusion of the solute into the pores of the adsorbent and finally, the adsorbate is adsorbed onto the interior surface of the adsorbent solid (76).

Under certain conditions in a liquid-solid system, any of these three steps can be the rate-controlling step. For example, in a batch type experiment in which there is a high degree of agitation and mixing, the rate-limiting factor is most likely diffusion into the pores. In a continuous-flow system that is operating under normal flow conditions, the rate-limiting factor will most likely be film diffusion.

Adsorption Isotherms

For a simple adsorption system, a curve can be drawn to express the relationship of the solute concentration in the solid phase to the solute concentration in the aqueous phase (50). Isotherm experiments are used to determine the equilibrium adsorption capacity of an adsorbent such as activated carbon. At equilibrium there is a particular ratio of the solute between the liquid and solid phases.

A simple isotherm (or batch) experiment involves setting up different ratios of liquid-to-solid in containers that are agitated for a set period of time at a constant temperature. The amount of solute removed (X , milligrams) is calculated by subtracting the equilibrium concentration of solute detected in the solvent from the original concentration and multiplying by the volume of liquid (78). The specific adsorption capacity, X/M , is found by dividing the amount of solute adsorbed, X (mg), by the mass of adsorbent (M , mg) utilized in the experiment.

Several adsorption models have been developed to illustrate the relationship between X/M and the initial concentration of solute in solution. The Langmuir and Freundlich equations are the most widely utilized and each will be discussed briefly in the following section.

Langmuir and Freundlich Equations

The Langmuir equation for single layer adsorption was originally developed for the adsorption of gases onto solids. Three assumptions were made in the development of the Langmuir isotherm (78):

1. The maximum adsorption possible is a complete monolayer.
2. The energy of adsorption is constant at all adsorption sites.
3. There is no interaction between adsorbed molecules, such as translational migration.

The equation can be written as (78):

$$Q = X/M = \frac{abC_{eq}}{1 + bC_{eq}} \quad [1]$$

where b is a constant related to the energy of adsorption and k is the amount of adsorbate required to form a complete monolayer.

The equation may also be expressed in the linear form as:

$$1/Q = M/X = 1/a + 1/abC_{eq} \quad [2]$$

If the Langmuir isotherm applies, plotting the reciprocal of the amount of solute adsorbed per unit mass solid, $1/Q$, as a function of the reciprocal of C_{eq} will give a straight line with an intercept of $1/a$ and a slope of $1/ab$.

The Freundlich equation was developed empirically, but can be derived from Langmuir relations (78). This equation is used for heterogenous surface energies in which K , the energy constant, varies due to variations in the heat of adsorption (76). The equation is written as:

$$X/M = KC_{eq}^{1/n} \quad [3]$$

where K and n are constants (78). The equation is generally used in the following form which can be derived by taking the log of each side of equation 3:

$$\text{Log } X/M = \text{Log } K + 1/n \text{ Log } C_{eq} \quad [4]$$

where $1/n$ represents the slope of the isotherm. Linear forms for the graphical illustration of the Langmuir and Freundlich isotherms are provided in Figures 5 and 6 (78).

There are advantages and disadvantages to using both models. It is important to analyze the limitations of both in relation to the experimental parameters to be used before choosing a model for analysis of data. For example, one of the differences between the two types of isotherms is that the Freundlich isotherm does not reduce to linear

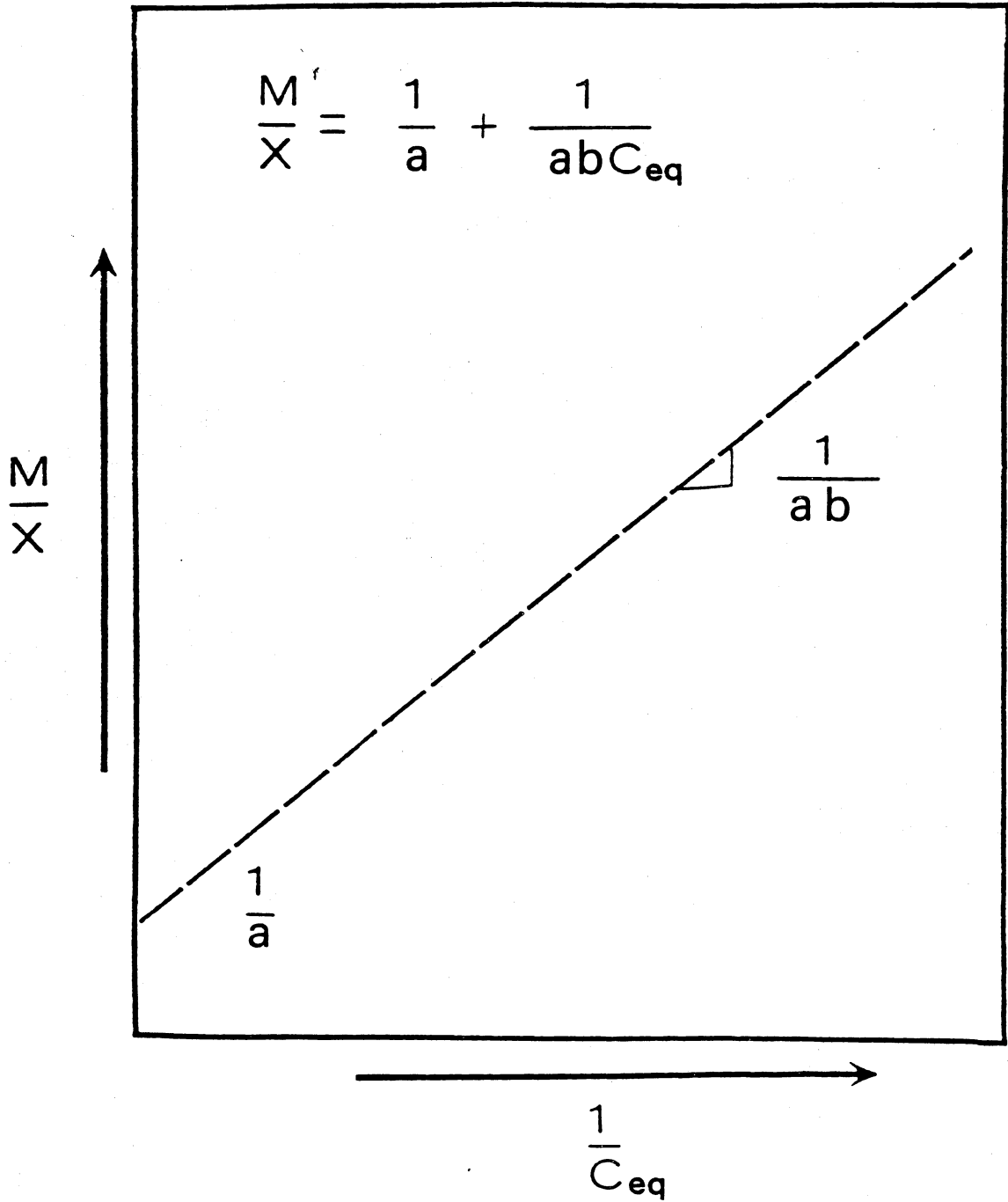


Figure 5. Evaluation of Langmuir constants (78).

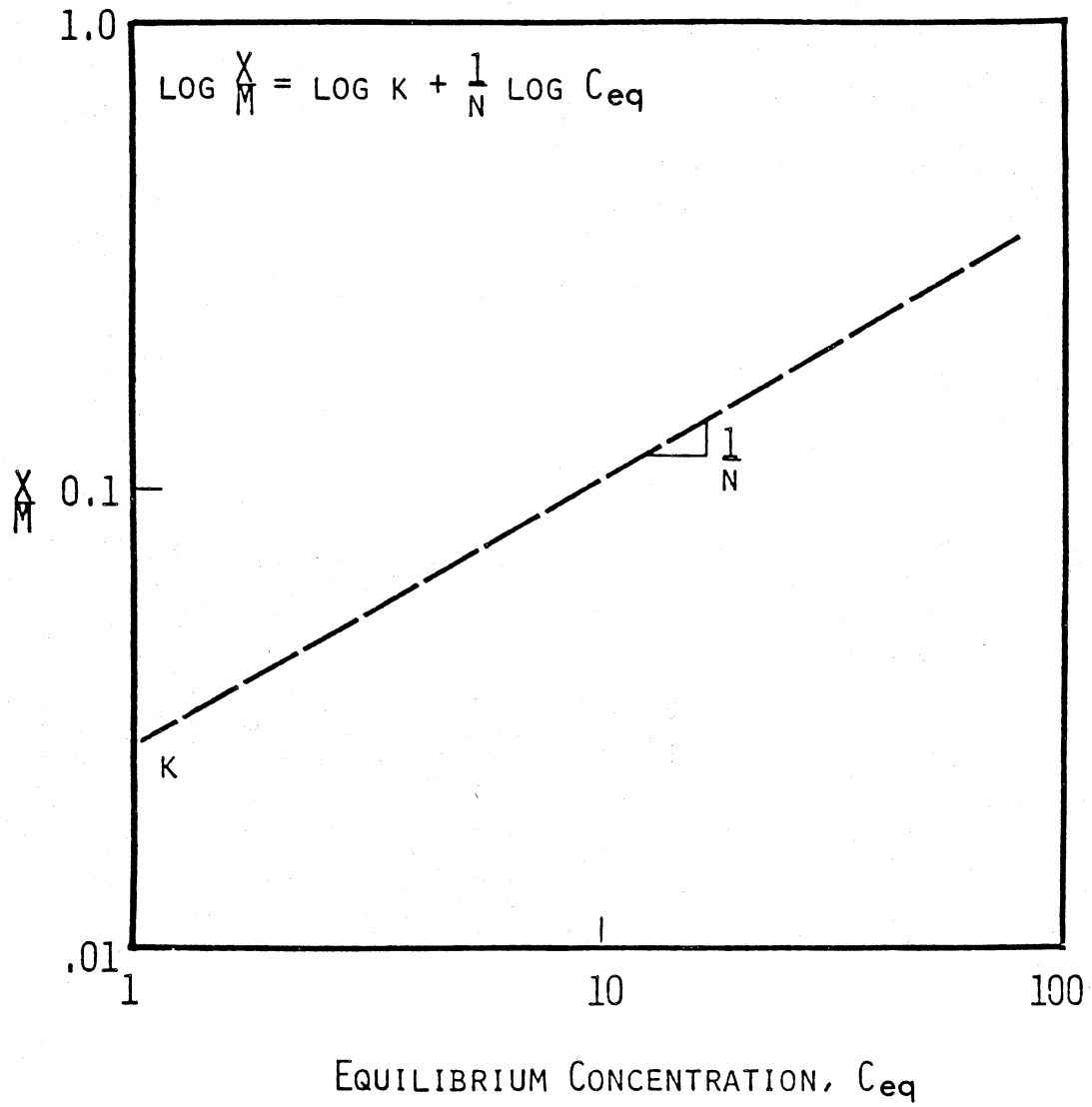


Figure 6. Evaluation of Freundlich constants (78).

adsorption at very low concentrations like the Langmuir. Nor does it agree with the Langmuir at high concentrations (76).

Chapter III

MATERIALS AND METHODS

Two types of laboratory experiments were performed in this study: batch experiments and continuous-flow, column experiments. The shale samples were obtained from the Department of Energy's (DOE) Laramie Project Office in Laramie, Wyoming. The four types of shale considered were:

1. a medium rich raw shale from Anvil Points, Colorado
2. Oxy 6 spent shale, retorted by Occidental Oil Shale, Inc.
3. Antrim spent shale (an eastern shale), retorted at Laramie
4. Run 16 spent shale (a Colorado shale), retorted at Laramie

Two particle sizes of shale were used. Particles which passed through an 8-mesh sieve and were retained on a 30-mesh sieve were used in the continuous-flow, column experiments. The material that passed through the 30 mesh sieve (fines) was used in the batch studies. The larger size particles were used to reduce headloss in columns, while finer particles were used in the batch experiments so that equilibrium would be reached sooner.

Physical properties of the shale that were determined included bulk density, solid density, and porosity. The minimum and maximum bulk-densities were determined by the method described in Soil Mechanics Laboratory (79) which utilized a Proctor Mold having a volume of 944 cc (cubic centimeters or $1/30 \text{ ft}^3$) (79). The shale was poured into the Proctor Mold and was leveled even with the top of the mold. The weight of the shale contained in the mold was determined and divided by the volume of the mold to obtain the minimum bulk density. Maximum bulk density was determined in a similar way, except that the mold and shale were vibrated until no further settling occurred and then the mold was weighed.

The solid density of the shales was determined by using the specific gravity determination method (79). A pycnometer was used instead of a volumetric flask to increase the accuracy of the method. Some of the shales tended to be hydrophobic, so methanol, instead of water, was used in the procedure. The molecular structure of methanol enhanced entry of the solute into the pores of the shale particles.

Porosity was calculated from the bulk density and solid density values. Minimum and maximum porosities were computed as follows:

$$\text{Porosity} = 1 - (\text{Bulk Density} \div \text{Solid Density})$$

BATCH EXPERIMENTS

Batch reactor studies were divided into elution and sorption experiments. The elution trials were performed to examine the materials released from the shale into distilled, deionized water and the sorption experiments were designed to reveal the behavior with solid material of several inorganic ions introduced into bulk solution.

Batch Elution Experiment

Approximately 4.5 grams (g) of shale fines were placed in 250 milliliter (mL), glass, Erlenmeyer flasks with 150 mL of distilled, deionized water and sealed with Parafilm (Grenwich, CT). The samples were then placed in a shaking water bath (Fisher, Pittsburgh, PA; Model 129) set at 25 \pm 3°C and 120 strokes/minute. Two flasks were removed from the water bath at each of the following time intervals: 4, 8, 12, 24, 36, 48, 60, 72, 96, 120, 144, and 168 hours.

The fluid (150 mL) in each flask was filtered through a 0.45 μ m membrane filter (Gelman, Ann Arbor, MI; GA-6 Metrical). The filtrate from each flask was treated in the following way. Approximately 50 mL of sample from each flask was acidified with HNO₃ in preparation for analysis of arsenic (As), cadmium (Cd), calcium (Ca), iron (Fe), and potassium (K) on an atomic absorption (AA) spectrophotometer

(Perkin-Elmer, Norwalk, CT; Model 703). The remaining 100 mL of sample from each flask was used for analyses of pH, conductivity (YSI conductance meter, Yellow Springs, OH; Model 32), redox potential (Fisher; platinum combination electrode), and fluoride (Orion, Cambridge, MA; fluoride electrode). Alkalinity and sulfate analyses were performed in accordance with Standard Methods (80).

Batch Sorption Experiment

The sorption experiments were conducted in basically the same manner as the elution experiments, except that only one flask per experimental condition was prepared. Three liquid-to-solid (L:S) ratios, [33:1 (4.5 g shale), 20:1 (7.5 g shale), and 10:1 (15 g shale)], were considered. The amount of liquid in each case was 150 mL. The elements studied were As, Cd, Fe, and F. A solution of approximately 10 milligrams/liter (mg/L) of each ion was prepared by adding the appropriate amount of stock solution to distilled, deionized water. Commercial atomic absorption standards (1000 mg/L) were used to prepare the arsenic, cadmium and iron solutions. Fluoride solutions were prepared from an Orion fluoride standard (100 mg/L). Because the metal stock standards were dissolved in an acid solution, the pH of the final 10 mg/L solution was adjusted to approximately 5.5 with NaOH.

The ion solutions (150 mL) were added to the shale fines in 250-mL glass, Erlenmeyer flasks and sealed with Parafilm. The fluoride sorption study was performed with 250-mL, polycarbonate, Erlenmeyers flasks to prevent interference due to the sorption of fluoride on glass. The samples were immediately placed on the shaking water bath set at batch set at $25 \pm 3^\circ\text{C}$ and 120 strokes/minute. A 5-mL sample was removed with a glass syringe at 1, 3, 6, 12, 24, 48 and 120 hours and filtered through a $0.45 \mu\text{m}$ membrane filter (Gelman, GA-6 Metricel). The sample, contained in a glass test tube, was acidified with HNO_3 , after the pH had been recorded. Fluoride samples were placed in a plastic sample bottle and measured, as before, with the Orion fluoride electrode. Analyses for metals were again performed on the AA.

Controls for Sorption Experiment

For each ion solution-to-shale ratio in the sorption experiments an accompanying control flask was prepared which consisted of 10 mg/L ion in leachate that had been generated by shaking the specified amount of shale with 150 ml of distilled, deionized water for 120 hours. The shale/water mixture was filtered through a $0.45 \mu\text{m}$ membrane filter and then the filtrate was used to prepare the ion solution.

CONTINUOUS-FLOW COLUMN EXPERIMENTS

Column experiments were also divided into elution and sorption studies. The elution study consisted of leaching columns of shale with distilled, deionized water and measuring various parameters in the column effluents. In the sorption experiments certain ions, alone and in mixtures, were pumped through columns for 48 hours. The period for sorption was immediately followed by a desorption phase in which the column was leached with distilled, deionized water. The experimental system for the column experiments is shown in Figure 7.

The glass columns chosen for this work were chromatography columns manufactured by LKB (Gaithersburg, MD) (no. 2137). The columns were fitted with a water-jacket to regulate temperature and adjustable plungers that could be moved to accommodate the amount of material placed in the columns. The plungers were covered with a removable polyester/polypropylene mesh filter disk to prevent solids from escaping the column in the effluent. After a preliminary trial, the influent disk was replaced by a disk having larger pores because plugging of the finer-meshed, filter disk was causing excessive headloss.

A circulating water bath (Lauda K-2/R) was used to keep the feed solution and column of shale at $25 \pm 3^\circ\text{C}$. The feed

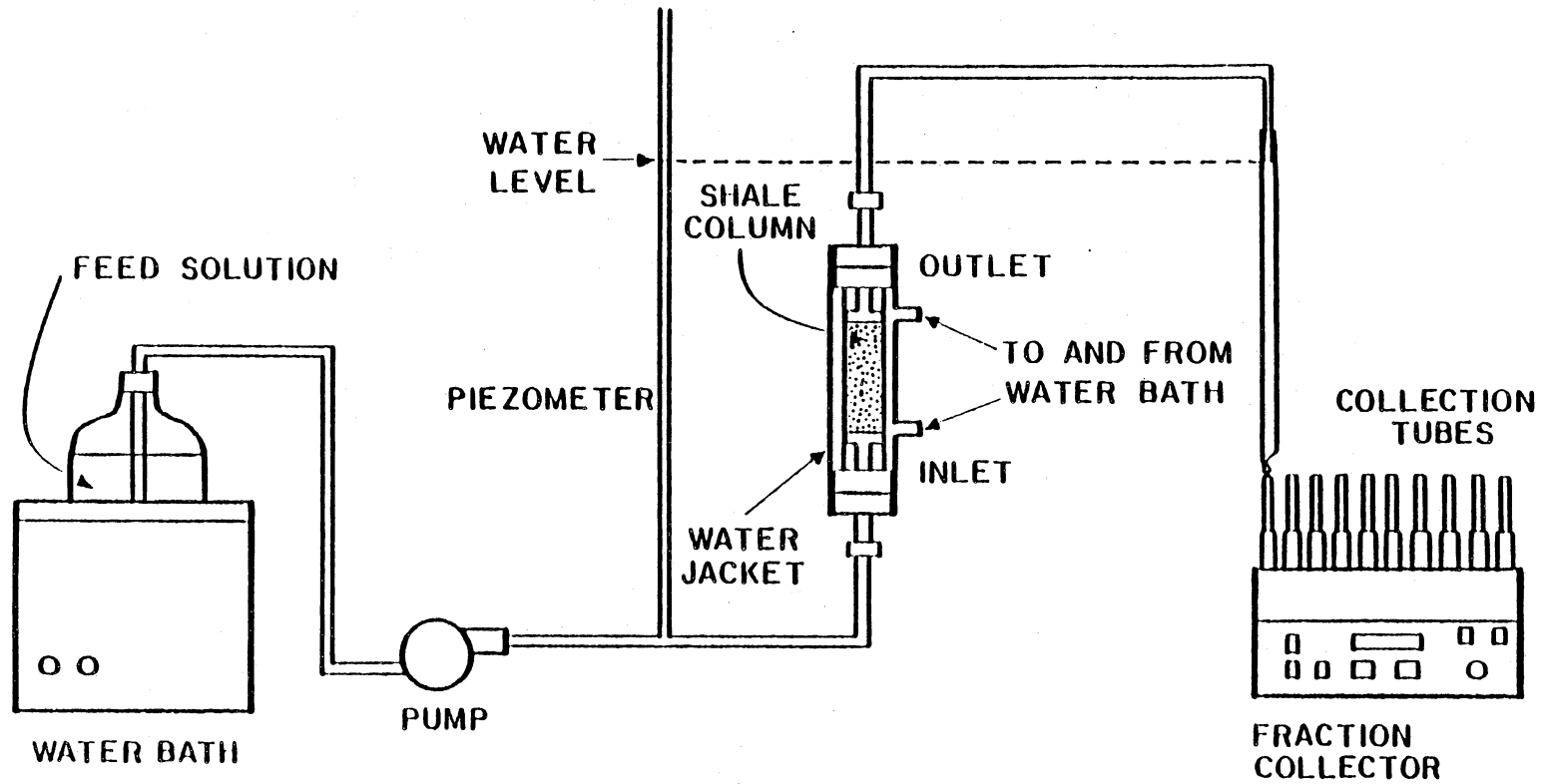


Figure 7. Design of the continuous-flow column system.

solution was contained in a glass carboy and pumped (FMI lab pump RP-G50) to the column through teflon tubing at a flow rate of approximately 1.0 ml/min. The solution entered the bottom of the shale column in order to expel air and insure complete wetting of the shale material. The effluent from the column traveled to a teflon collection tube which directed the solution to an ISCO fraction collector holding glass, screw-capped, test tubes. Each tube held approximately 15 ml of solution.

Column Elution Experiments

Approximately 100 g of 8 to 30 mesh shale was placed in a glass column and was tamped until no further settling occurred. The feed tank was filled with distilled deionized water (pH 5.5 - 6.0). Triplicate columns of each shale type were prepared in this way and each was eluted for 48 hours. The volume of effluent leaving the column was expressed as the number of pore volumes that had passed through the shale column. Pore volume was calculated in the following way:

1. Volume occupied by the shale.

$$V \text{ (cm}^3\text{)} = \frac{\text{Length of shale column (cm)}}{\text{Area (cm}^2\text{)}} \times \text{Area (cm}^2\text{)}$$

2. Bulk density of the column.

$$\text{Bulk Density} = \frac{\text{Mass of shale (g)}}{\text{Volume (cm}^3\text{)}}$$

3. Porosity of the column.

$$\text{Porosity} = 1 - (\text{Bulk Density} \div \text{Solid Density})$$

4. Calculation of pore volume.

$$\text{Pore Volume (cm}^3\text{)} = \text{Porosity} \times \text{Volume (cm}^3\text{)}$$

Not all of the effluent samples were analyzed. Samples were collected at various intervals and the pore volume of that sample recorded. In order to have enough sample for all the analyses, three consecutive samples of effluent (total of 45 mL) from the fraction collector were combined and filtered through a 0.45 μm membrane filter into a glass sample bottle. Approximately 30 ml was acidified with HNO_3 and analyzed for As, Cd, Ca, Fe and K on the AA. Alkalinity, pH, conductivity, fluoride and sulfate were analyzed as previously discussed in the batch elution experiments.

Column Sorption Experiments with Single Ion Solutions

The column configuration for the sorption study was the same as that utilized in the elution experiment; however, the feed tank was filled with an ion solution which was pumped through columns of each of the four shale types. The ions considered were As, Cd, Ca, F, Fe and K. The concentration of the ions in each trial was 10 mg/L, the same as that used in the batch sorption experiment. Solution pH levels were adjusted to approximately 5.5. The

solutions were then pumped through columns at a rate of 1 ml/min for 48 hours. The effluent was collected and filtered as in the column elution study and the pH and conductivity were recorded. The samples were then acidified and analyzed for metal levels on the AA. Fluoride was analyzed with the Orion Fluoride electrode.

After the the sorption phase, columns were immediately eluted with distilled, deionized water for 48 hours. A sorption/desorption trial for each of the ions mentioned earlier was performed with each shale type. However, an exception was made with the Antrim and Run 16 spent shales. The batch elution data indicated that high concentrations of calcium (190 and 250 mg/L, respectively) and potassium (160 and 200 mg/L, respectively) leached from these shales. Therefore, it was decided that the sorption of Ca and K on these shales would not be considered.

Column Sorption/Desorption with a Combination of Ions

In the final phase of the continuous-flow experiments, solutions containing 10 mg/L each of As, Cd, Ca, F and K (pH \approx 5.5) were pumped through columns of each shale type. All experiments were performed in triplicate. Iron was not included because it precipitated from solution. The 48-hour sorption phase was followed by 48 hours of desorption with

distilled, deionized water. Samples were collected and analyzed, as was described in the single-ion sorption/desorption studies.

Chapter IV

RESULTS

The results of this investigation are presented in the following chapter. The presentation of results derived from the two major types of experiments (batch and continuous-flow trials) has been further subdivided into subsections in which the results of the elution, sorption, and desorption studies are presented.

PHYSICAL PROPERTIES

Table 14 presents the type of retort process and the maximum retorting temperature experienced by Oxy, Antrim and Run 16 shales. Oxy shale, a modified in situ (MIS) retorted shale, encountered the highest temperatures ranging from 800 to 1000°C (81). Antrim and Run 16 were retorted in simulated, MIS retorts and the maximum bed temperatures (793 and 660 °C, respectively) were less severe than those in the Oxy retort (82).

The bulk and solid densities and porosities of the four shale types are presented in Table 15. Bulk densities of Antrim spent and Anvil raw shale were similar, ranging from 0.97 to 1.37 g/cm³. Oxy and Run 16 bulk densities ranged from 0.88 to 1.11 g/cm³. There was little variation between

TABLE 14

RETORT PROCESS FOR ANTRIM, OXY 6 AND RUN 16 SHALES ¹

	Shale Type		
	Oxy 6	Antrim	Run 16
Type of Retort	MIS ²	simulated MIS (10 ton)	simulated MIS (150 ton)
Retort Gas	air and steam	air and recycle	air and recycle
Maximum Bed Temperature, (°C)	800 to 1000	793	660
Length of run, (days)	330	5.54	22.56

1. Taken from references 81 and 82

2. Modified in situ retort

these values for fines and the 8-30 particle size. This is also true for the solid density measurements; fines and 8-30 particle sizes differed no more than 0.18 g/cm^3 . Run 16 and Antrim spent shales had the greatest solid densities, 2.66 and 2.56 g/cm^3 respectively, followed by Anvil then Oxy shale, 2.25 and 2.08 g/cm^3 respectively. The porosities of the shales, from most porous to least porous were: Run 16, Antrim, Anvil and Oxy. The porosities of the latter two were similar, ranging from 0.42 to 0.57. Run 16 and Antrim shales exhibited greater porosity values of 0.67 and 0.60, respectively. In most cases, the fines had greater porosities than the larger particle size.

BATCH ELUTION STUDIES

Recall that the batch elution experiments consisted of shaking flasks of water and shale (L:S = 33:1) in a temperature-controlled bath for 168 hours. Table 16 provides the time at which equilibrium was reached for the parameters measured and their concentrations at that time period. Appendix A contains figures that illustrate the equilibrium isotherms for the variables studied. Wherever possible, the results of contacting a given agent with all four shales were plotted on one graph so that comparisons of the different shales can be made easily. It is apparent

TABLE 15

PHYSICAL PROPERTIES OF ANVIL, ANTRIM, OXY 6 AND RUN 16 SHALES

Property	Anvil (raw)		Antrim (spent)		Oxy 6 (spent)		Run 16 (spent)	
	fines	8-30 mesh	fines	8-30 mesh	fines	8-30 mesh	fines	8-30 mesh
Minimum Bulk Density (g/cm ³)	0.966	1.043	1.022	1.010	0.891	0.940	0.867	0.906
Maximum Bulk Density (g/cm ³)	1.238	1.215	1.365	1.202	1.078	1.111	1.078	1.104
Solid Density (g/cm ³)	2.25	2.24	2.56	2.52	2.08	1.90	2.64	2.66
Minimum Porosity	0.450	0.458	0.467	0.523	0.482	0.415	0.582	0.594
Maximum Porosity	0.571	0.534	0.601	0.599	0.572	0.505	0.672	0.659

after examination of the graphs that the inorganics eluted from the shale reached an equilibrium state within 24 hours of the experiment. There were a few exceptions, however, and these will be pointed out.

One of the more important parameters measured throughout the elution experiments was the pH of the eluents because pH impacts upon the solubility of metal ions. The pH's of the four eluents ranged from 8.5 to 11.5 (Figure 8). Run 16 spent shale created an eluent with an extremely high pH (greater than 11.0). Antrim shale also produced a basic eluent (approximately 10.6), while the pH of Anvil raw shale and Oxy spent-shale eluents ranged from 8.5 to 9.6. Note also that the pH of these latter two eluents tended to decrease somewhat throughout the experiment.

In most cases, Run 16 and Antrim spent-shales released greater amounts of material than Oxy and Anvil shales. For example, Anvil and Oxy eluents contained approximately 20 mg/L of Ca and K, compared to 125 to 250 mg/L, respectively, in Run 16 and Antrim eluents. The same was true for sulfate. Anvil and Oxy released approximately 10 and 50 mg/L SO_4 , respectively, while Antrim and Run 16 released much greater levels, approximately 380 and 470 mg/L, respectively (Table 16).

TABLE 16

SUMMARY OF DATA DERIVED FROM BATCH ELUTION EQUILIBRIUM ISOTHERMS

Shale	<u>Parameter</u>										
	¹ Alk	² As	³ Ca	⁴ Cd	⁵ Con	⁶ F	⁷ Fe	pH	⁸ K	⁹ RP	¹⁰ SO ₄
Anvil											
¹¹ C _{eq}	65.0	8.0	14.0	5.0	0.24	11.8	0.02	8.7	2.9	+198	51.0
¹² T _{eq}	116	60	93	¹³ n.a.	48	144	n.a.	109	30	36	35
Oxy 6											
C _{eq}	60.0	16.0	11.0	5.0	0.13	0.72	0.10	8.6	2.1	+120	9.1
T _{eq}	66	144	69	n.a.	68	118	132	48	46	126	20
Antrim											
C _{eq}	70.0	18.0	180.0	5.0	1.78	0.74	0.02	10.6	166.0	-19	383.0
T _{eq}	36	108	72	n.a.	77	43	n.a.	12	44	80	78
Run 16											
C _{eq}	265.0	4.3	238.0	5.0	1.85	5.4	0.02	11.5	195.0	-9	470.0
T _{eq}	106	50	58	n.a.	115	131	n.a.	120	36	48	43

1. Alkalinity as mg/L CaCO₃

2. Arsenic, µg/L

3. Calcium, mg/L

4. Cadmium, µg/L

5. Conductivity, mmhos/cm

6. Fluoride, mg/L

7. Iron, mg/L

8. Potassium, mg/L

9. Redox Potential, mv

10. Sulfate, mg/L

11. Concentration at equilibrium

12. Time for C_{eq}, hours

13. Not applicable

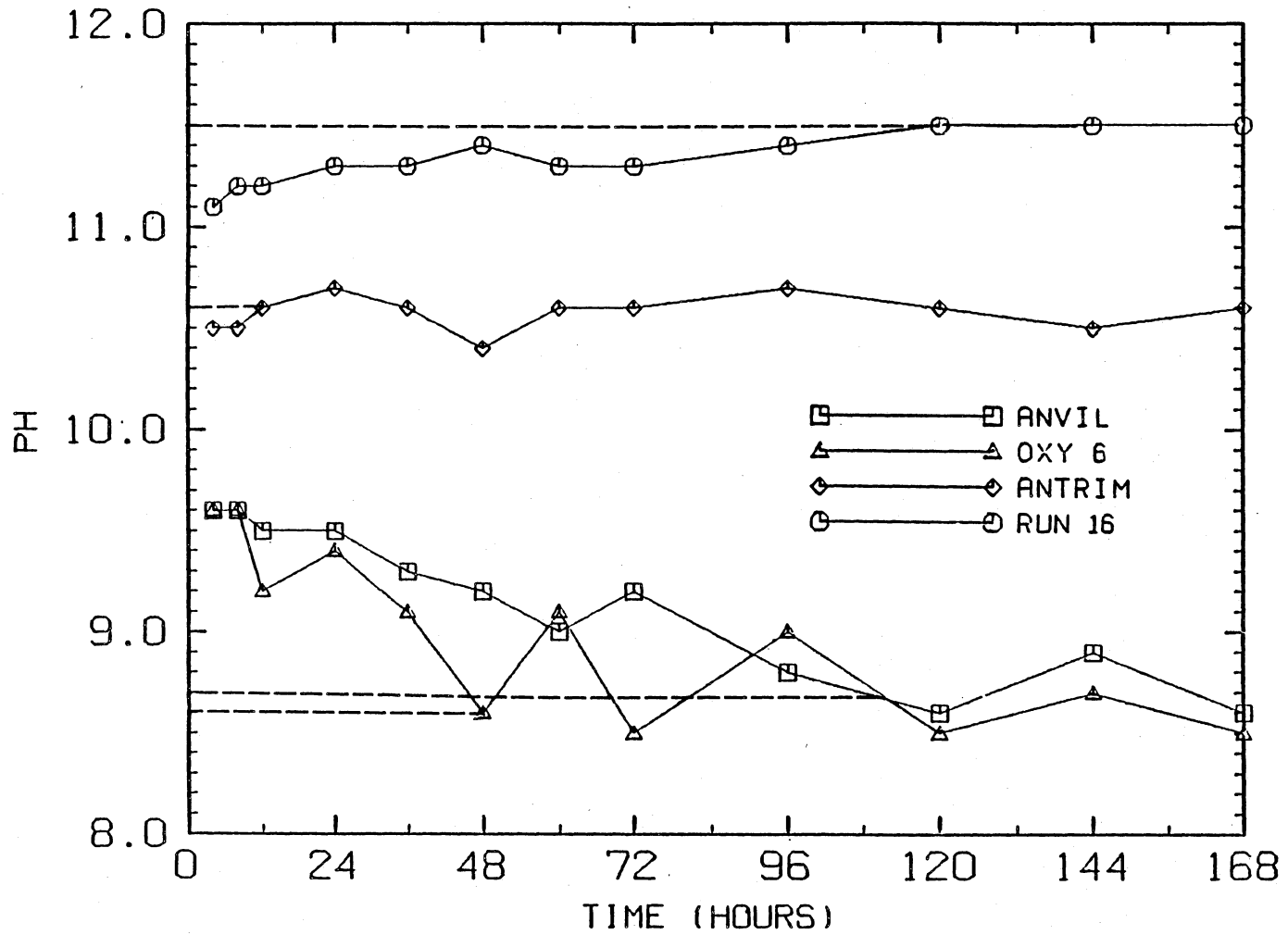


Figure 8. Variation in pH of batch eluents for the various shales. Dashed line represents concentration at equilibrium.

Conductivity reflects the amount of dissolved solids in a sample and tended to verify the calcium, potassium and sulfate concentrations just presented (Figure 9). Run 16 and Antrim shale eluents had the highest conductivity ranging from 1.2 to 1.9 millimhos/cm, while the values associated with Anvil and Oxy eluents were many times less, 0.1 to 0.3 millimhos/cm.

The redox potentials of the eluents of the Run 16 and Antrim shales were negative, indicating that these eluents had reducing tendencies. Anvil and Oxy eluents, in contrast, exhibited positive redox potential (100 to 200 mv) (Figure 10).

The eluents from Anvil, Oxy, and Antrim shales exhibited alkalinity levels ranging from 30 to 80 mg/L as CaCO_3 , while the alkalinity of Run 16 eluents ranged from 125 to 325 mg/L (Figure 11). While alkalinity concentrations in Anvil, Oxy, and Antrim eluents reached an equilibrium within the experimental time period, it is possible that the alkalinity of Run 16 eluents would have continued to increase after 168 hours.

The arsenic and fluoride isotherms deviated from the behavior of the variables mentioned previously. Arsenic values were measured in $\mu\text{g/L}$. At such low levels there is a greater opportunity for error and variability in results.

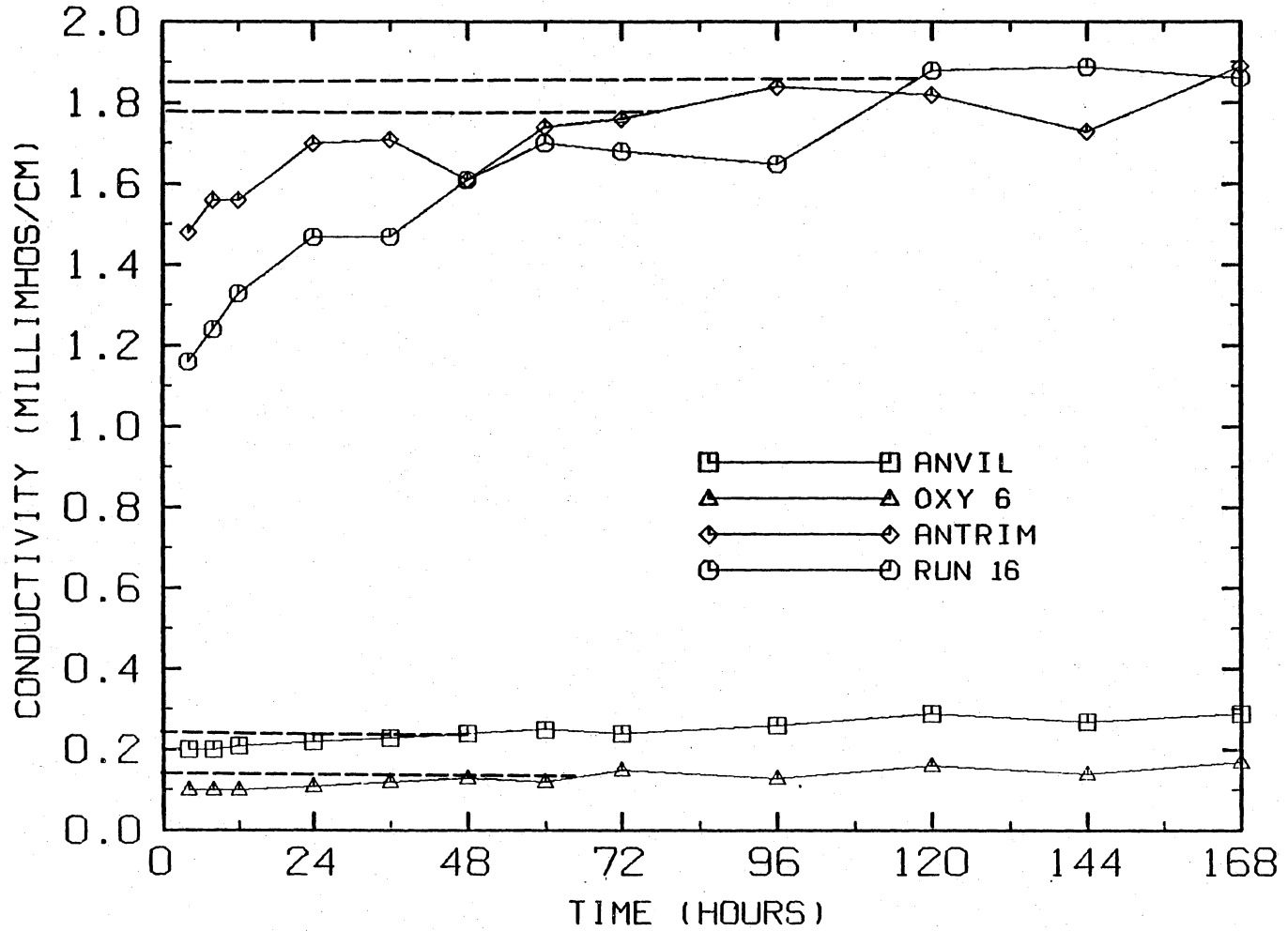


Figure 9. Variation in conductivity of batch eluents for the various shales. Dashed line represents concentration at equilibrium.

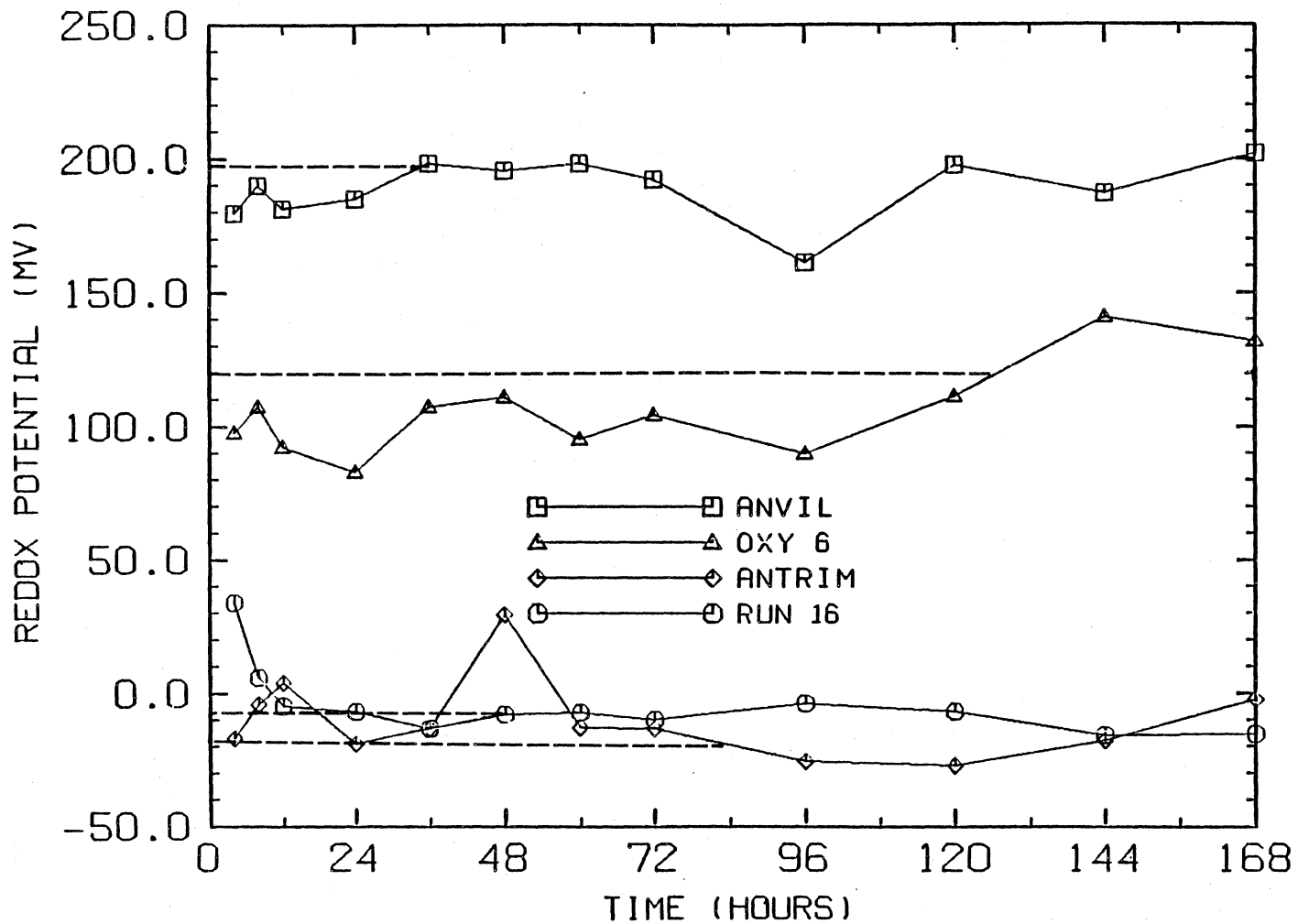


Figure 10. Variation in redox potential of batch eluents for the various shales. Dashed line represents concentration at equilibrium.

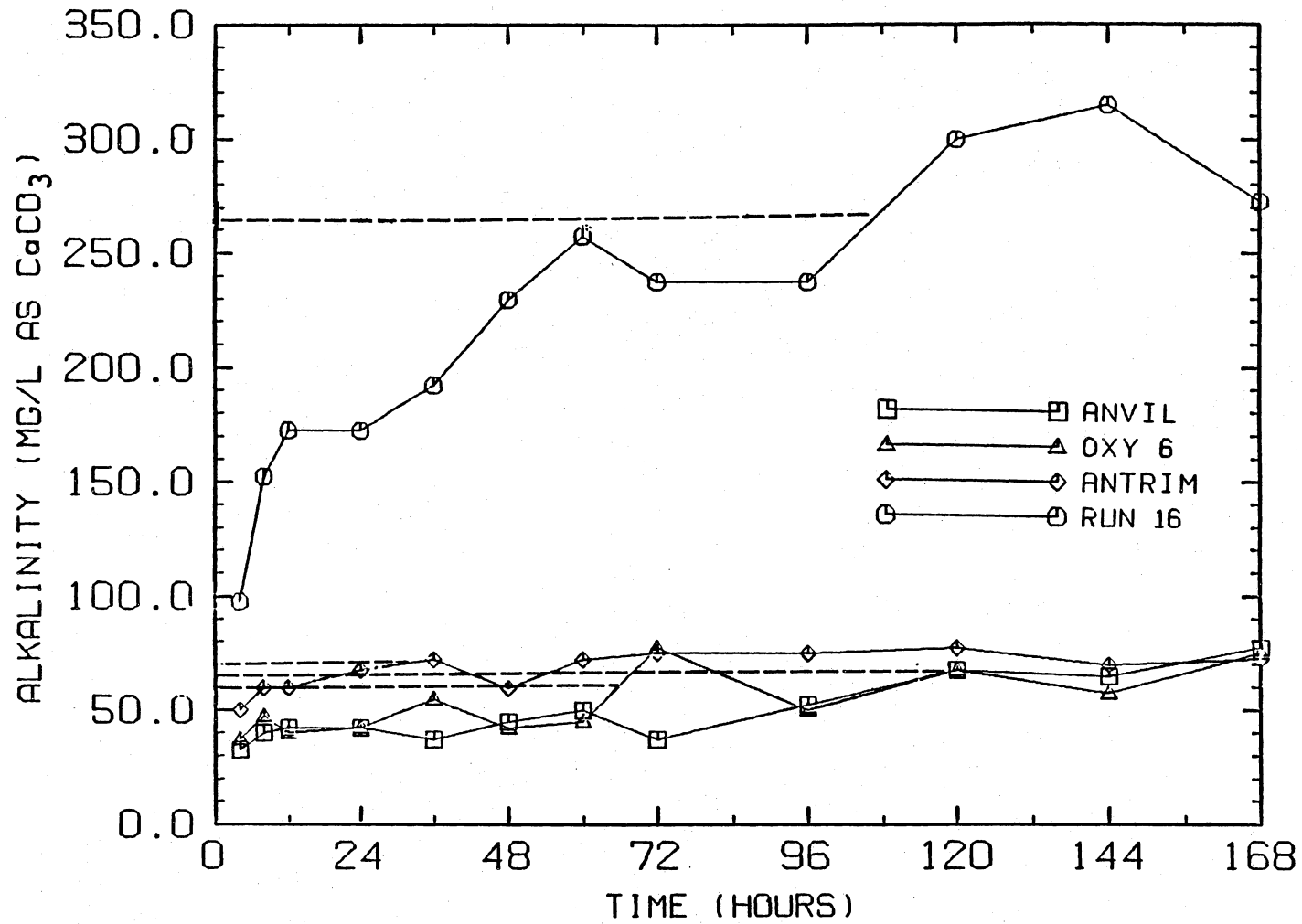


Figure 11. Variation in alkalinity of batch eluents for the various shales. Dashed line represents concentration at equilibrium.

Generally, the arsenic concentrations of all of the shale eluents were somewhere between 3 and 21 $\mu\text{g/L}$ (Figures 12,13). Anvil raw shale produced the greatest fluoride levels in the eluent (3 to 12 mg/L) and it appears that this shale would have continued to elute fluoride had the experiment been continued (Figure 14). Fluoride levels in the Run 16 eluent reached equilibrium at approximately 5 mg/L . Oxy and Antrim eluents did not yield concentrations greater than 1 mg/L (Table 16).

Iron and cadmium levels in the eluents were generally below detection on the AA, iron less than 0.02 mg/L and cadmium less than 0.005 mg/L .

BATCH SORPTION RESULTS

The data for the batch sorption experiments are presented in two ways. First, the concentration of ions remaining in solution (Y), in both the sorption and control flasks, is plotted versus the sample time (X) (Appendix B). Ion concentrations in control flasks for the three ratios of water-to-shale were averaged and plotted as one curve. Batch adsorption data are also presented in the form of adsorption isotherms where the amount of ion adsorbed is plotted against time (Appendix B). Representative graphs are included in this section.

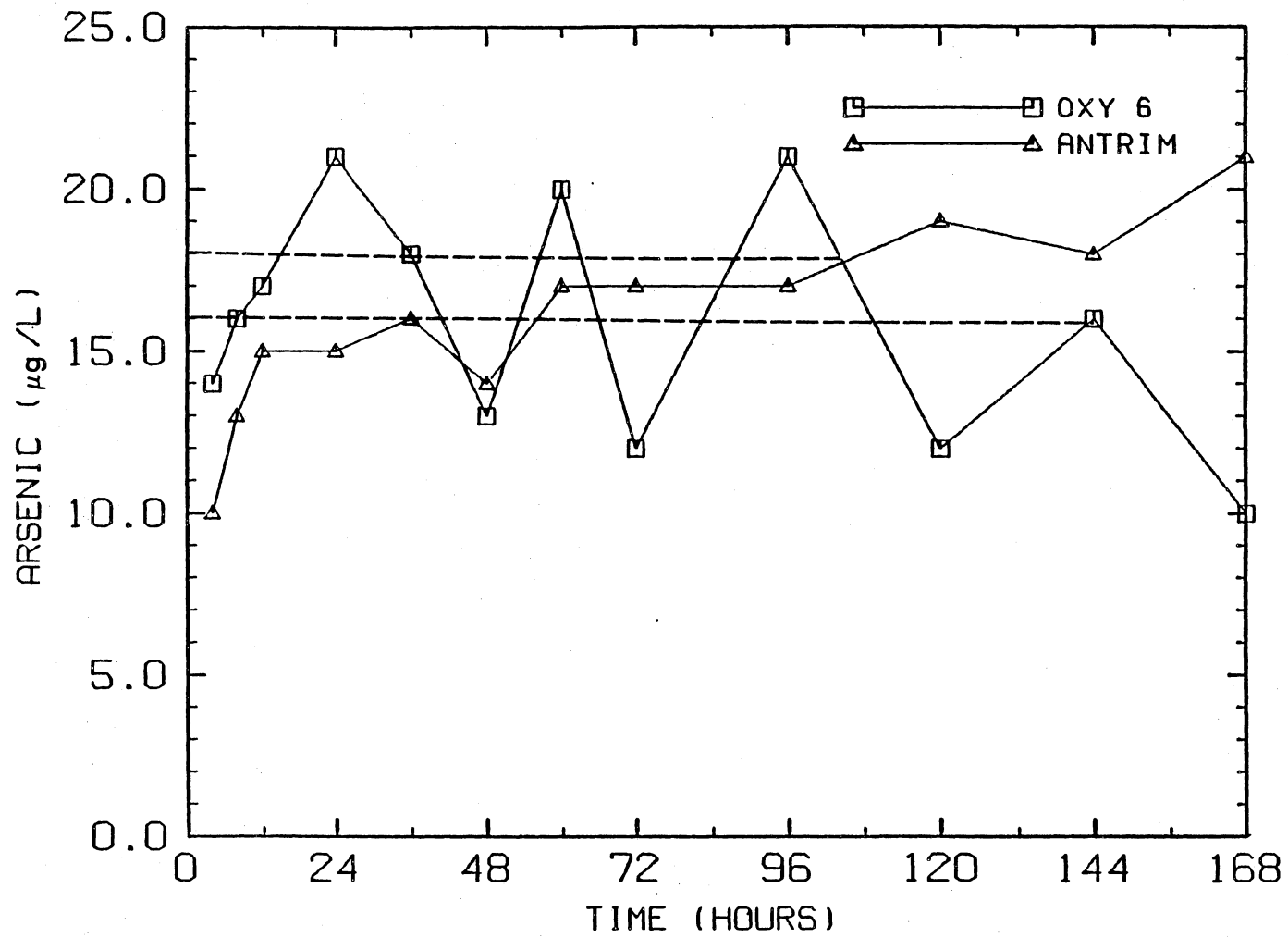


Figure 12. Variation in arsenic of batch eluents for Oxy and Antrim shales. Dashed line represents concentration at equilibrium.

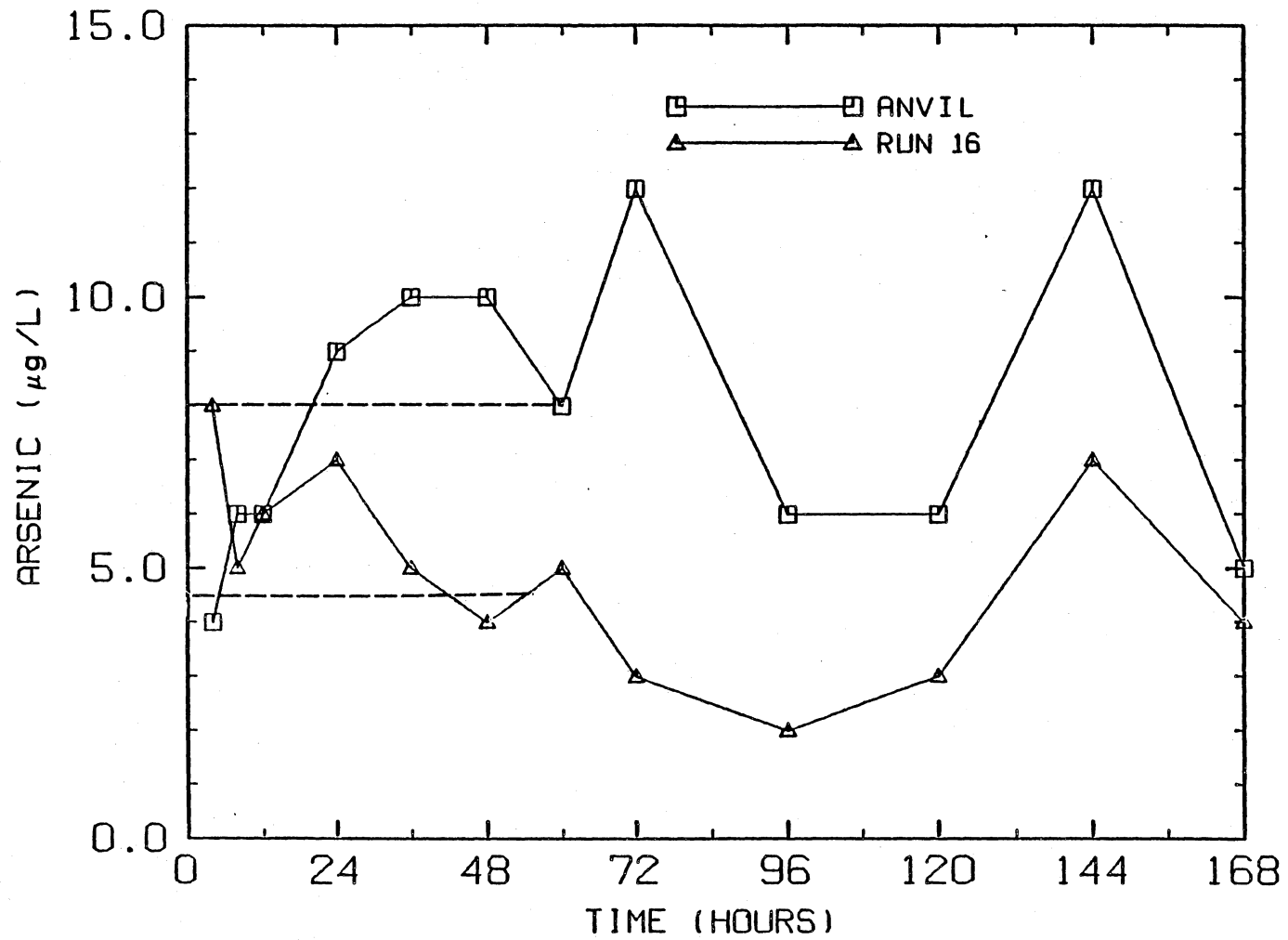


Figure 13. Variation in arsenic of batch eluents for Anvil and Run 16 shales. Dashed line represents concentration at equilibrium.

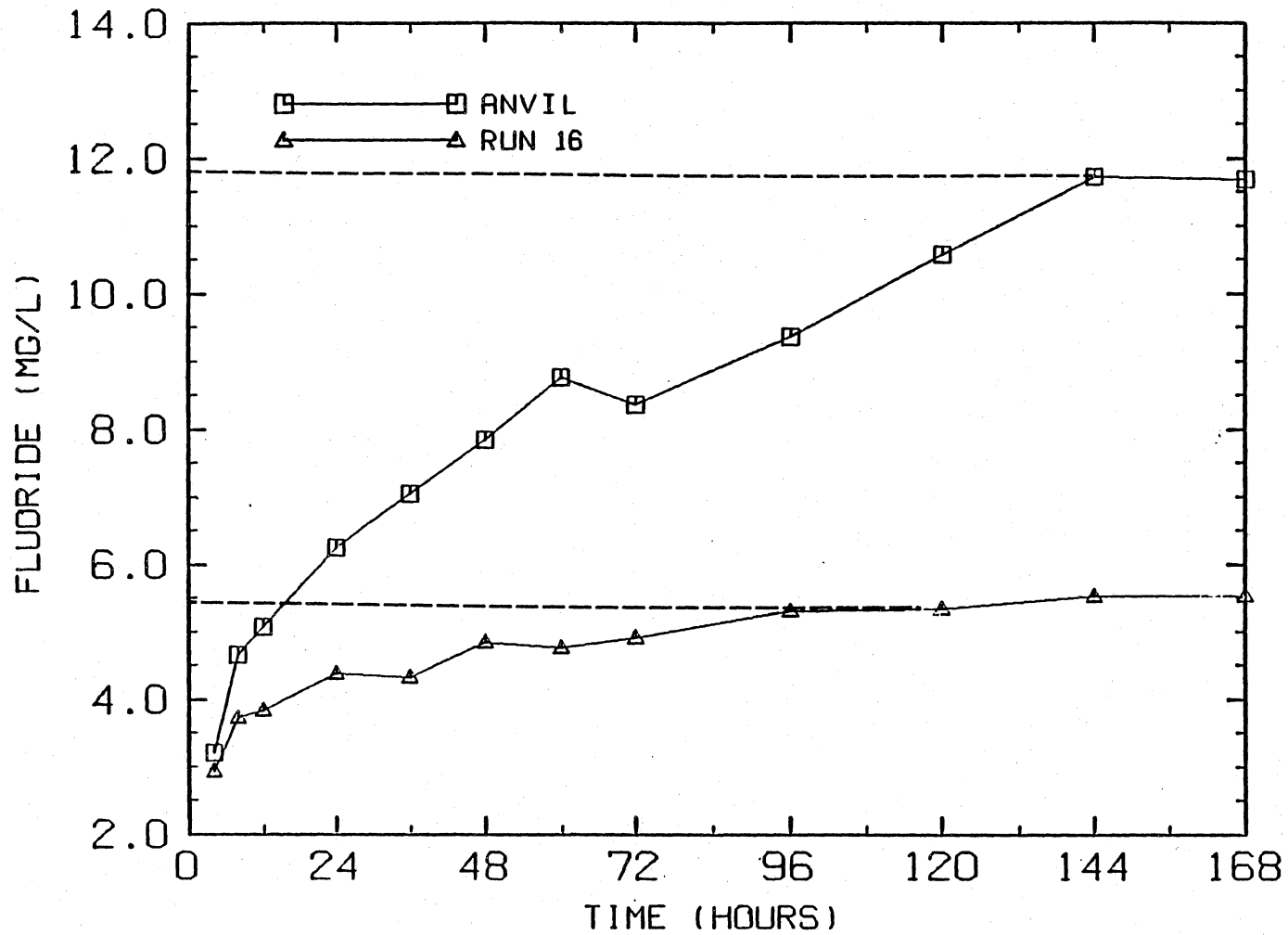


Figure 14. Variation in fluoride of batch eluents for Anvil and Run 16 shales. Dashed line represents concentration at equilibrium.

The purpose of the control test was to illustrate the effect of pH and other leachate constituents on the solubility of the ions of interest in the absence of a solid phase that might act as an adsorbent. Therefore, the concentration of ions in the control flasks represents the amount of ion available for adsorption after other reactions such as precipitation and/or complexation occurred.

The control flask ion concentrations resulted from two sources; those eluted from shale (background level), and the addition of 10 mg/L of a particular ion. As presented earlier in the batch elution section, the background level of constituents was generally insignificant. However, Run 16 and Anvil eluents did contain high background levels of fluoride (Table 16).

Table 17 displays the concentrations (C_{eq}) of the ions studied that were remaining in solution at equilibrium. The concentration of ion adsorbed when C_{eq} was obtained, C_{ad} , was found by simply taking the difference between the amount of ion added (10 mg/L) and that left in solution. In many instances, the ion introduced adsorbed and/or precipitated to such an extent that the concentration left in solution was below the detection limits of the AA instrument. In these cases, the detection limit was reported as C_{eq} along

with the approximate time at which this occurred. Because these values cannot be plotted, there are no graphs showing these data.

Generally, all of the ions except for fluoride were almost completely adsorbed and/or precipitated within 24 hours of the beginning of the experiment. The data obtained from analysis of the arsenic control flasks indicated that arsenic remained soluble in the eluents to a large extent, so reductions in As levels when shale was present were due to association of the ion with the shale (Figure 15). Figure 16 illustrates the amount of arsenic adsorbed by Antrim shale.

The only data collected from cadmium sorption experiments were obtained in the experiments with Oxy shale (Figure 17). After 48 hours, the Cd levels in the adsorption flasks were less than 1.0 mg/L. The pH values increased from 6.6 in the initial sample to 8.2 for the final sample. The control flasks prepared for the Anvil, Antrim and Run 16 shales indicated that the cadmium added was almost completely removed within 24 hours through precipitation. The pH values measured in these flasks were all greater than 7.8. Cadmium levels in the adsorption flasks of these shales were below the detection limits of the AA within 24 hours (≤ 0.005 mg/L). Iron behaved in a

TABLE 17
SUMMARY OF BATCH SORPTION RESULTS

Shale	Parameter											
	Arsenic			Cadmium			Fluoride			Iron		
	¹ C _{eq}	² C _{ad}	³ Time	C _{eq}	C _{ad}	Time	C _{eq}	C _{ad}	Time	C _{eq}	C _{ad}	Time
Anvil												
⁴ 33:1	0.61	9.39	48	⁵ <0.01	⁶ n.a.	24	⁷ n.a.	⁵ n.a.	⁵ n.a.	⁵ <0.03	⁶ n.a.	⁶ n.a.
20:1	0.20	9.80	84	<0.01	n.a.	12	n.a.	n.a.	n.a.	<0.03	n.a.	n.a.
10:1	⁵ <0.01	⁵ n.a.	96	<0.01	n.a.	6	n.a.	n.a.	n.a.	<0.03	n.a.	n.a.
Oxy 6												
33:1	0.32	9.68	75	0.45	9.55	78	9.1	0.7	87	⁵ <0.03	⁶ n.a.	⁶ n.a.
20:1	0.24	9.56	84	0.40	9.60	47	9.2	0.6	87	<0.03	n.a.	n.a.
10:1	0.28	9.54	84	0.30	9.70	24	8.9	0.9	48	<0.03	n.a.	n.a.
Antrim												
33:1	0.20	9.80	9	⁵ <0.01	⁶ n.a.	6	7.0	2.8	32	⁵ <0.03	⁶ n.a.	⁶ n.a.
20:1	0.90	9.10	29	<0.01	n.a.	6	6.1	3.7	73	<0.03	n.a.	n.a.
10:1	0.80	9.20	78	<0.01	n.a.	6	4.4	5.4	24	<0.03	n.a.	n.a.
Run 16												
33:1	0.20	9.80	50	⁵ <0.01	⁶ n.a.	6	9.4	0.4	45	⁵ <0.03	⁶ n.a.	⁶ n.a.
20:1	0.15	9.85	50	<0.01	n.a.	3	9.5	0.3	21	<0.03	n.a.	n.a.
10:1	0.10	9.90	50	<0.03	n.a.	3	9.1	0.7	32	<0.03	n.a.	n.a.

- | | |
|--|--|
| 1. Concentration (mg/L) in solution at equilibrium | 5. Detection limit of AA for that ion |
| 2. Amount of ion adsorbed at C _{eq} (mg/L) | 6. Not applicable |
| 3. Approximate time of C _{eq} + C _{ad} (hours) | 7. No sorption occurred;
background levels were eluted. |
| 4. Water-to-shale ratio | |

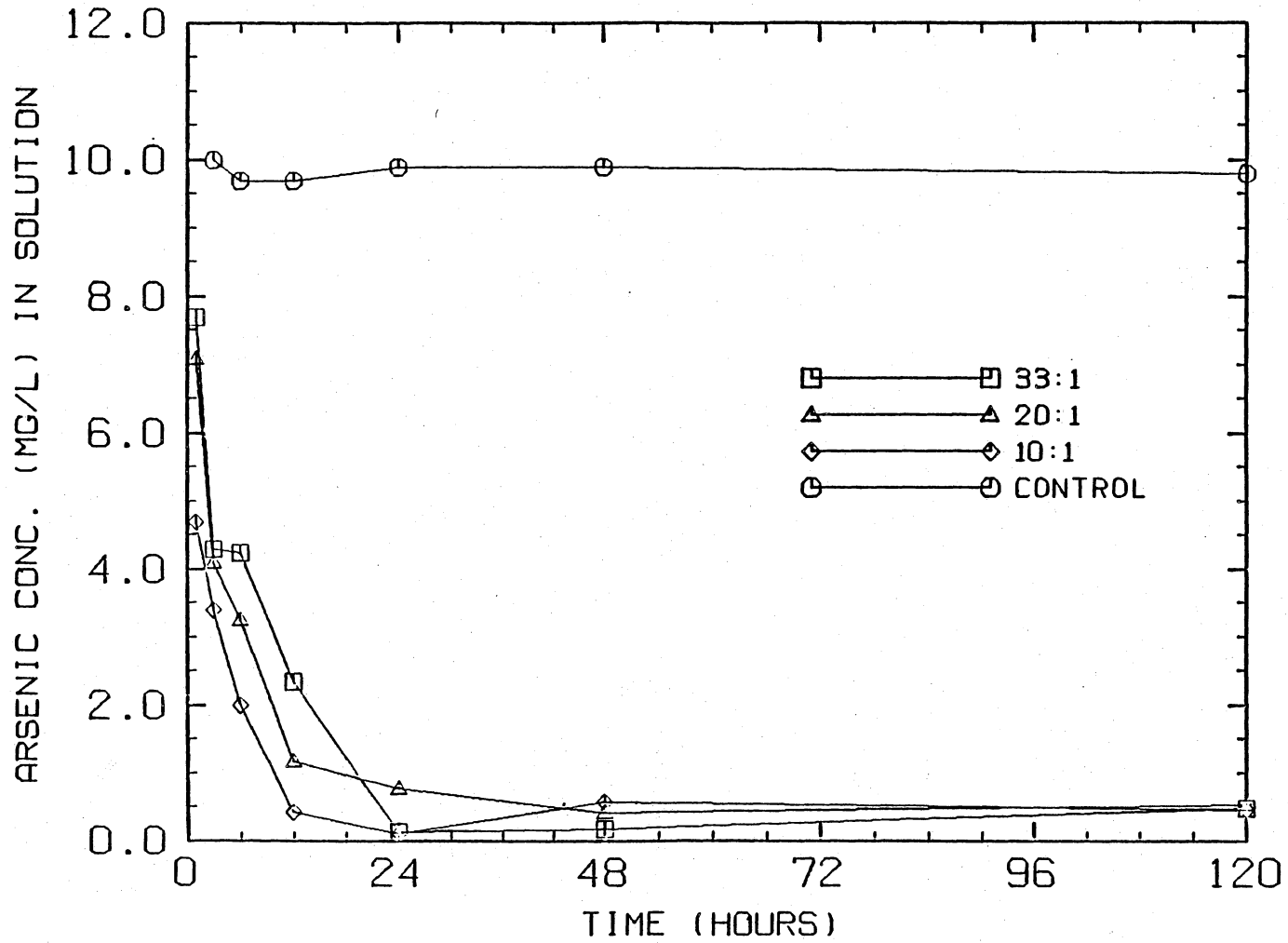


Figure 15. Comparison of arsenic concentrations remaining in solution during the batch sorption and control experiments with Oxy spent shale.

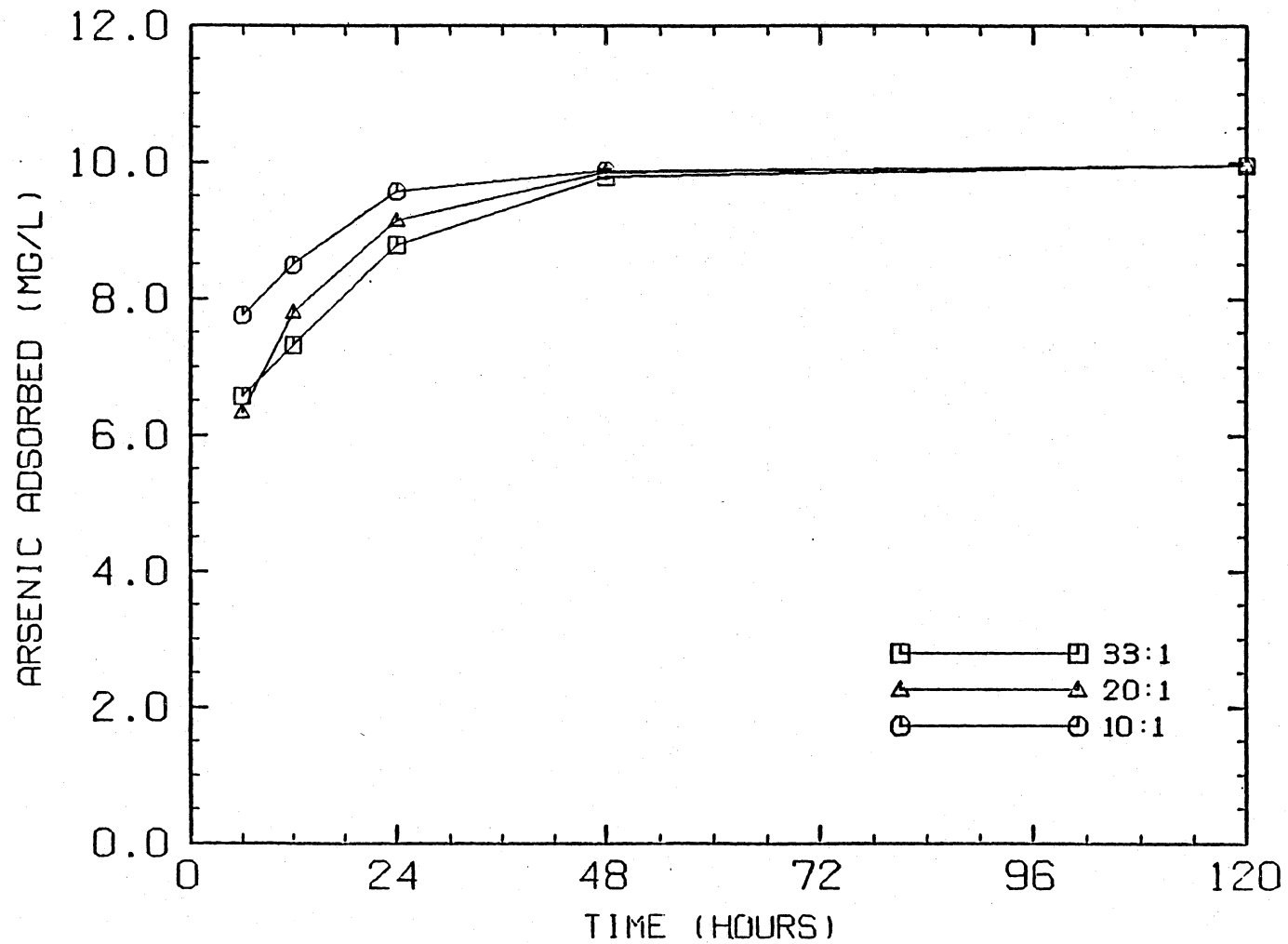


Figure 16. Arsenic adsorbed as a function of time for three liquid-to-solid ratios of water to Run 16 spent shale.

similar way. Generally this ion was completely removed from solution in the control and adsorption flasks within three to six hours.

Oxy and Anvil shales did not adsorb fluoride. High levels of fluoride eluted from the Anvil shale and contributed to the fluoride that had been added to the water (Figure 18). Oxy and Run 16 spent shales removed less than 1.0 mg/L fluoride from solution (Table 17). Run 16 shale eluted approximately 5 mg/L in the control flask; however, this background level of fluoride did not contribute to the fluoride level in the batch adsorption flask, as it did in the Anvil shale sorption flasks. Figure 20 illustrates fluoride adsorption on Antrim shale for the three L:S ratios. The flask containing the greatest amount of shale (15 g, 10:1) adsorbed the most fluoride, approximately 5.5 mg/L.

COLUMN ELUTION RESULTS

The continuous-flow elution experiments provided information about the background levels of inorganics expected to elute during column adsorption studies and the peak background levels of inorganics that might be anticipated. Appendix C contains equilibrium isotherms of the parameters monitored. Representative graphs are

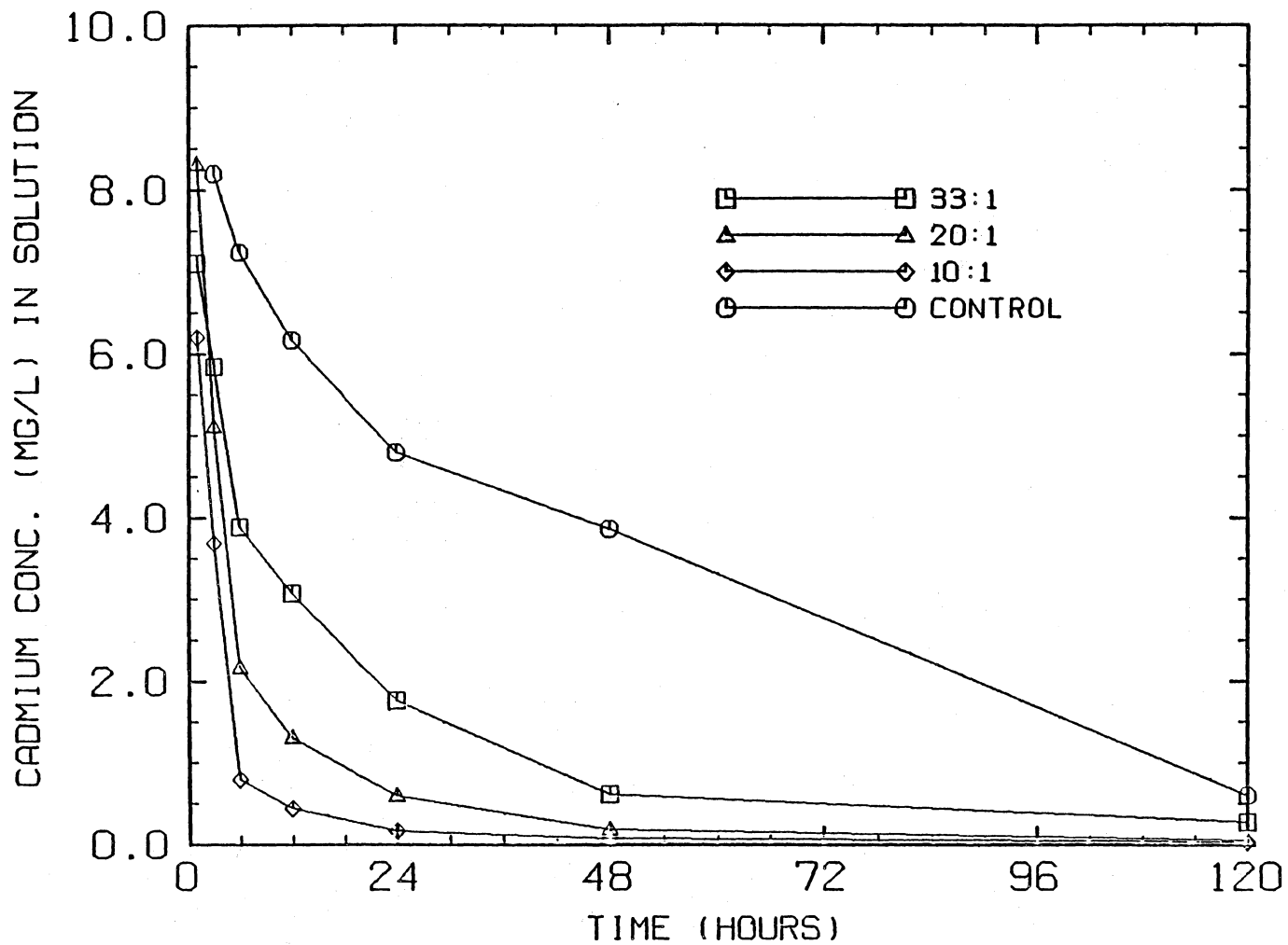


Figure 17. Comparison of cadmium concentrations remaining in solution during the batch sorption and control experiments with Oxy spent shale.

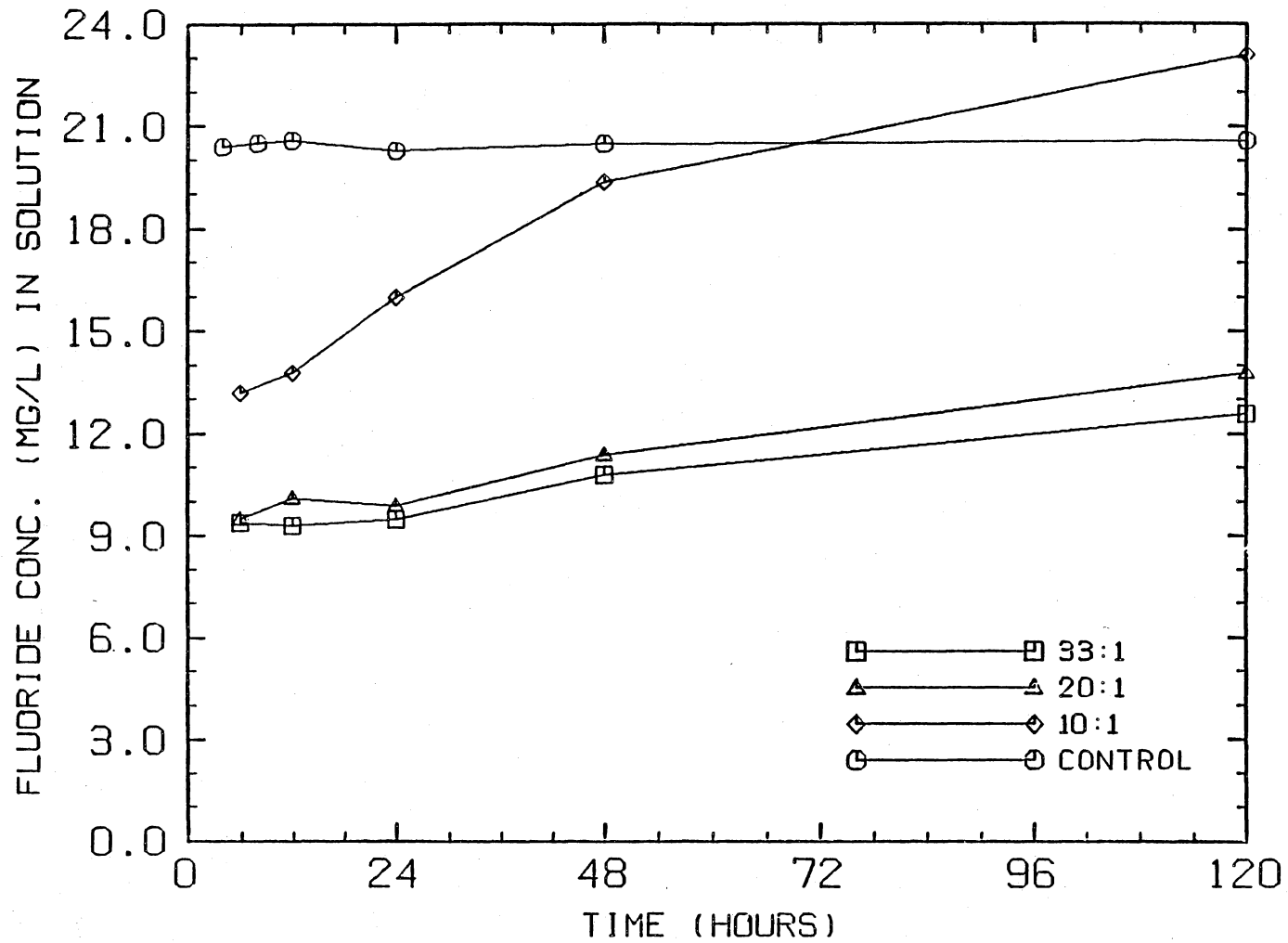


Figure 18. Comparison of fluoride concentrations remaining in solution during the batch sorption and control experiments with Anvil raw shale.

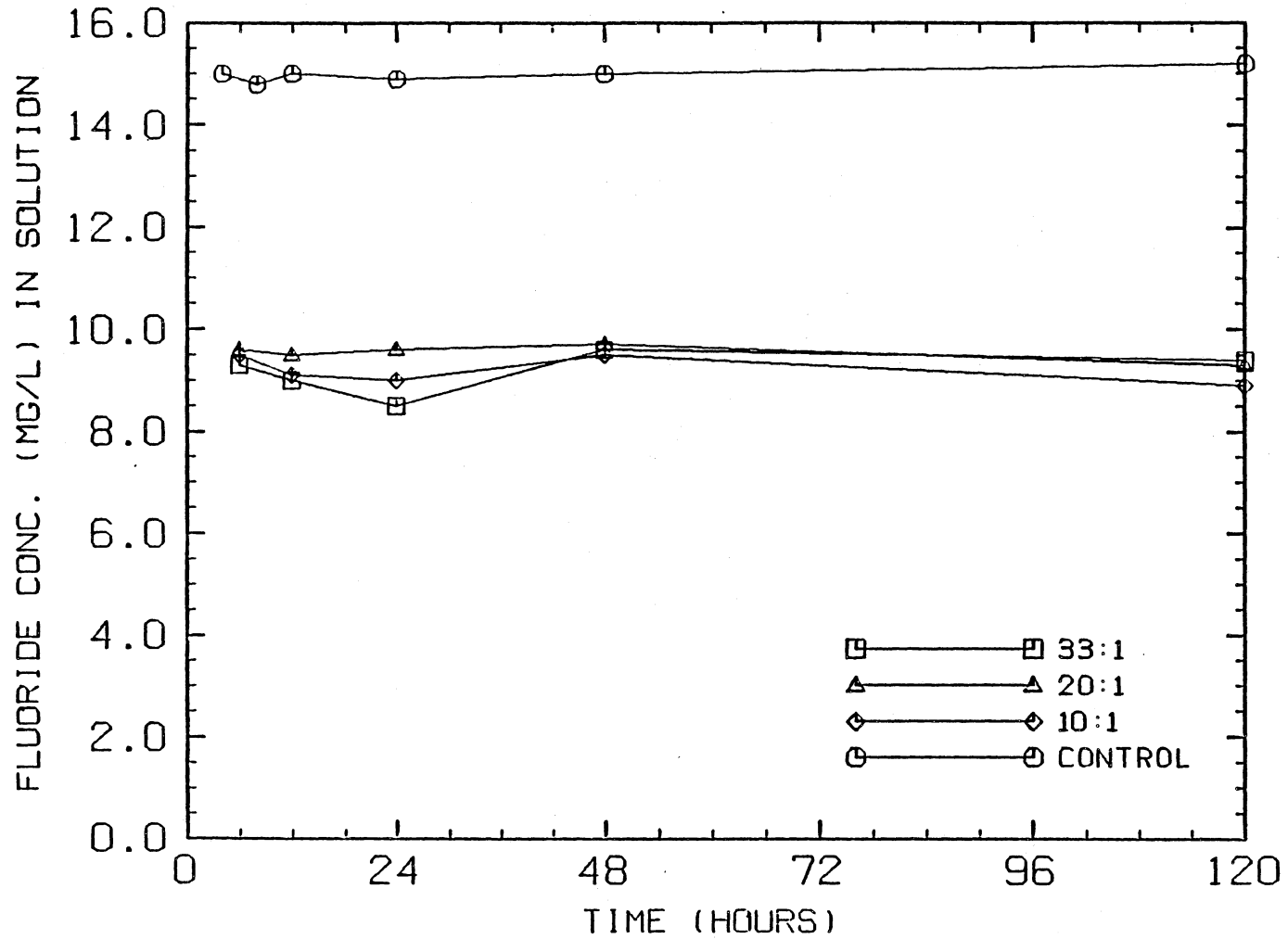


Figure 19. Comparison of fluoride concentrations remaining in solution during the batch sorption and control experiments with Run 16 spent shale.

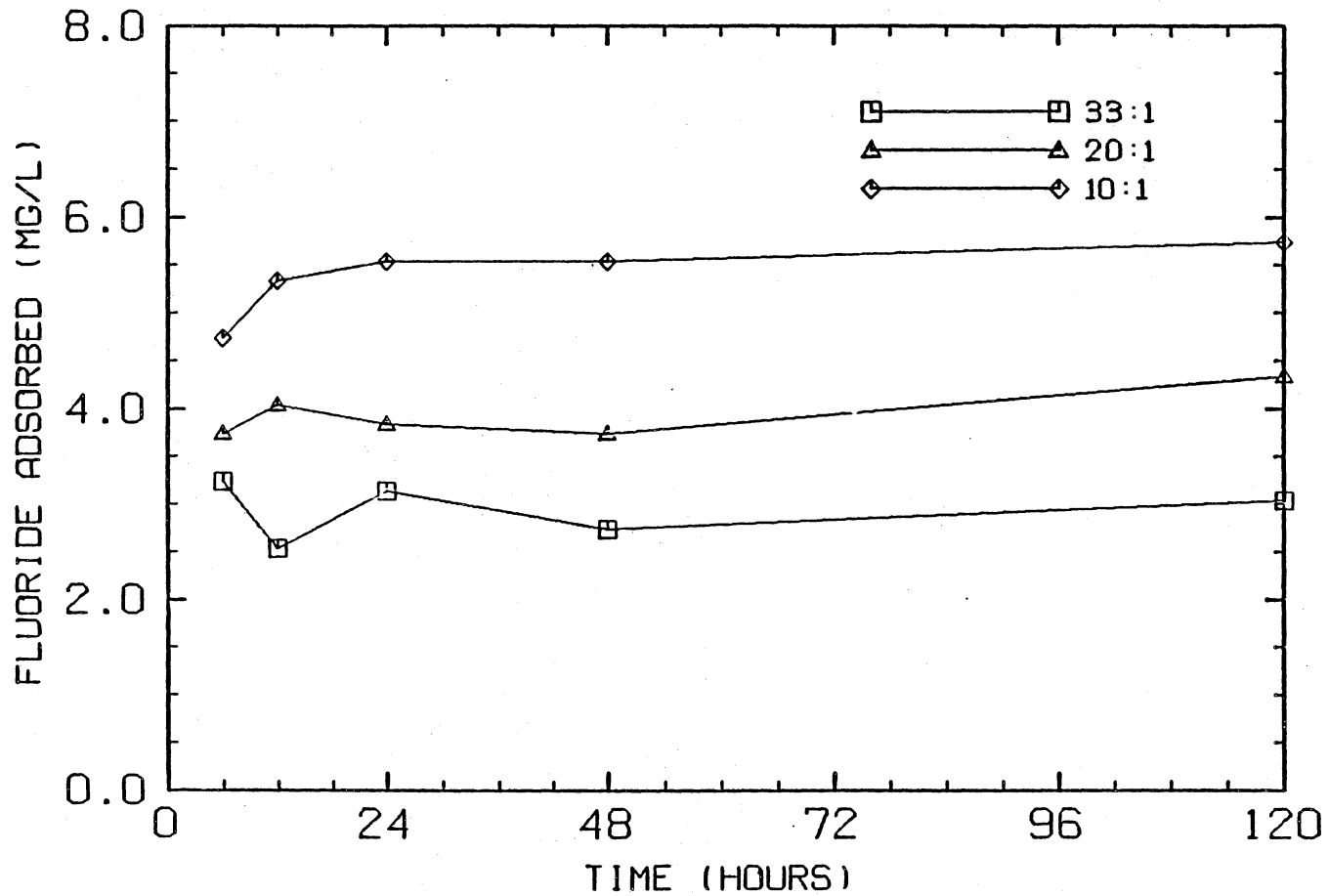


Figure 20. Fluoride adsorbed as a function of time for three liquid-to-solid ratios of water to Antrim spent shale.

included in the text of this section. Triplicate elution experiments were performed with each shale, so each figure contains three curves. Table 18 contains the equilibrium values of each variable measured and the pore volume at which this concentration occurred.

Upon examination of the graphs, it is evident that most of the inorganics were flushed out of the column by the passage of 5 to 8 pore volumes of distilled water through the column. The peak concentrations measured and the corresponding pore volumes were therefore also included in Table 18. Iron, cadmium and arsenic were below detection limits on the AA for many of the samples collected during the 48 hour elution period, so it was not possible to graph these results. However, in some cases the peak concentration was measurable and these values were included in Table 18.

Peak arsenic levels in the eluents from the columns containing Oxy, Antrim, Run 16 and Anvil shales, respectively, were as follows: 106, 38, 26 and 11 $\mu\text{g/L}$. Cadmium levels in all effluents were below detection; i.e., $\leq 5 \mu\text{g/L}$. Anvil, Oxy and Antrim eluents contained maximum concentrations of 0.11, 0.06 and 2.18 mg/L iron, respectively. Run 16 eluents contained no more than 0.05 mg/L Fe (Table 18).

TABLE 18
SUMMARY OF COLUMN ELUTION EQUILIBRIUM ISOTHERMS

Shale	Parameter										
	¹ Alk	² As	³ Ca	⁴ Cd	⁵ Con	⁶ F	⁷ Fe	pH	⁸ K	⁹ RP	¹⁰ SO ₄
Anvil											
¹¹ C _{eq}	25	21	4.9	5.0	120	1.5	0.02	9.0	0.6	170	120
¹² PV _{eq}	63	7.0	59	¹³ n.a.	14	1.9	11	70	42	14	27
¹³ C _p	225	11	8	n.a.	3240	6.5	0.11	9.4	5.8	n.a.	690
¹⁴ PV _p	2.1	1.0	1.1	n.a.	1.2	2.4	1.0	76	1.2	n.a.	2.4
Oxy 6											
¹¹ C _{eq}	26	10	4.1	5.0	53	0.19	0.02	9.2	0.9	125	125
¹² PV _{eq}	36	35	66	n.a.	25	36	5	50	38	27	35
¹³ C _p	231	106	4.2	n.a.	1190	1.1	0.06	10.1	3.3	n.a.	500
¹⁴ PV _p	2.2	1.1	71	n.a.	1.1	2.1	1	2.2	1.1	n.a.	1.9
Antrim											
¹¹ C _{eq}	21.0	30	14.0	5.0	90	0.25	0.02	9.3	8.9	-58	175
¹² PV _{eq}	55	30	50	n.a.	36	61	15.0	61	8	60	23
¹³ C _p	50	38	596	n.a.	12000	0.98	2.18	9.7	494	n.a.	4020
¹⁴ PV _p	1.9	40	2.8	n.a.	0.9	7.7	0.9	66	0.9	n.a.	2.0
Run 16											
¹¹ C _{eq}	212	5	85	5.0	575	1.7	0.05	11.2	4.4	-27	510
¹² PV _{eq}	55	28	45	n.a.	52	62	n.a.	43	30	44	37
¹³ C _p	235	26	578	n.a.	7100	9.4	n.a.	11.4	220	n.a.	2390
¹⁴ PV _p	35	0.9	0.8	n.a.	0.9	1.7	n.a.	25	0.9	n.a.	1.7

1. Alkalinity as mg/L CaCO₃ 5. Conductivity μ mhos/cm 9. Redox Potential (mv) 13. Peak conc. during elution
 2. Arsenic, μ g/L 6. Fluoride, mg/L 10. Sulfate, mg/L 14. Pore volume at C_p
 3. Calcium, mg/L 7. Iron, mg/L 11. Conc. at equilibrium 15. Not applicable^P
 4. Cadmium, μ g/L 8. Potassium, mg/L 12. Pore volume at C_{eq}

The behavior of pH was generally the same as in the batch experiment; i.e., the pH of Oxy and Anvil effluents tended to decrease during the elution period, while it increased in Run 16 experiments. Antrim shale eluents had fairly low pH values of 7.0 to 7.5 in the first 18 pore volumes. However, the pH increased sharply in the following 10 pore volumes and the final pH values were in the area of 9.3 (Figure 21).

As mentioned previously, most of the inorganic constituents in shale columns were flushed out in the first 5 to 8 pore volumes, depending on the shale and the parameter measured (Appendix C). There were a few interesting cases in which this behavior was not displayed. For example, alkalinity reached a relatively constant, equilibrium value for all shales except Run 16 where alkalinity values increased initially to 225 mg/L, then decreased to approximately 175 mg/L at 40 pore volumes, after which values increased again to 225 mg/L (Figure 22). This behavior was similar to that described in batch elution experiments.

Elution of calcium from Anvil and Oxy shales was unusual in that following the initial flush of Ca in the first three pore volumes ($C_p = 8$ and 1.8 mg/L, respectively, Table 18) an equilibrium state was not established (Figures

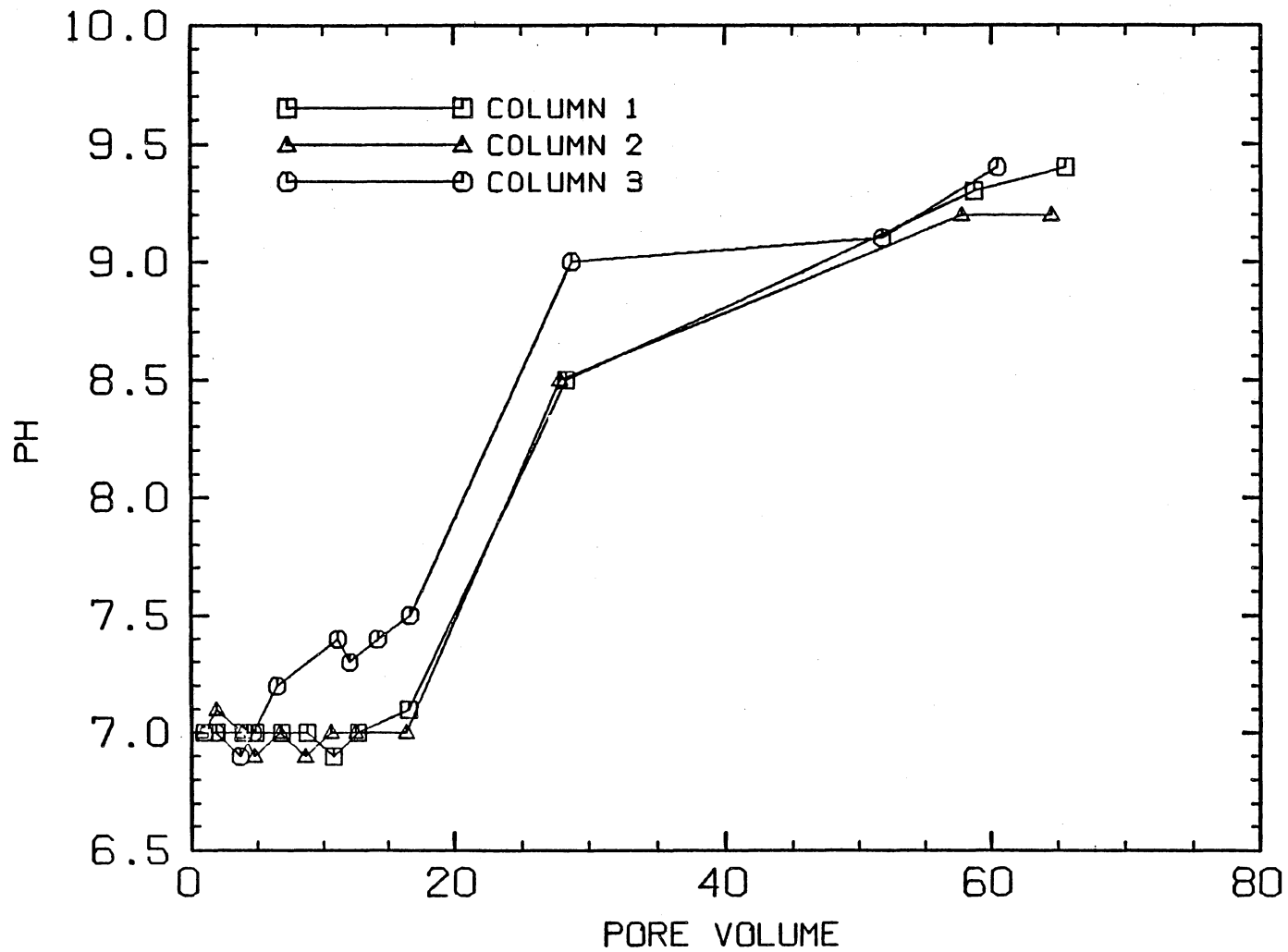


Figure 21. Variation in pH during column elution of Antrim spent shale.

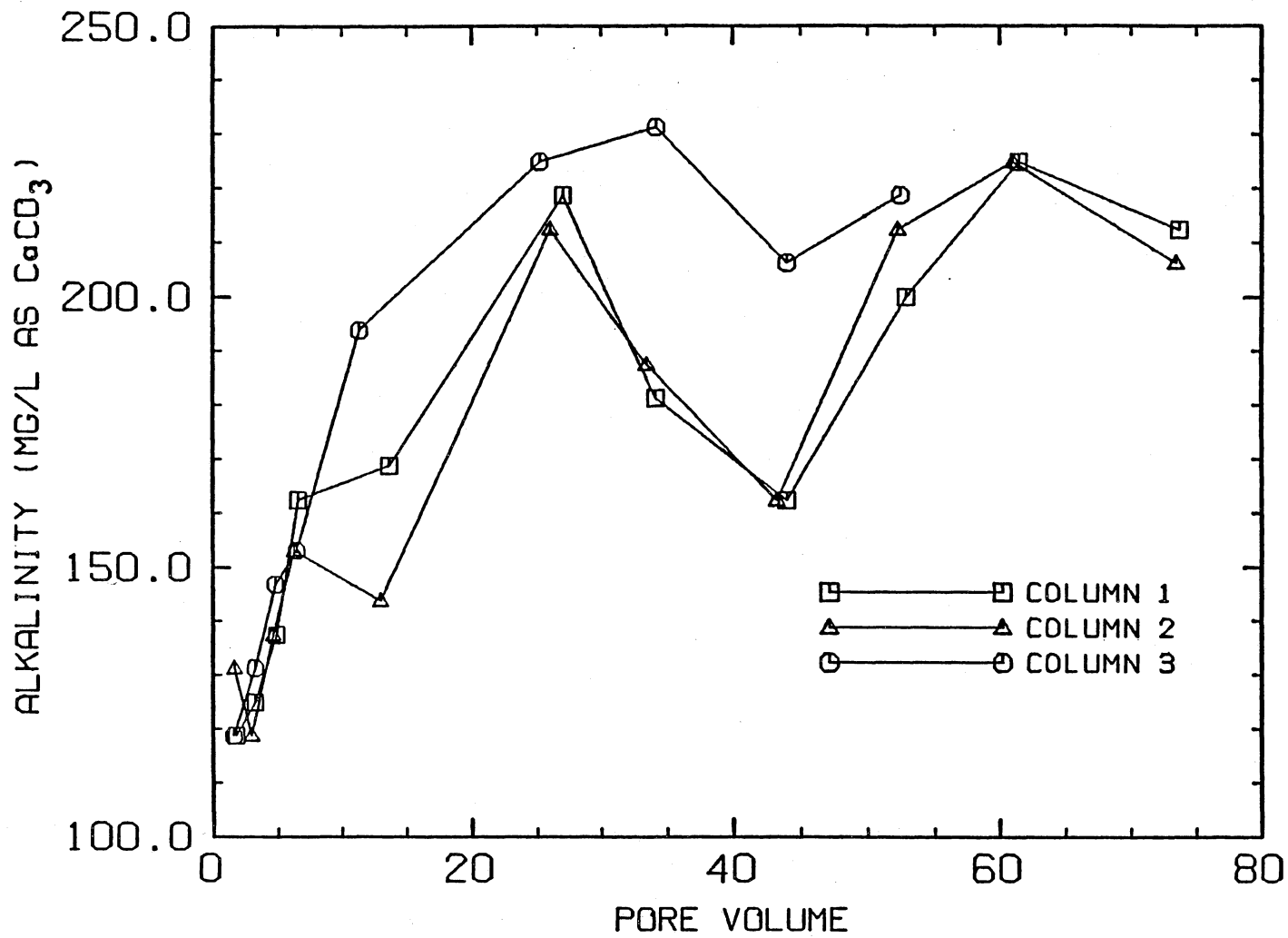


Figure 22. Variation in alkalinity during column elution of Run 16 spent shale.

23 and 24). Instead, Ca levels increased gradually to approximately 5 mg/L. Antrim and Run 16 shales did not display this behavior but eluted similar amounts of calcium with peak concentrations of 596 and 578 mg/L, respectively (Figures 25 and 26). There was, however, a slight lag period before the effluent exhibited these peak levels, after which time the Ca was uniformly eluted to equilibrium concentrations.

Fluoride elution from Antrim shale was unlike that seen for the other shales in that flushing occurred in the first couple of pore volumes (Figure 27). As in the case of Ca, fluoride levels increased initially to a peak concentration of 0.98 mg/L before decreasing uniformly to equilibrium of 0.25 mg/l.

Antrim and Run 16 shales produced eluents with much higher potassium levels than the other two shales. The peak concentrations flushed from Anvil and Oxy shale columns were less than 5.8 mg/L, while Antrim and Run 16 shales eluted peak concentrations of 490 and 270 mg/L, respectively (Table 18).

Maximum sulfate levels in Oxy and Anvil eluents were 500 and 690 mg/L, respectively. These values were greatly exceeded by the levels flushed from Antrim ($C_p = 4060$ mg/L) and Run 16 shales ($C_p = 2390$ mg/l). After the initial flush,

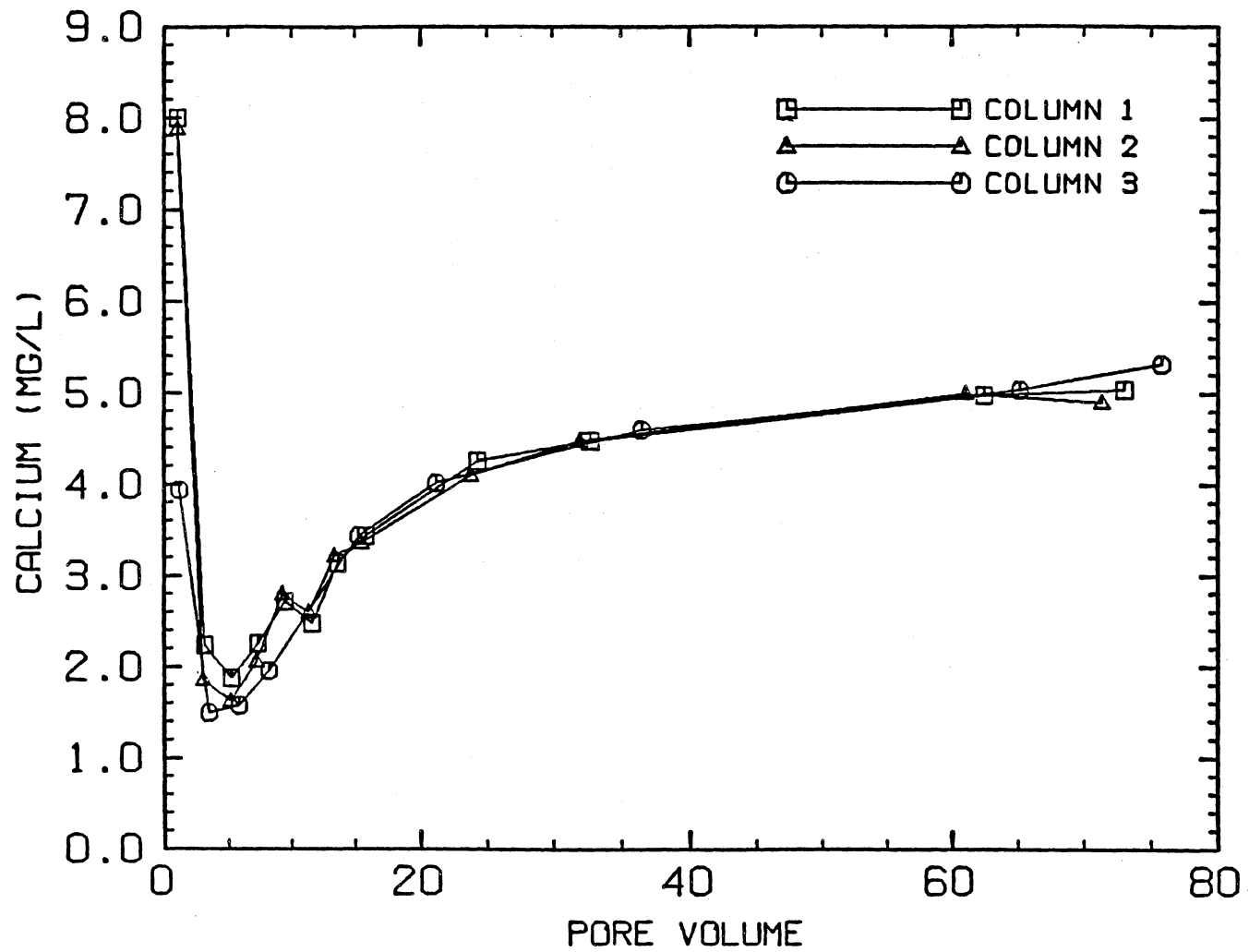


Figure 23. Variation in calcium during column elution of Anvil raw shale.

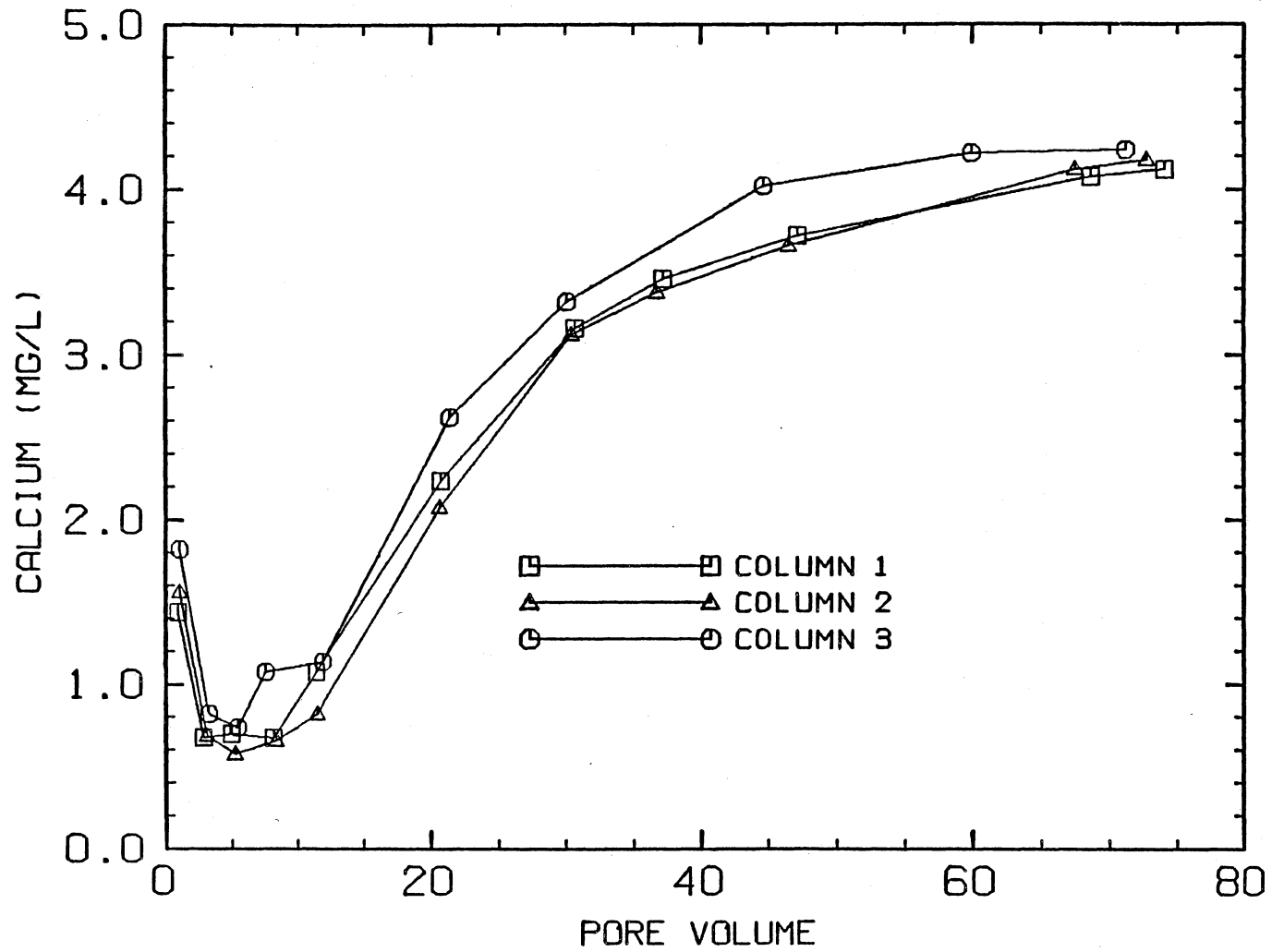


Figure 24. Variation in calcium during column elution of Oxy spent shale.

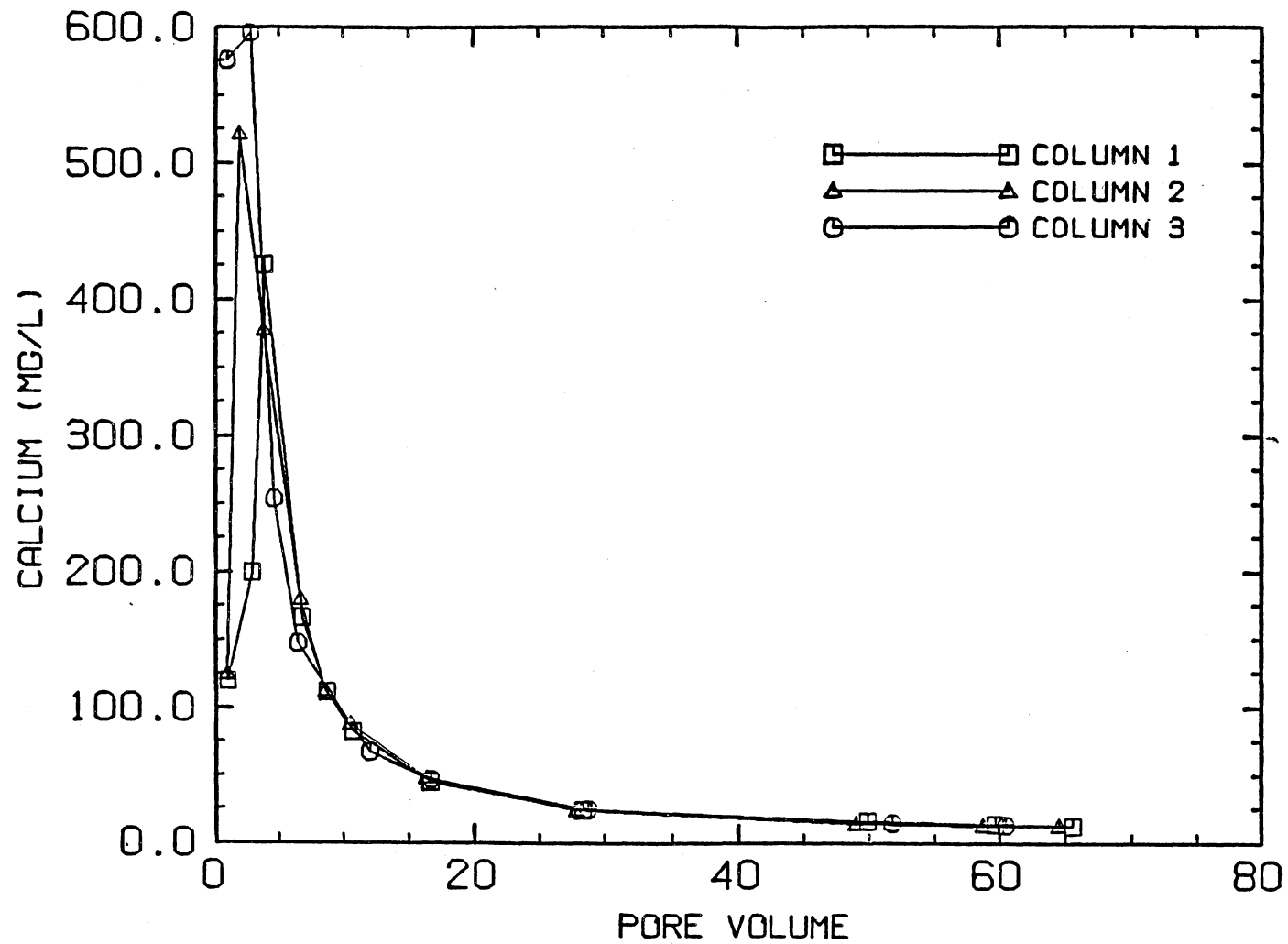


Figure 25. Variation in calcium during column elution of Antrim spent shale.

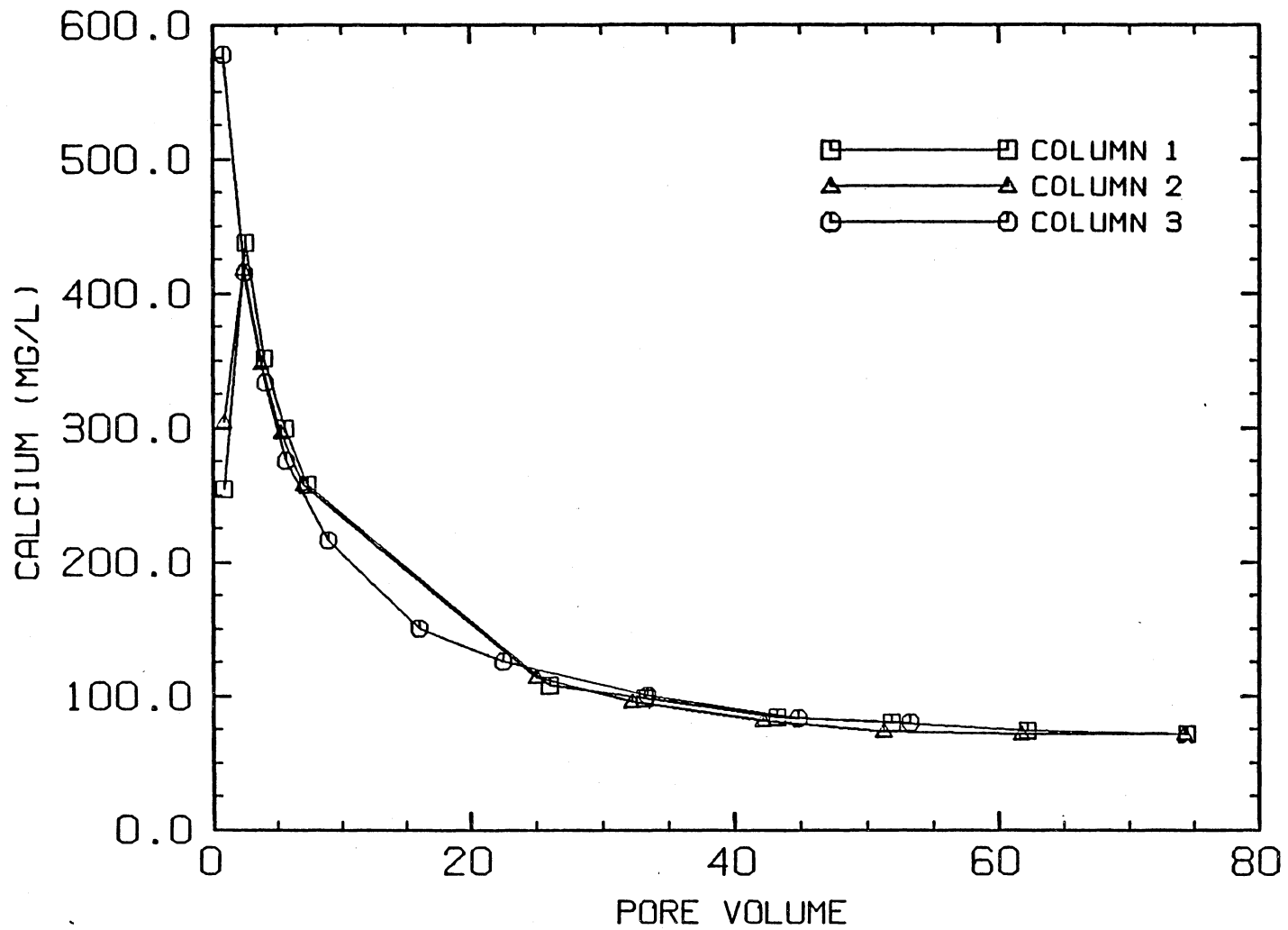


Figure 26. Variation in calcium during column elution of Run 16 spent shale.

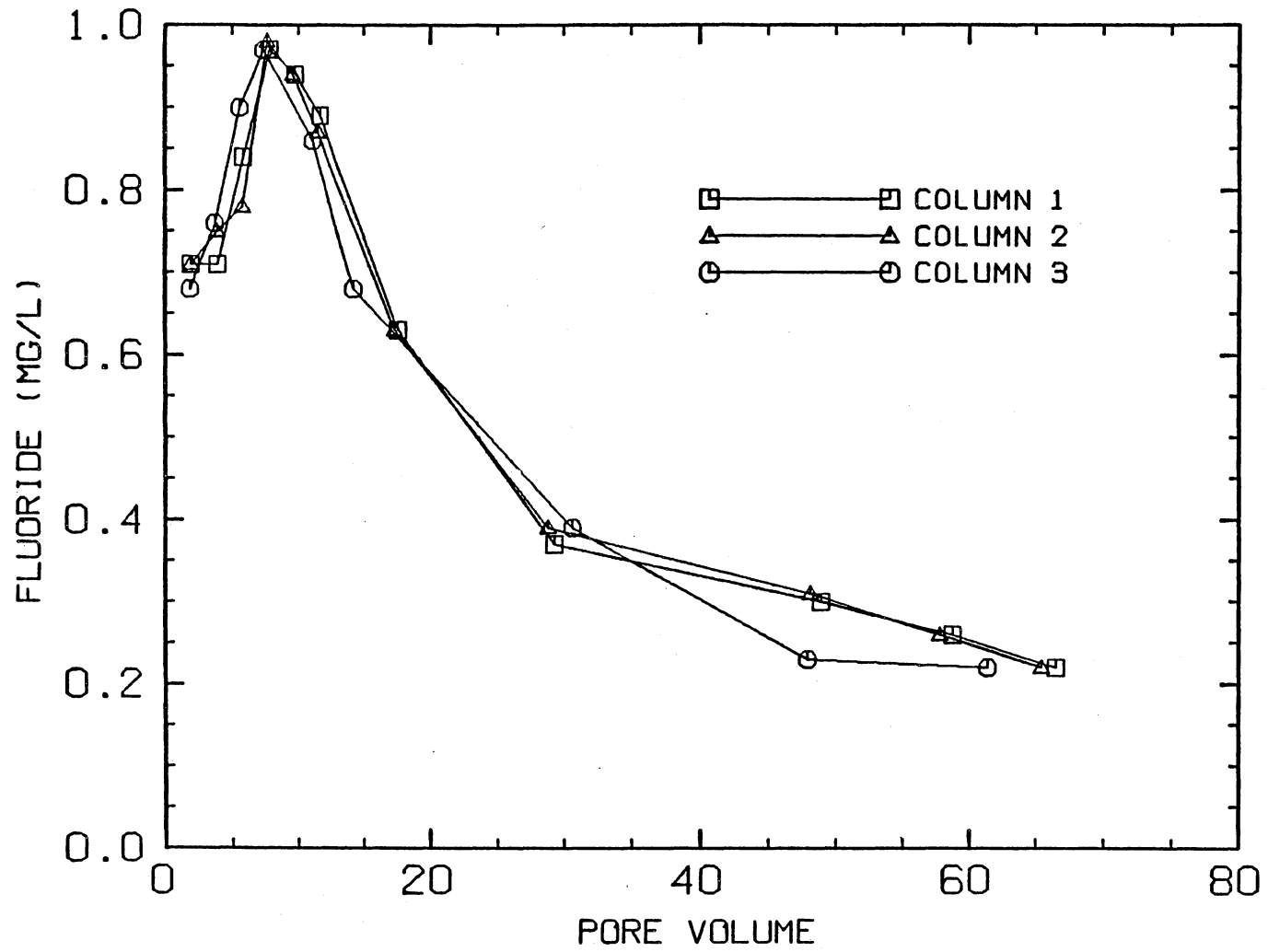


Figure 27. Variation in fluoride during column elution of Antrim spent shale.

elution of K and SO₄ continued at much lower levels (less than 500 mg/L SO₄ and 10 mg/l K, Appendix C).

Peak conductivity values of Antrim and Run 16 eluents were 12,000 and 7,100 μ mhos/cm, respectively. As in the batch elution trials, Anvil and Oxy shales produced eluents having much lower conductivities ($C_p = 3,240$ and 1,190 μ mhos/cm, respectively) than the former shale eluents. Conductivity values decreased to equilibrium values within 5 to 8 pore volumes (Appendix C).

Measurements of redox potential indicated that the aqueous conditions of the column eluents were similar to those of the batch experiments. Antrim and Run 16 eluents exhibited negative redox potentials ranging from 0 to -100 mv. The first 10 and 20 pore volumes of effluent from Run 16 and Antrim shale columns, respectively, exhibited positive redox potentials ranging from 0 to 175 mv. Anvil and Oxy eluents were positive throughout the trials, ranging from 100 to 200 mv (Appendix C).

SINGLE ION COLUMN ADSORPTION/DESORPTION

The adsorption data are presented herein as breakthrough curves where the concentrations of ions (Y) in the effluent from the column are plotted as a function of the pore volumes (X). Pore volumes of the four shales

ranged from 37 to 56 mL. This volume represented the void space in a 2.6 by 15 cm column of approximately 100 g of shale. Each graph is accompanied by one showing the desorption results. Recall that desorption experiments were performed immediately after the adsorption trials.

Table 19 contains the breakthrough values and equilibrium concentrations of the ions studied. Defining a consistent "breakthrough value" to report in the table of results was difficult because in many of the trials, the shales exhibited a very slight capacity for adsorption of the ions. In cases where adsorption resulted in almost complete removal of solute in the initial pore volumes, the breakthrough pore volume reported was that at which the concentration of ion in the effluent was approximately 1 mg/L. Breakthrough values reported for ions which were minimally adsorbed, were the ion levels in the initial to third pore volumes.

Iron and cadmium never reached breakthrough in the 48-hour adsorption period. The concentration of these ions in effluents from the columns was generally below detection with the AA; i.e., the detection (Fe, 0.05 mg/L; Cd, 0.005 mg/L).

Run 16 spent shale showed the greatest capacity for adsorption of arsenic. Arsenic levels in the effluent were

TABLE 19
SUMMARY OF SINGLE ION COLUMN ADSORPTION DATA

Shale	As	Ca	Parameter		Cd	Fe
			F	K		
Anvil						
¹ C _F	10.2	9.1	10.2	9.6	10.1	10.1
² C _{eq}	9.2	11.4	⁵ n.a.	7.7	n.a.	n.a.
³ PV _{eq}	47	50	n.a.	49	n.a.	n.a.
⁴ PV _b	3.5	15	n.a.	8	n.a.	n.a.
Oxy 6						
C _F	10.2	9.1	10.2	9.6	10.1	10.1
C _{eq}	9.0	9.6	n.a.	6.9	n.a.	n.a.
PV _{eq}	41	70	n.a.	32	n.a.	n.a.
PV _b	1.2	28	n.a.	12	n.a.	n.a.
Antrim						
C _F	9.8	⁶ -	9.7	⁶ -	10.2	16.8
C _{eq}	7.7	-	9.5	-	n.a.	n.a.
PV _{eq}	60	-	29	-	n.a.	n.a.
PV _b	18	-	5	-	n.a.	n.a.
Run 16						
C _F	9.8	-	9.5	-	10.2	16.8
C _{eq}	2.4	-	9.5	-	n.a.	n.a.
PV _{eq}	65	-	11.0	-	n.a.	n.a.
PV _b	35	-	1.0	-	n.a.	n.a.

1. Concentration of ion in feed solution, mg/L
2. Concentration of ion at equilibrium, mg/L
3. Pore volumes of that shale at C_{eq}
4. Pore volumes at breakthrough
5. Not applicable
6. Adsorption with this ion not performed

approximately 2 mg/L at the end of the sorption period. Antrim shale also exhibited an affinity for arsenic, reaching breakthrough at approximately 15 pore volumes, while Anvil and Oxy shales exhibited a small capacity for adsorption of this ion (Figure 28). Arsenic levels in the first five pore volumes of effluent from these shales ranged from 5 to 8.5 mg/L. By the time 10 to 15 pore volumes had passed through, the concentrations was leveling off at 9 mg/L. Desorption with distilled water resulted in peak As levels of 14 and 8 mg/L respectively, in the Antrim and Anvil eluents. These levels were approximately 2 and 5 mg/L in the Run 16 and Oxy eluents, respectively. For all of the shales, arsenic levels were less than 2 mg/L after five pore volumes of distilled water had passed through the columns (Appendix D).

As discussed in the Materials and Methods, Antrim and Run 16 shales were not subjected to Ca and K sorption experiments due to the high background levels of these ions released in the batch and column eluents. The first pore volumes from Oxy and Anvil shales yielded the following peak concentrations: 2 and 5 mg/L K and 1.8 and 10 mg/L Ca for Oxy and Anvil shales, respectively (Figures 29 and 30). Adsorption of Ca and K followed this initial flush and continued for 10 to 15 pore volumes. Note that the

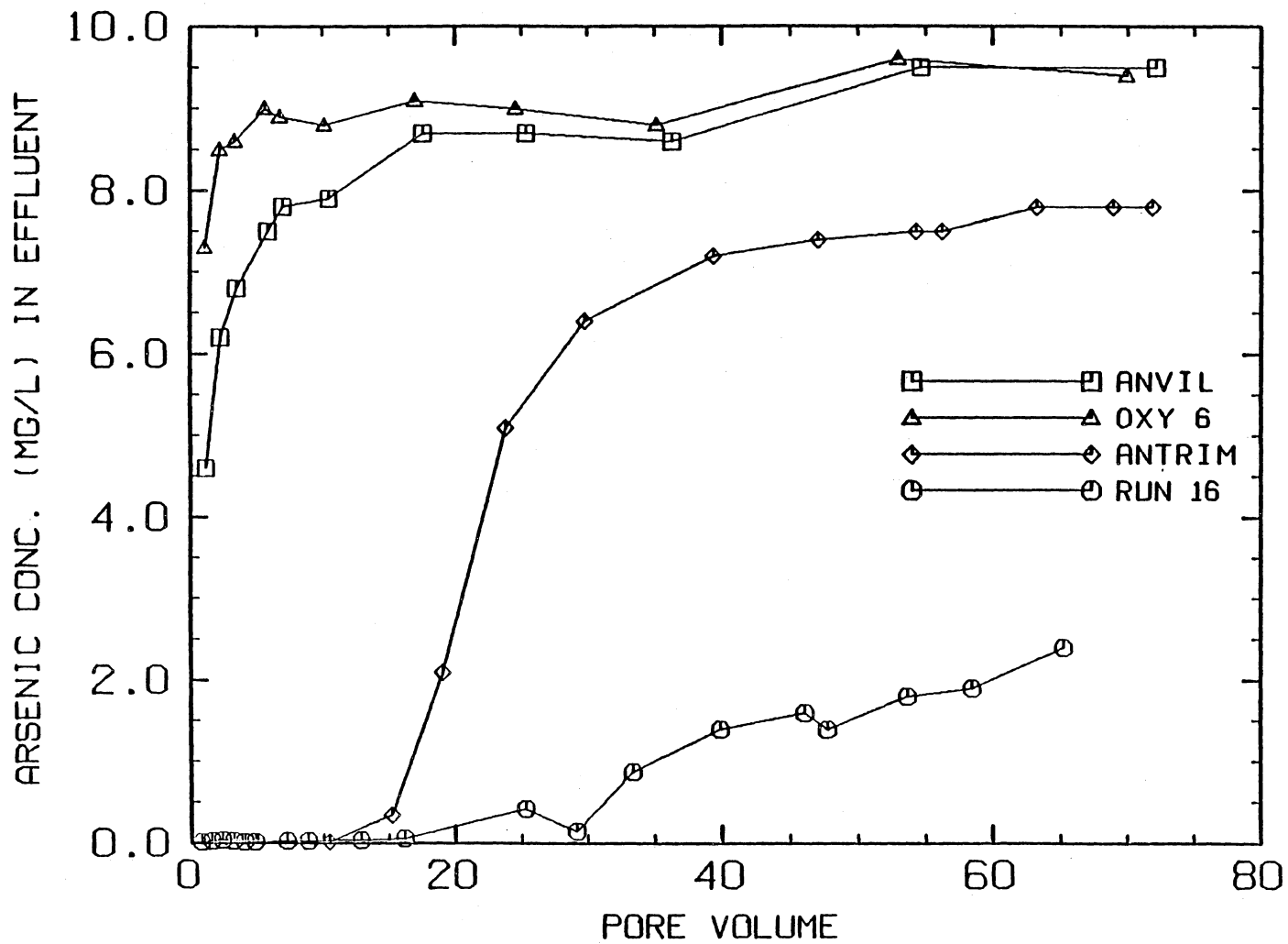


Figure 28. Breakthrough curves for arsenic in column adsorption experiments with various shales.

equilibrium concentration of Ca in Anvil eluents was approximately 1.0 mg/L greater than the feed solution (Table 19).

Desorption of Ca from Oxy and Anvil shales was interesting in that after the initial flush, ($C_p = 4.5$ and 7.5 mg/L, respectively), the effluent concentration increased rather than decreased, as was seen in desorption studies involving other ions. Ca concentrations increased to 8 and 4.7 mg/L in the Anvil and Oxy effluents, respectively (Figure 31). Both shales exhibited uniform desorption of K to a concentration less than 2 mg/L after the initial flush.

Fluoride levels in the first pore volumes of effluent from the Anvil and Oxy shale columns were 22 and 13 mg/L, respectively (Figures 32 and 33). These levels decreased to approximately 10 mg/L, which was roughly the feed concentration (Table 19). Antrim spent shale displayed an affinity for fluoride; breakthrough occurred at approximately five pore volumes (Figure 33). Run 16 shale seemed to have much poorer capacity to adsorb fluoride; breakthrough occurred within the first pore volume. The distilled water desorption of fluoride indicated fluoride eluted from all four shales to concentrations less than 3 mg/L after 5 to 10 pore volumes (Appendix D).

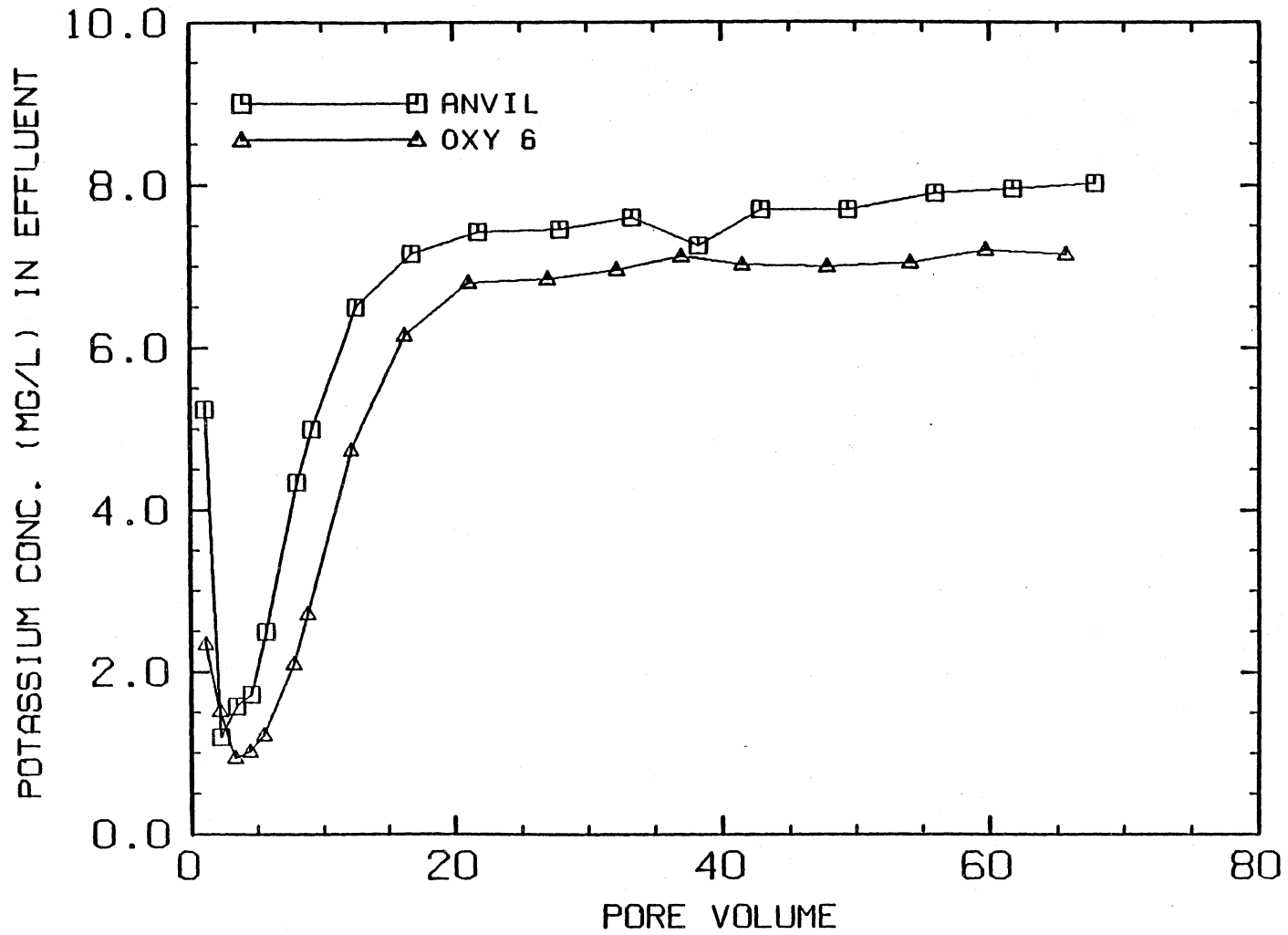


Figure 29. Breakthrough curves for potassium in column adsorption experiments with Anvil raw and Oxy spent shales.

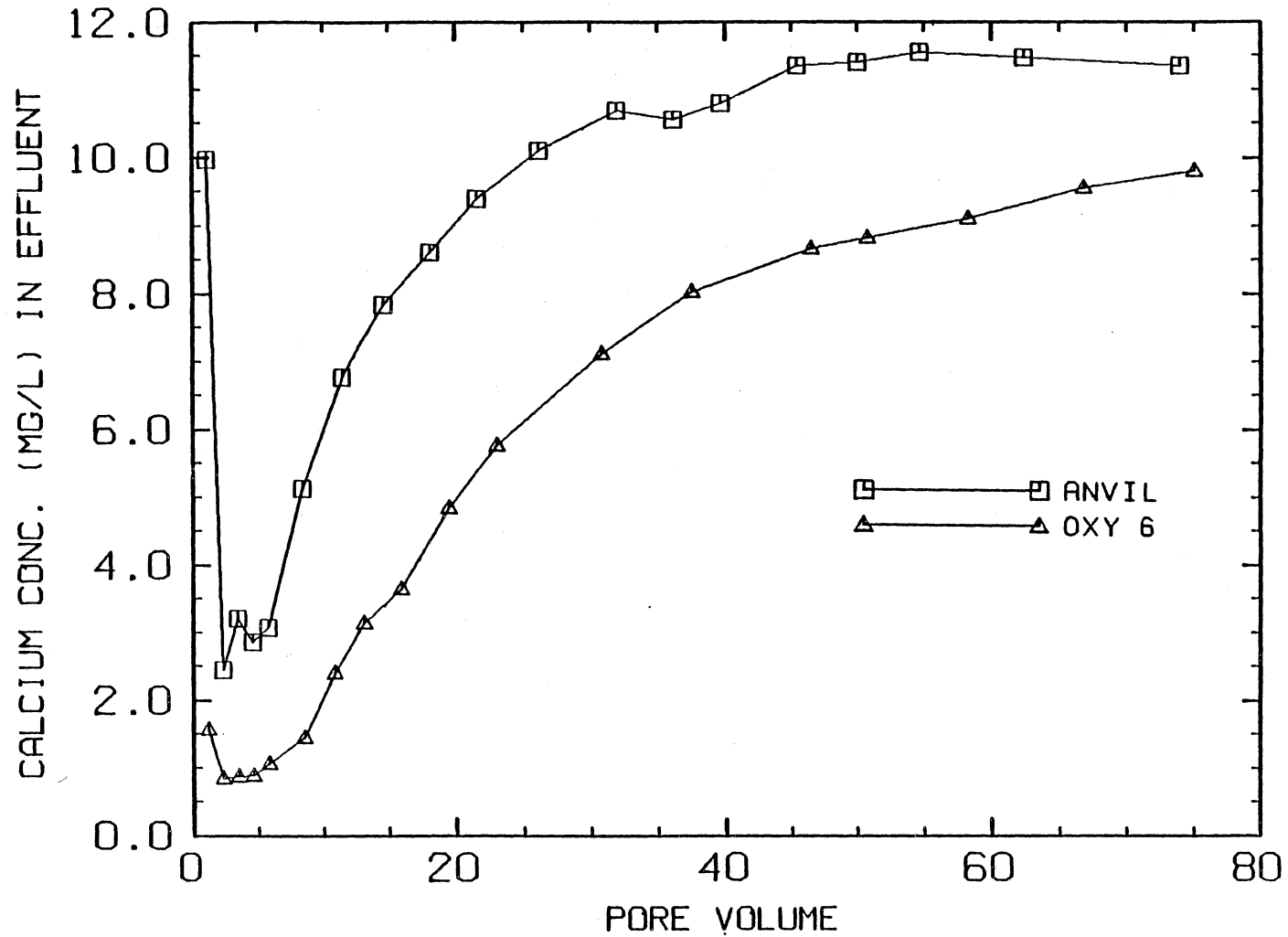


Figure 30. Breakthrough curves for calcium in column adsorption experiments with Anvil raw and Oxy spent shales.

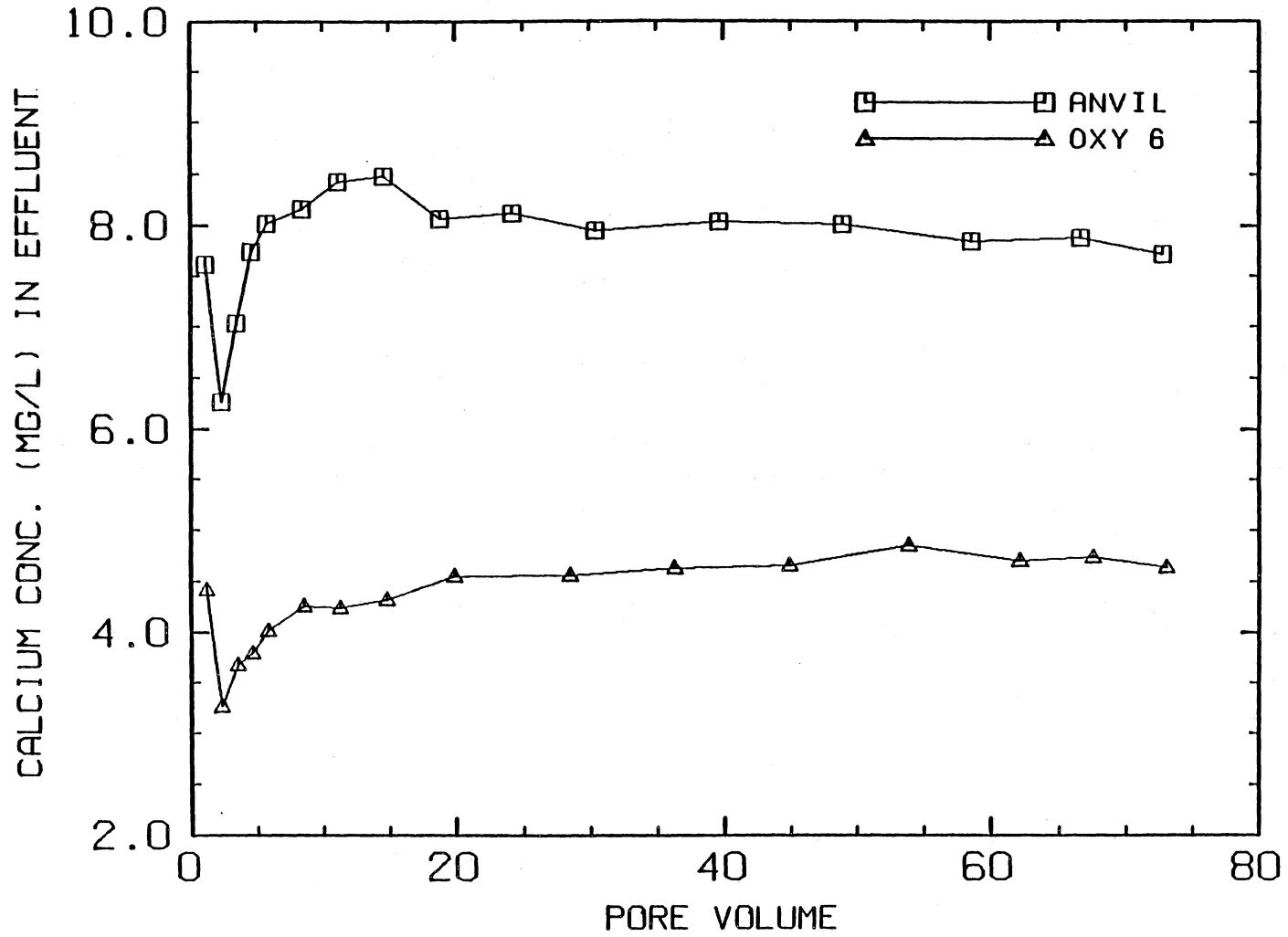


Figure 31. Desorption of calcium from shale columns previously used in calcium adsorption trials.

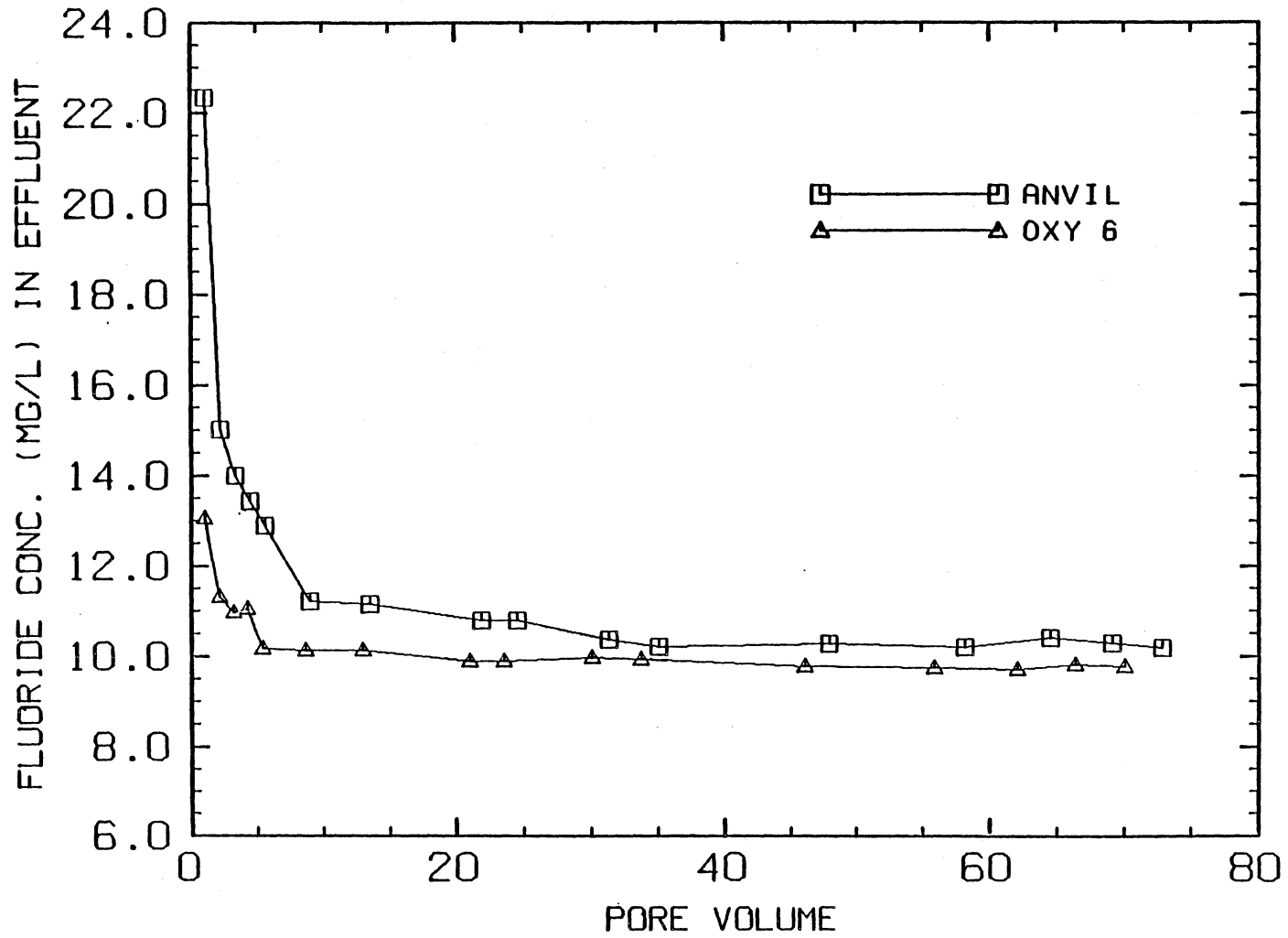


Figure 32. Breakthrough curves for fluoride in column adsorption experiments with Anvil raw and Oxy spent shales.

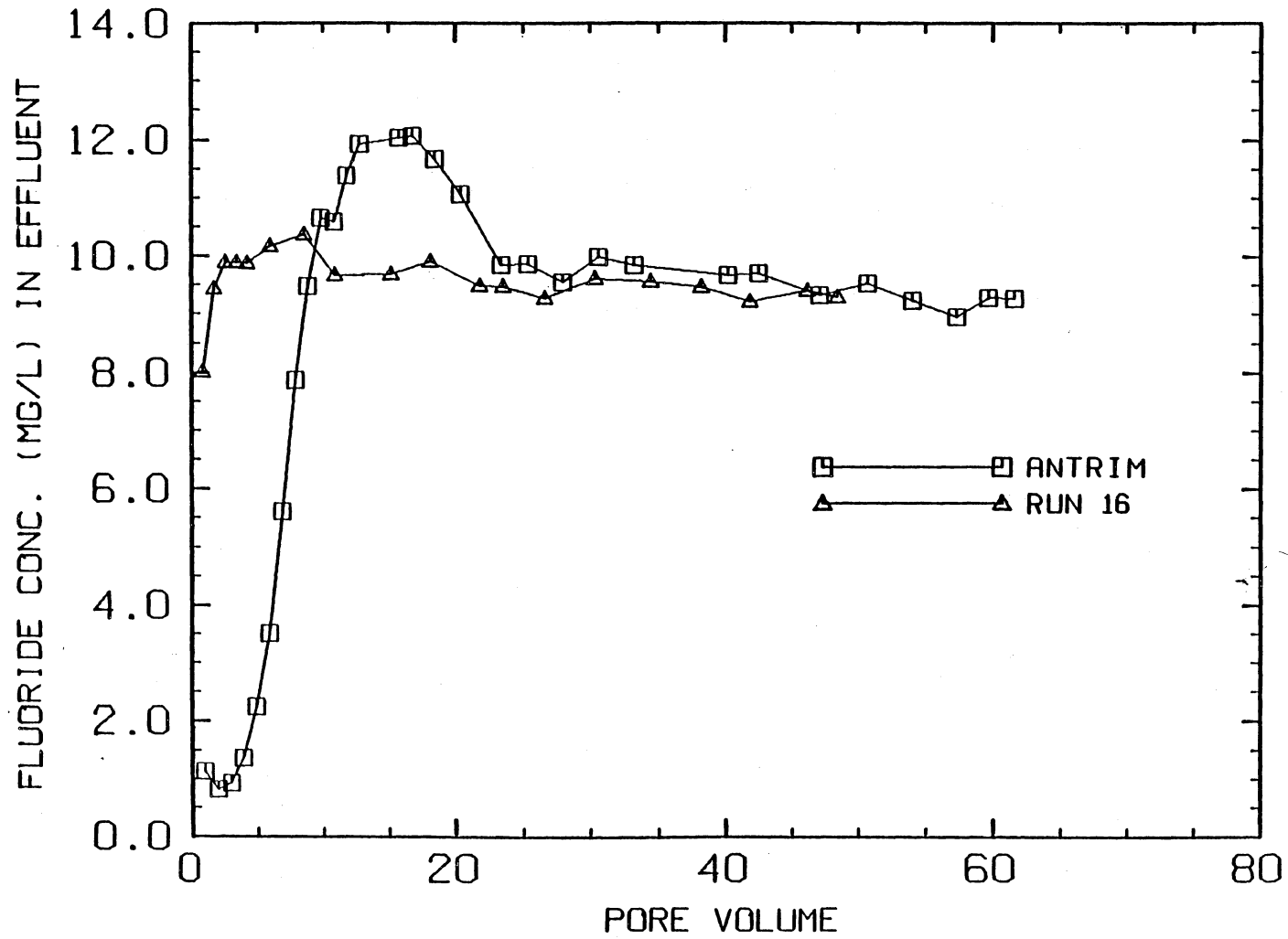


Figure 33. Breakthrough curves for fluoride in column adsorption experiments with Antrim and Run 16 spent shales.

SORPTION/DESORPTION IN A MULTI-ADSORBATE SYSTEM

Recall that the feed solution pumped through the shale columns contained approximately 10 mg/L each of As, Ca, Cd, F and K. Iron was eliminated from this experiment because it created a precipitate in the feed solution. Appendix E contains the breakthrough and desorption curves of the ions investigated. Arsenic and cadmium levels in many of the effluent samples were below the detection limits of the AA and, therefore, could not be plotted (0.05 mg/L for As and 0.005 mg/L for Cd). Table 20 summarizes the results of the multi-adsorbate experiments.

Antrim and Run 16 spent shales exhibited a capacities for removal of arsenic and cadmium. Arsenic levels in Run 16 eluents were less than 0.05 mg/L until the very end of the sorption trials when the effluent contained 1.3 mg/L As. The first ten pore volumes from the Antrim shale contained less than 0.05 mg/L. At approximately sixteen pore volumes, As levels began to increase and ranged from 5 to 6 mg/L at the end of the sorption trial (Figure 34). The desorption phase removed very little arsenic; all Antrim and Run 16 effluent samples contained less than 0.04 and 0.8 mg/L As, respectively.

Antrim effluent samples never contained greater than 0.23 mg/L Cd throughout the sorption trials, and Run 16

TABLE 20

Summary of Multi-adsorbate Column Results

Parameter	As	Ca	F	K	Cd
Anvil					
¹ C _F	9.85	9.93	9.88	10.00	9.72
² C _{eq}	9.90	⁵ n.a.	10.10	9.80	⁶ n.e.
³ PV _{eq}	35	n.a.	25	41	n.e.
⁴ PV _b	2.5	n.a.	n.a.	2.5	60
Oxy 6					
C _F	9.95	10.40	9.85	10.40	9.98
C _{eq}	9.61	12.20	10.10	10.40	n.e.
PV _{eq}	38	70	20	24	n.e.
PV _b	1.5	2.5	n.a.	2.0	50
Antrim					
C _F	10.05	9.75	9.90	10.30	9.80
C _{eq}	n.a.	n.a.	9.80	n.a.	n.a.
PV _{eq}	n.a.	n.a.	25	n.a.	n.a.
PV _b	19	n.a.	5.0	n.a.	⁷ n.b.
Run 16					
C _F	9.80	10.00	⁸ 8.8	10.40	9.80
C _{eq}	n.a.	n.a.	⁹ 10.20	n.a.	n.a.
PV _{eq}	n.a.	n.a.	¹⁰ 15	n.a.	n.a.
PV _b	n.b.	n.a.	1.0	n.a.	n.b.

1. Concentration of ion in feed solution, mg/L
2. Concentration of ion at equilibrium, mg/L
3. Pore volumes at equilibrium
4. Pore volumes at breakthrough
5. Not applicable, background level flushed out was much greater than the concentration in the feed
6. Equilibrium not reached within 48 hours
7. Breakthrough was not reached in the 48-hr. experiment
8. 8.8 mg/L for columns 1 & 2, 11.0 mg/L for column 3
9. 9.55 mg/L for columns 1 & 2, 10.81 mg/L for column 3
10. 22 pore volumes for column 3

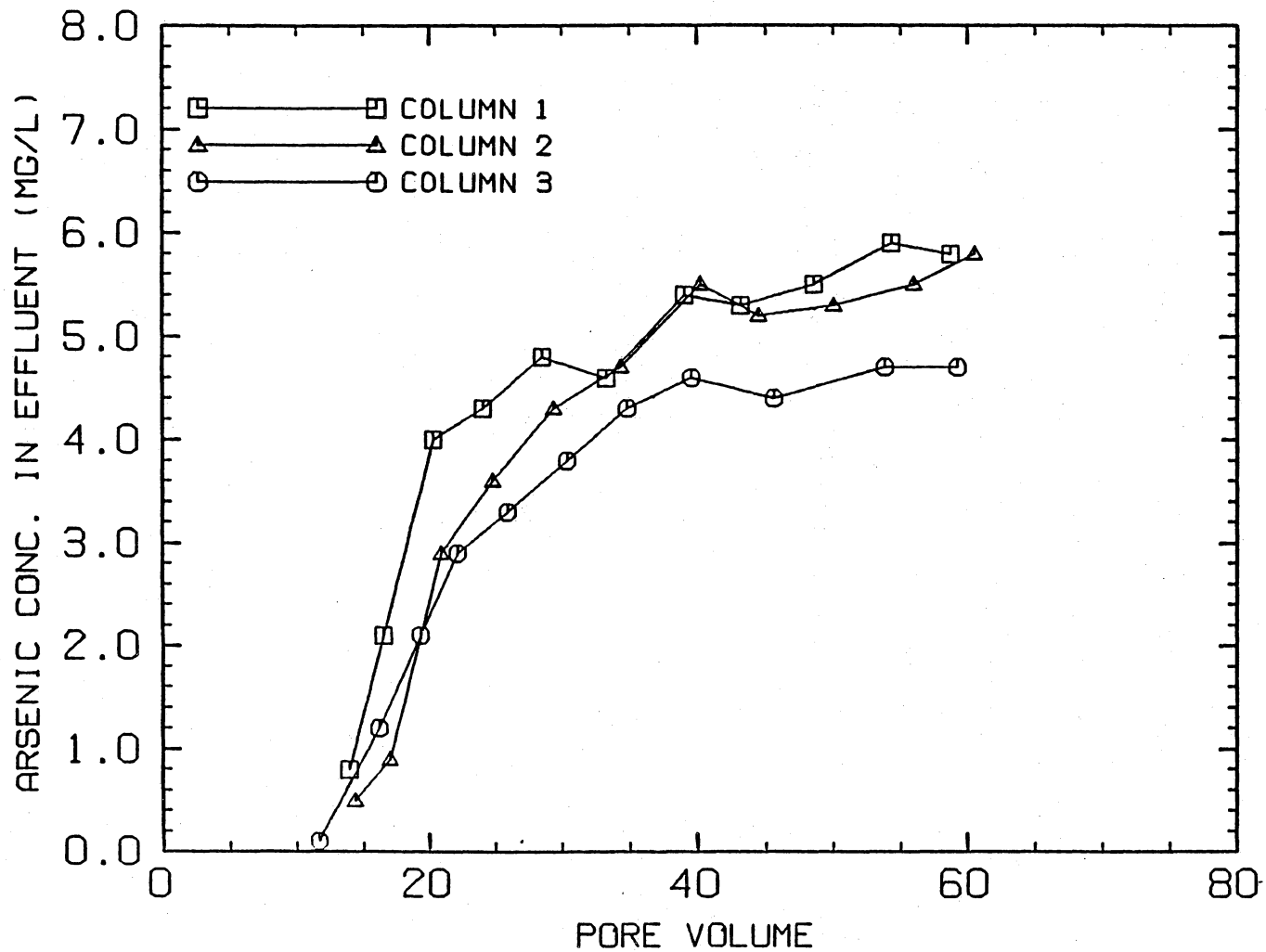


Figure 34. Breakthrough curve for arsenic in multi-adsorbate column trials with Antrim spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

samples all contained less than 0.008 mg/L Cd. The desorption trials indicated that cadmium was not easily removed from the shale; the effluent concentrations were all less than 0.04 mg/L for Antrim, and less than 0.007 mg/L for Run 16 shale.

Breakthrough of As occurred at approximately 2.5 and 1.5 pore volumes for Anvil and Oxy shales, respectively. The behavior of As in Anvil and Oxy multi-adsorbate systems did not differ from that noted in the single-ion trials (Figures 35 and 36). Distilled water desorption of these columns yielded C_p values of 8 and 5 mg/L for Anvil and Oxy shales, respectively. At five pore volumes, the eluents contained less than one mg/L As.

Breakthrough of cadmium for Anvil and Oxy shales occurred at approximately 60 and 50 pore volumes, respectively, and by the end of the sorption trial the Cd concentration in the effluent was 4 to 5 mg/L. Distilled water desorption of these shale columns yielded an eluent containing a maximum of 0.66 mg/L Cd. Recall that in the single-ion column trials, breakthrough of cadmium did not occur for any of the shales

Anvil and Oxy fluoride adsorption in the multi-adsorbate trials paralleled the results from the single-ion trials; i.e., background levels of fluoride were flushed out

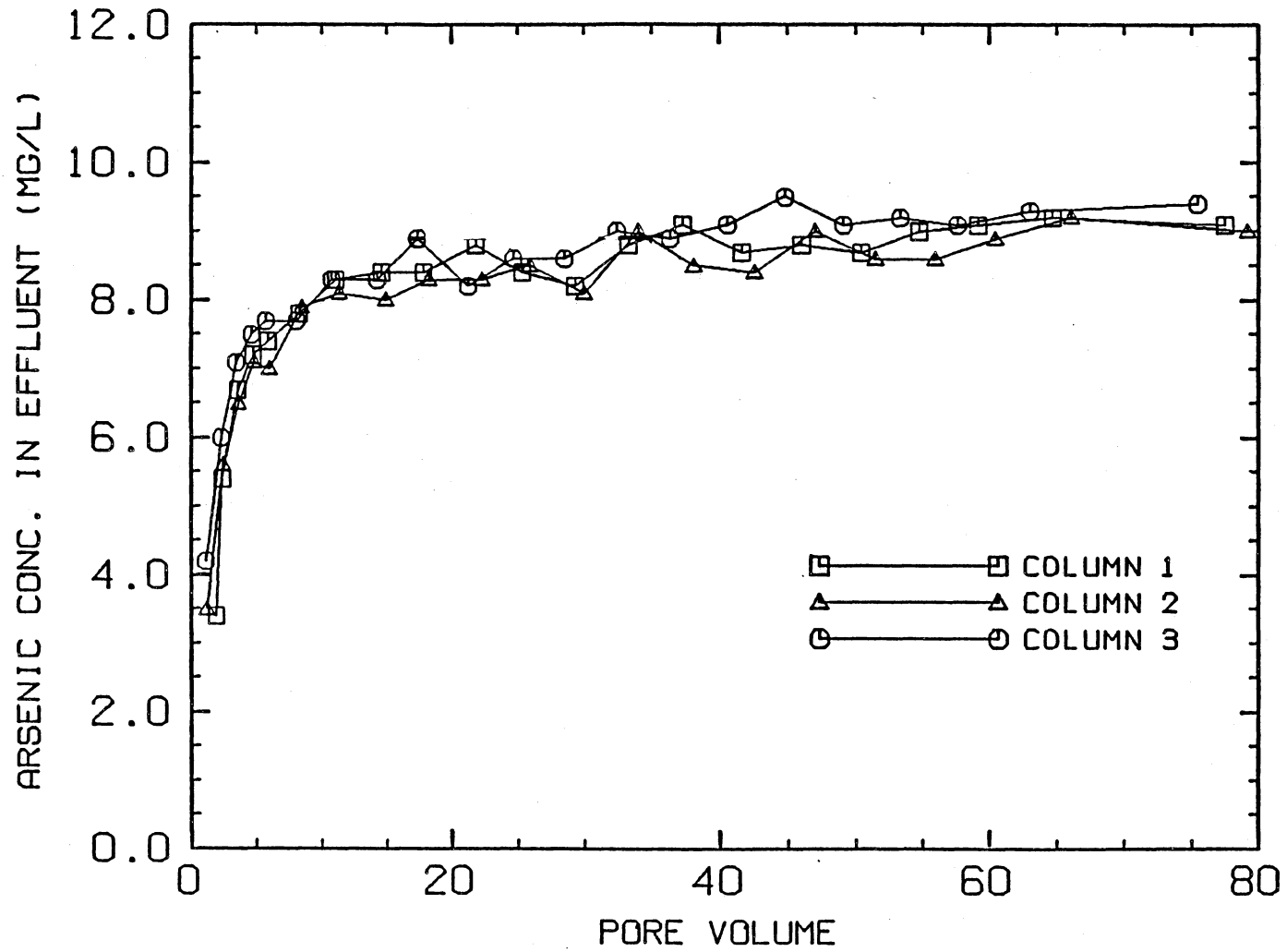


Figure 35. Breakthrough curves for arsenic in multi-adsorbate column trials with Anvil raw shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

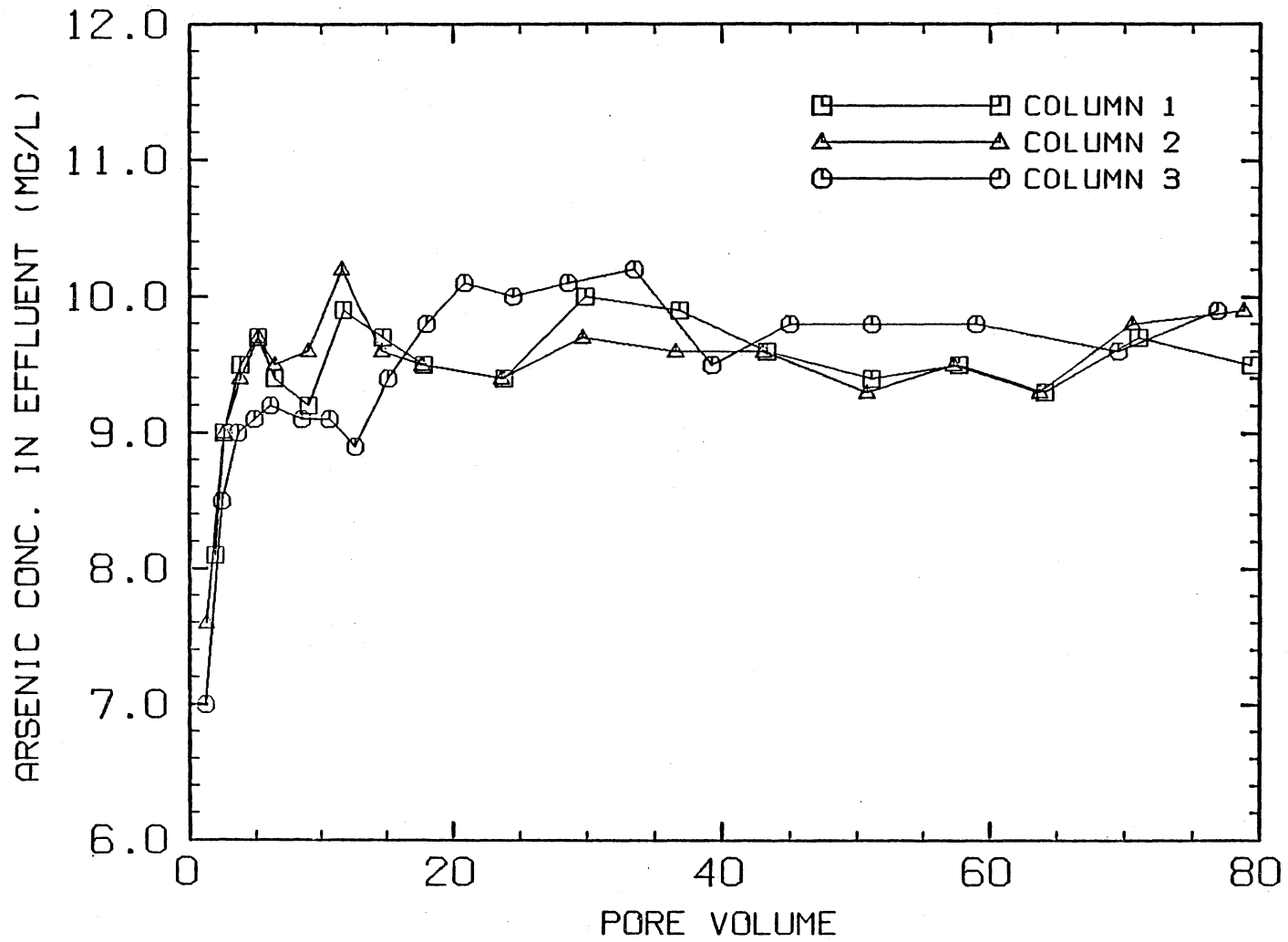


Figure 36. Breakthrough curves for arsenic in multi-adsorbate column trials with Oxy spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

in the first few pore volumes, after which time the eluents yielded concentrations similar to the influent, level of 10 mg/L (Figures 37 and 38). Note that the peak concentration of F in the Anvil eluents was only 12 mg/L, whereas in the single-ion fluoride trial, the peak concentration flushed from the column was almost 22 mg/L. In the desorption trials, fluoride was flushed out at levels less than 1.1 mg/L after peak concentration of approximately 9 and 5 mg/L for Anvil and Oxy shales, respectively (Appendix E).

Antrim and Run 16 shales showed a capacity for fluoride adsorption in a multi-adsorbate system which was similar to that seen in the single-ion sorption trials (Figures 39 and 40). Antrim was the better adsorbent; breakthrough occurred at approximately four pore volumes. Run 16 showed only a small capacity for adsorption in the first pore volume. Desorption of these shale columns yielded an effluent containing approximately 11 mg/L F in the first couple of pore volumes. Fluoride levels were then eluted to values less than 1.0 mg/L (Appendix E).

High background levels of Ca and K were eluted from the Antrim and Run 16 shale columns, so the concentration of the two elements in the feed solution had little impact on the shales (Appendix E). Anvil and Oxy shales, on the other hand, had much smaller background levels of these ions.

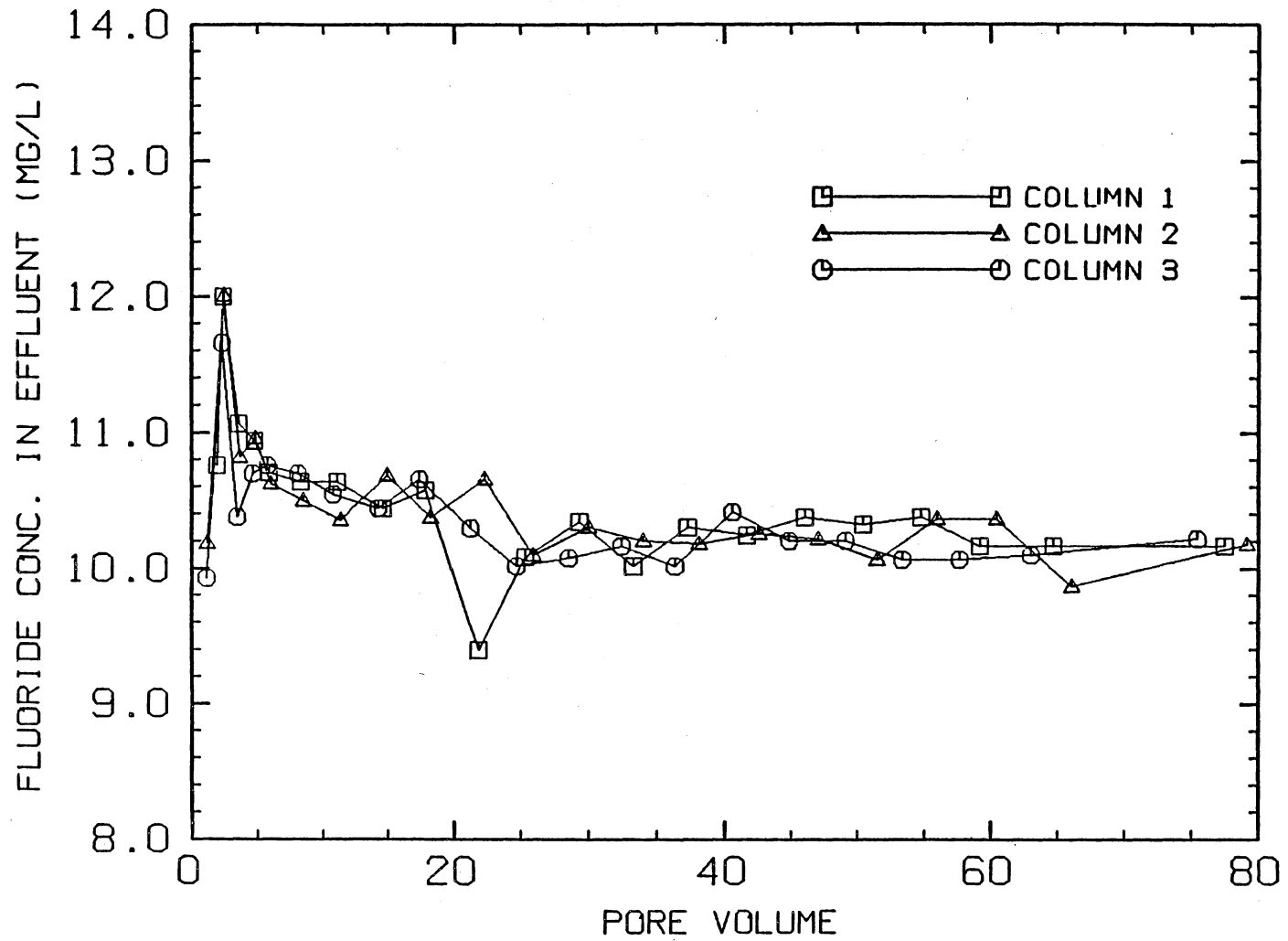


Figure 37. Breakthrough curves for fluoride in multi-adsorbate column trials with Anvil raw shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

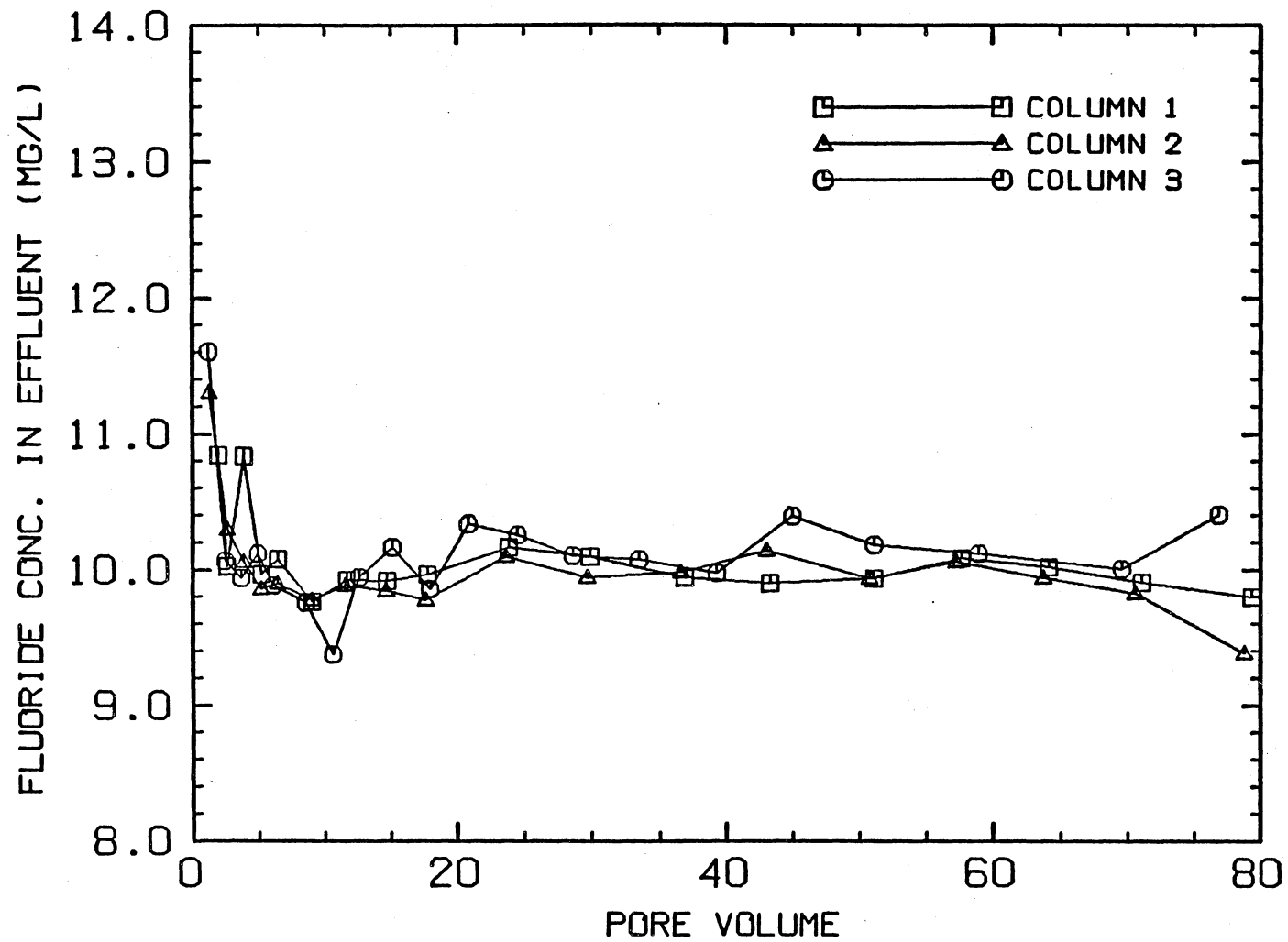


Figure 38. Breakthrough curves for fluoride in multi-adsorbate column trials with Oxy spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

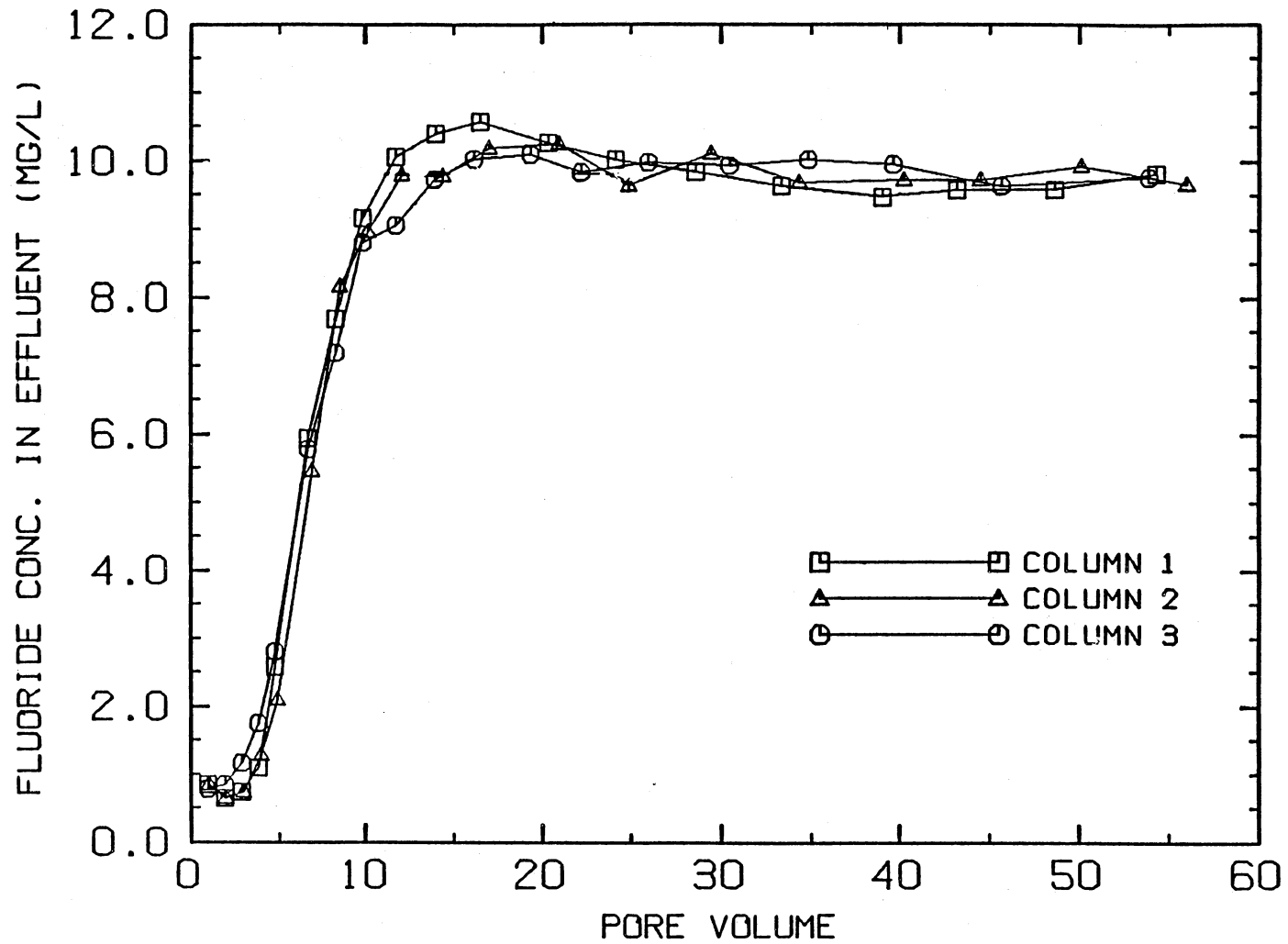


Figure 39. Breakthrough curves for fluoride in multi-adsorbate column trials with Antrim spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

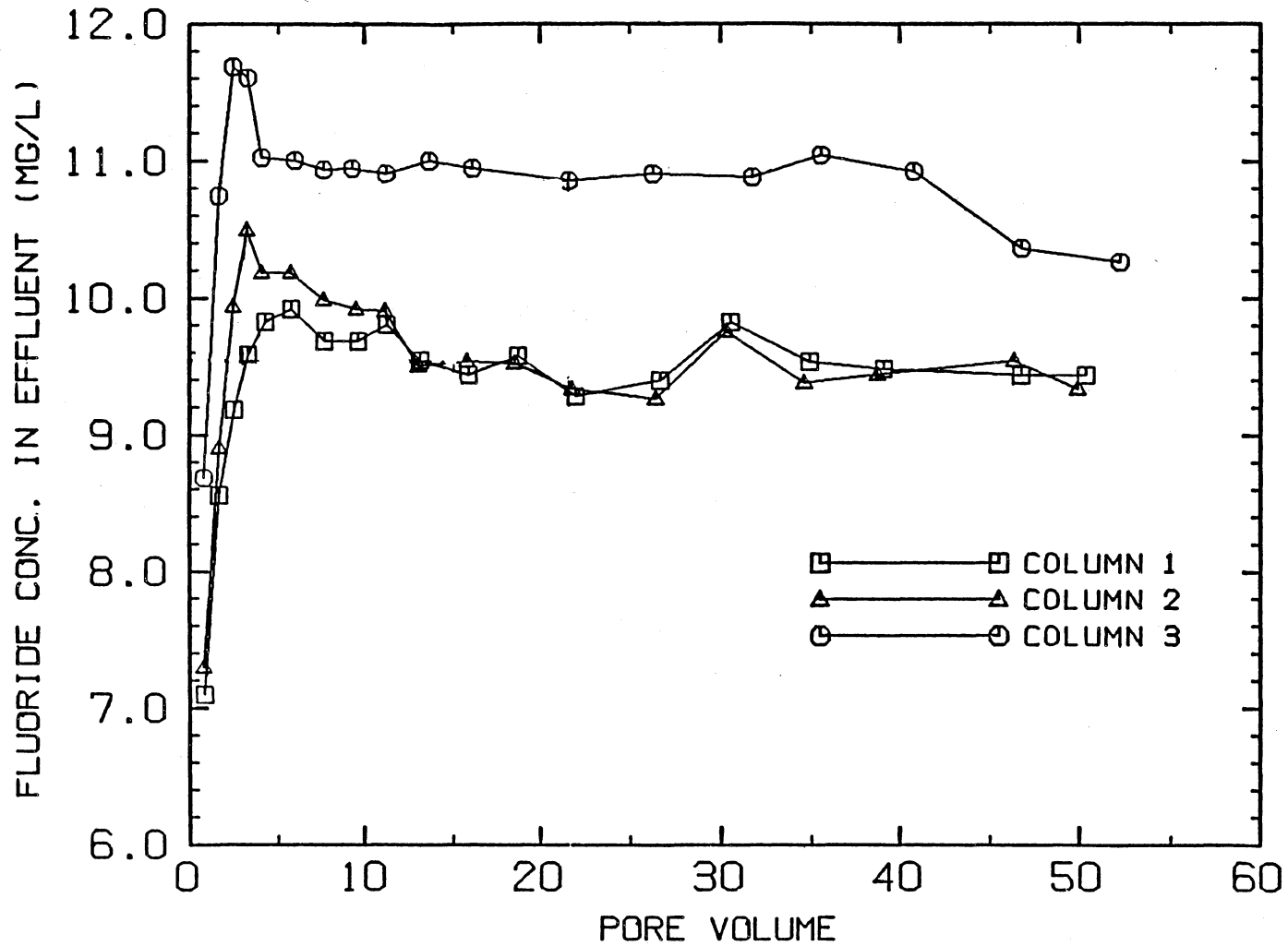


Figure 40. Breakthrough curves for fluoride in multi-adsorbate column trials with Run 16 spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

Calcium behaved differently in the Anvil multi-adsorbate trials than in the single-ion trials. Figure 41 shows that initial pore volumes contained 28 to 33 mg/L Ca, after which time concentrations stabilized at about 13 to 18 mg/L. Recall that Ca was adsorbed in the single-ion sorption trials with this shale. The adsorption of Ca on Oxy shale in the multi-adsorbate trials did paralleled the behavior seen in the single-ion trials; however, the concentration of Ca at equilibrium was 2 to 5 mg/L greater than the influent level (Table 20).

Calcium desorption curves for the Anvil and Oxy shales were similar to those of the single-ion desorption trials. The peak concentrations in the eluents from Anvil, Oxy and Antrim shales ranged as follows: 5 to 7, 2.5 to 3 and 14 to 17 mg/L Ca. As in the single-ion desorption trials, after the initial flush of Ca levels in the columns, eluent concentrations of Ca began to increase gradually (Figures 42 and also Appendix E). The final pore volumes of eluents from Anvil, Oxy and Antrim shales contained the following (approximate) Ca levels: 2.0, 3.0 and 8.0 mg/L Ca.

Potassium levels in the first pore volume of fluid from the multi-adsorbate trials with Anvil shale ranged from 8 to 9.5 mg/L. Eluents from pore volumes 3 to 5 contained approximately 6.5 mg/L K. After this point, adsorption of K

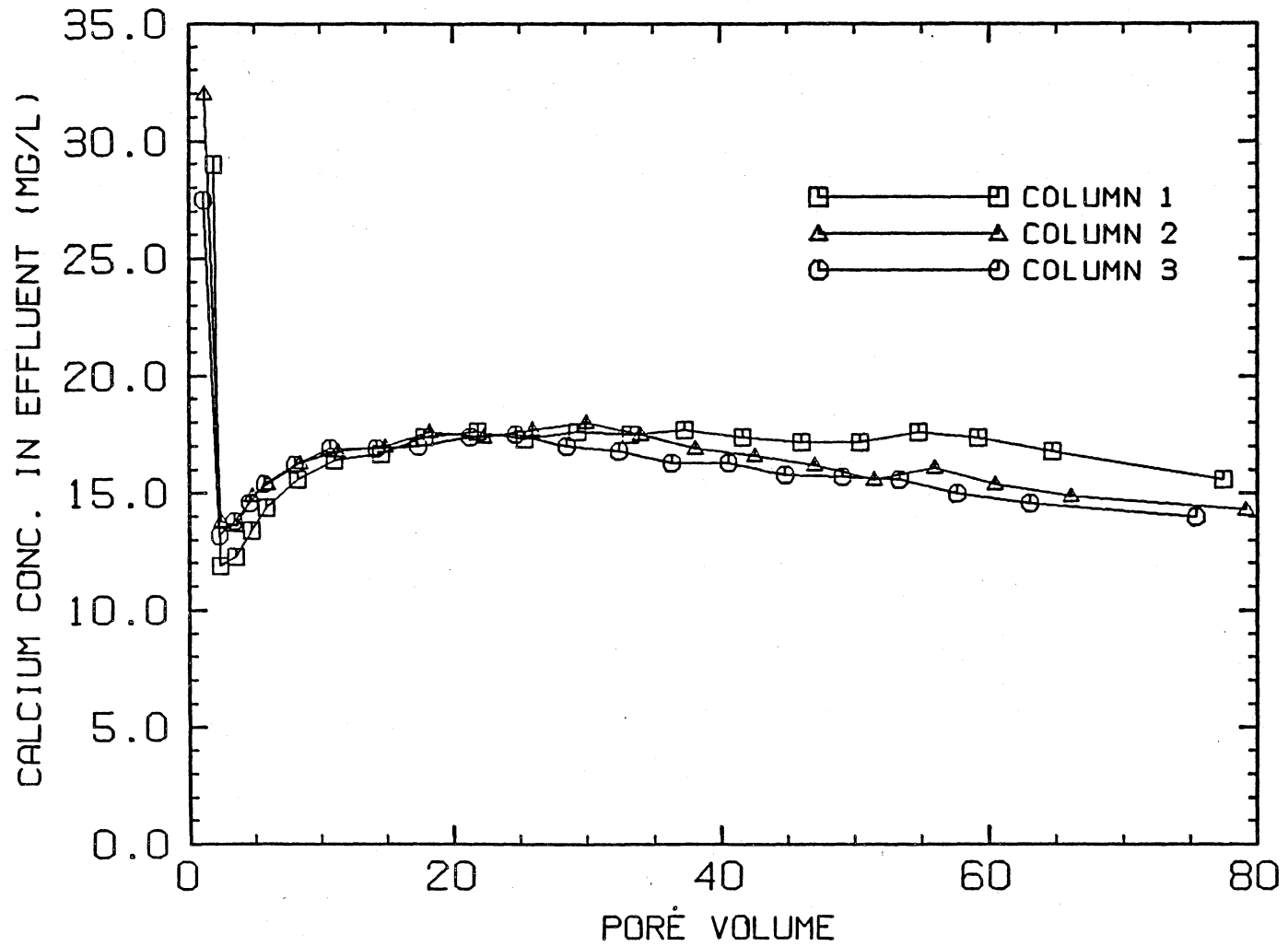


Figure 41. Breakthrough curves for calcium in multi-adsorbate column trials with Anvil raw shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

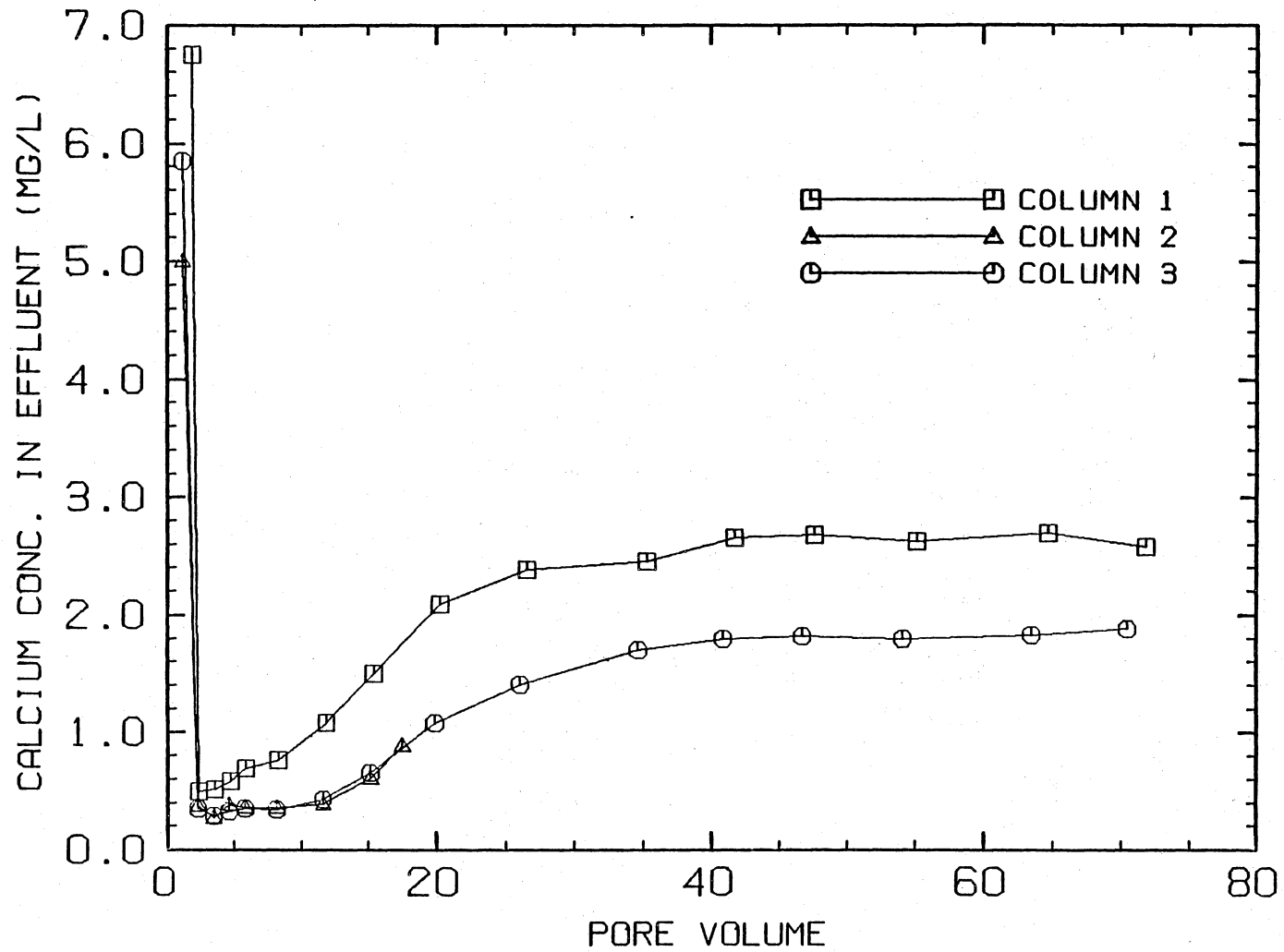


Figure 42. Desorption of calcium from columns of Anvil raw shale which were previously used in multi-adsorbate experiments; results of three trials provided.

occurred for nearly 20 pore volumes until effluent levels approached those of the influent (Figure 43). There was no initial flush of K from the Oxy shale column. A small amount of adsorption occurred in the first 10 to 15 pore volumes, after which time the equilibrium concentration was approximately 10 mg/L (Figure 44). Desorption of all four shales produced K levels ranging from 3 to 13 mg/L in the first few pore volumes. After five pore volumes of distilled water had passed through the shales, K levels were less than 2 mg/L.

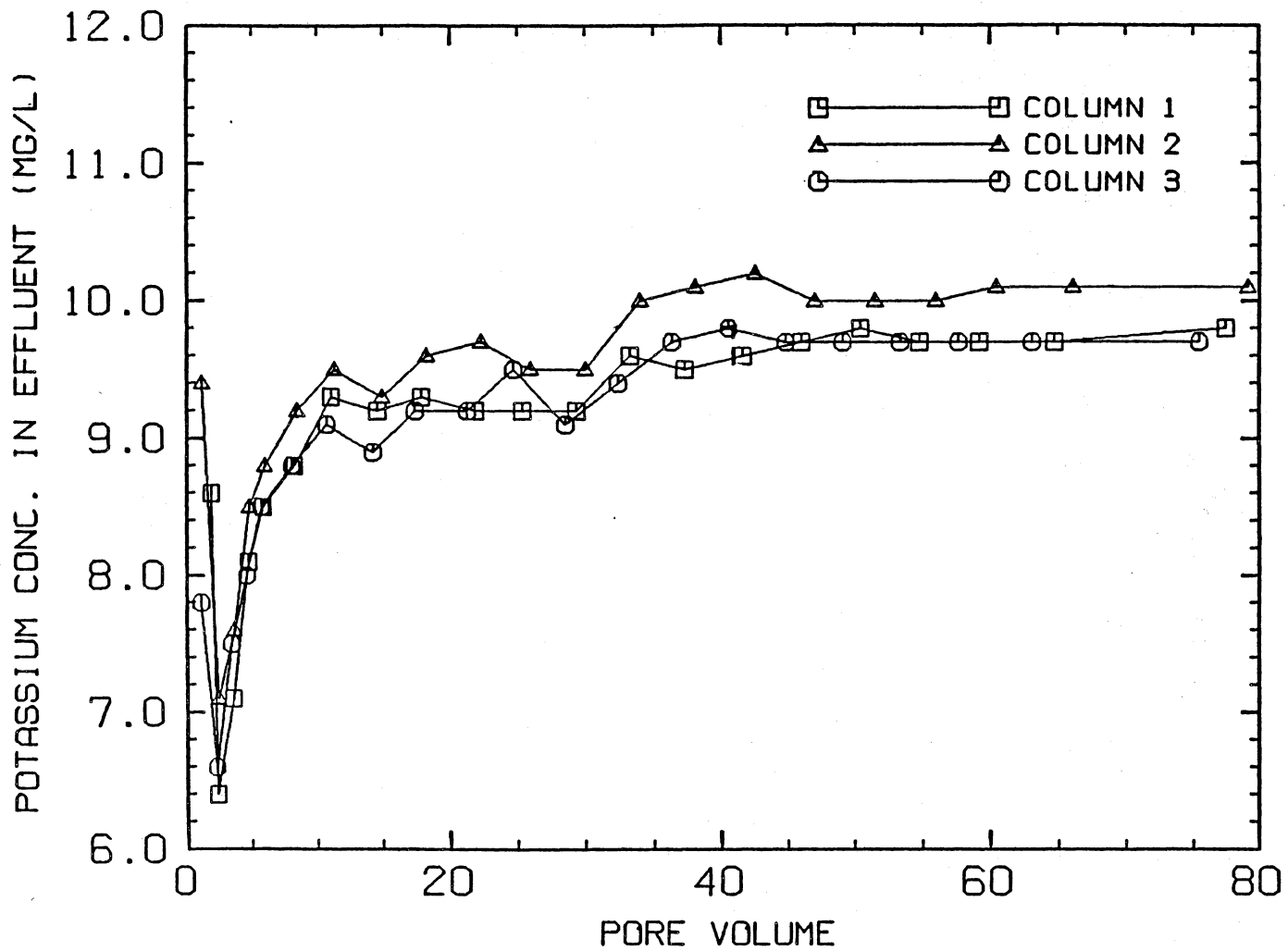


Figure 43. Breakthrough curves for potassium in multi-adsorbate column trials with Anvil raw shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

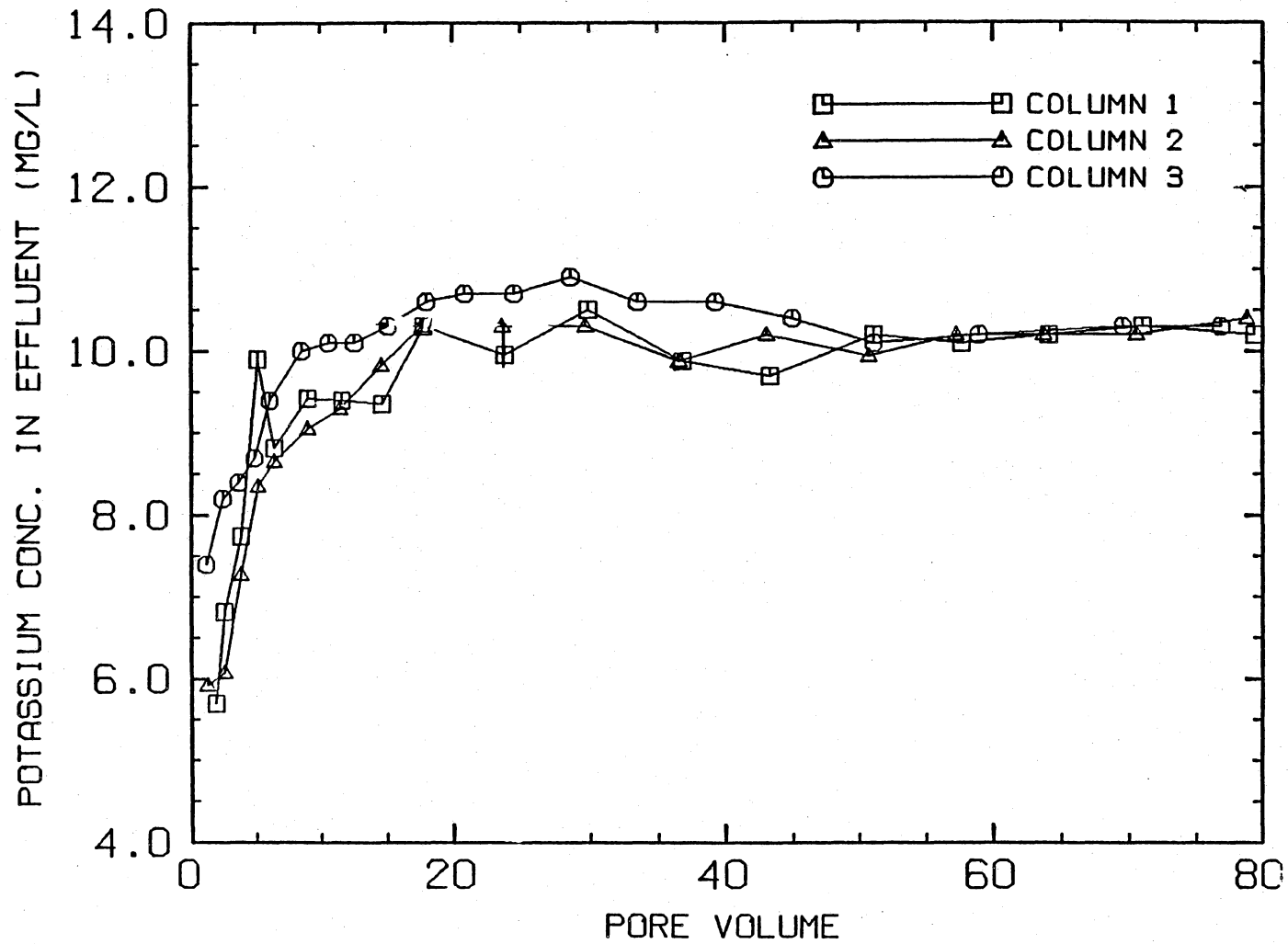


Figure 44. Breakthrough curves for potassium in multi-adsorbate column trials with Oxy spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

Chapter V
DISCUSSION

APPLICATION OF RESULTS

Leachates produced by the addition of either rain or process waters to raw or spent shale may pose a serious contamination threat to surface and groundwater supplies. Under controlled disposal conditions, leachates can be collected and sent for disposal or treatment. Therefore, it is important to know the potential contaminants in the several types of leachates that may be generated under various conditions.

The results from the five different experiments which utilized batch and continuous-flow column methods can be used to analyze and evaluate the environmental consequences involving leachates generated in the following ways:

1. Rainwater percolating through:
 - a) surface disposal piles
 - b) landfilled spent shale
 - c) raw shale exposed by mining
 - d) in situ retorts
2. Retort water is used to moisten spent shale before disposal (dust control) and/or is co-disposed with the spent shale in a landfill.

3. A "clean" water is used to moisten shale before landfill disposal and remains contained in the landfill, possibly percolating downward through the shale.
4. Packed beds of crushed spent shale are used as a treatment phase in a process water treatment scheme.
5. Retort water is piped through in situ retorts to remove salts from the spent shale and to potentially remove harmful metals through adsorption or precipitation.
6. Rainwater percolates through surface piles of spent shale which had been previously moistened with retort water for dust control.

Although the experiments conducted in this study cannot directly simulate these environmental situations, they give a good indication of the potential contaminants in leachates and are useful for assessing the behavior of metals in various shale-water systems. The results from these experiments can be used to evaluate potential consequences of the previously mentioned conditions where leachates are generated from raw and spent shale.

BATCH AND COLUMN ELUTION RESULTS

The results of the batch elution experiments indicated that the concentration of most inorganic materials considered during this study reached equilibrium within 24 to 48 hours. Plots of time (X) versus ion concentration (Y) illustrated that two stages were involved in the elution experiments. There first appeared to be a noticeable increase in concentration within the first 24 hours of agitation, followed by a more gradual increase throughout the remaining elution period. The initial increase was most likely due to dissolution of readily soluble inorganic salts present on the surface of the shale. In a second stage, materials in the eluents increased as a result of the dissolution of less soluble salts or transfer of agents through pores in the shale to the bulk solution.

The continual agitation of the shale particles (fines) in the flasks for seven days may also have been responsible for release of additional inorganics caused by the abrasive action of the particles bumping against one another. Cote and Constable (40) in an evaluation of different experimental conditions in batch trials, found that agitation methods might cause fragmentation of solid particles, thereby creating additional surface area for a leachate to contact.

Recall that in the batch elution study the entire contents of the flasks were filtered and the eluents analyzed for inorganics. Quality of water at each sample period was determined by a different aliquot of shale. Although it is assumed that the shales are homogenous after crushing and sieving, there is still the possibility for variation in individual samples.

CONSTITUENTS OF LEACHATES FROM RAW AND RETORTED SHALES

The differences in leachates produced from low- and high-temperature, retorted shales were discussed in the Literature Review. It is known that shales which subjected to retort temperatures of 600 to 800°C produce leachates with high pH values (16 - 19 and 29). At temperatures greater than 800°C, relatively insoluble minerals are formed (18 and 19).

The elution results and retort temperatures of the shales investigated in this project indicated that:

1. Oxy 6 spent shale, a modified, in situ (MIS) retorted shale that had ben subjected to extreme retort temperatures, 800 to 1000°C, released lower levels of inorganics and eluents having a lower pH in elution experiments than the other shales considered.

2. Antrim spent shale, an eastern shale retorted in a simulated MIS retort, experienced lower retort temperatures (maximum bed temperature = 793°C) and produced a leachate with a high content of inorganic salts and a high pH.
3. Run 16 spent shale, also a simulated MIS spent shale (maximum bed temperature = 660°C), yielded eluents with extremely high levels of inorganics and a high pH.

Eluents generated from Anvil raw shale were similar to those of the Oxy retorted shale; i.e., pH of 8.5-9.5 and inorganic levels, except for fluoride, that were relatively low. Others (8,18 and 19) have also reported that in situ spent shale produces a leachate similar to that produced from raw shale. The levels of the following inorganics in the eluents from Anvil raw shale were similar to those produced by raw shale in a batch study conducted by Peterson and Wagner (18): calcium, sulfate, pH, conductivity and arsenic.

In general, spent shale eluents yield greater levels of inorganic materials than do raw shales. The eluents from Antrim and Run 16 shales contained much greater levels of inorganics than those of the Anvil raw shale. These data support the work of Stollenwerk and Runnells (83) who

TABLE 21

Concentration Ranges of Various Inorganic Constituents in
Batch Eluents from Raw Shales¹

Constituent	Peterson & Wagner (18)	Anvil Raw Shale ²
As	0.01 - 0.6	0.004 - 0.012
Ca	2.07 - 75.9	7.5 - 17.0
Cond. ³	345 - 750	200 - 300
pH	8.52 - 9.5	8.5 - 9.6
SO ₄	30 - 200	46 - 54

1. concentrations in mg/L
2. ratio of water-to-shale, 33:1
3. conductivity in $\mu\text{mhos/cm}$

compared column leachates from TOSCO and Paraho retorted shales to their raw counterparts. These surface-retorted shales were subjected to temperatures less than 800°C. Total dissolved solids and pH were much greater in the retorted eluents than in the raw shale leachates. However, Oxy shale, which was retorted at higher temperatures, produced eluents similar to the raw shale. Ranges of pH, conductivity, calcium, and sulfate in batch eluents produced by Oxy spent shale were comparable to those of a similar experiment conducted by Peterson (18) with MIS spent shale. These data verify the effect of high-temperature retorting on shale-leachate characteristics.

Relationship of Retort Temperature and pH of Leachates

The pH of leachates produced from spent shale is of great concern due to the influence pH has on the solubility of many toxic trace elements. Spent shale piles may yield leachates having very alkaline pH values, into ground or surface waters and have a harmful effect on aquatic life. Desirable pH levels in waters are approximately 6.5 to 8.0 (85). The pH of Antrim and Run 16 eluents were greater, pH 10.5 and above. The pH of Anvil raw shale and Oxy spent shale leachates were lower, ranging from 7.5 to 9.6. It is necessary to exercise caution when extrapolating results of

leaching tests with Antrim and Run 16 simulated-MIS retorts to field conditions involving true MIS retorts. The elution results obtained with Oxy shale indicated that true MIS retorts produce a shale that releases low levels of leachable inorganics. Antrim and Run 16 processes, which simulated a true MIS retort on a much smaller scale, did not produce a spent shale with the leaching characteristics of Oxy shale. It is obvious that retorting temperatures play an important role in the water quality of leachates from spent shales. The results of this study indicated that it is desirable to retort under extreme temperatures in order to produce a spent shale which is less likely to cause drastic pH changes in receiving waters.

There were specific trends noted in the pH characteristics of the eluents. Some of the Antrim column eluents were approximately pH 6.0, but, these values were measured in the earlier eluents. Later, the effluent pH's were about 9.0. Similar pH variations were observed in evaluation of Run 16 batch- and column eluents. As mentioned in the previous paragraph, these shales were retorted at lower temperatures, and it is likely that these conditions resulted in the decomposition of carbonates to calcium and magnesium oxides which, in contact with water, are converted to hydroxides. Hence a material is created

that will produce a high-pH leachate (8,16 and 46). The calcium oxide is flushed from the shale column during leaching with distilled water, and some of it be converted to calcium carbonate (86). Decreasing pH values in Anvil and Oxy eluents can then be explained by the slow dissolution and hydrolysis reactions of carbonate compounds in the eluent (46).

Fluoride Levels in Leachates

Run 16 and Anvil shales released the most fluoride in the batch and column trials. Anvil shale, in particular, eluted high levels of fluoride (approaching 12 mg/L) during the batch trials (Figure 14). Kuo et al. (19) also found high fluoride levels in leachate from raw shale. It has been suggested that high levels of fluoride are a result of a solid reservoir of fluoride in the shale (83 and 87). Fluoride levels in the Run 16 and Anvil eluents were also much greater than the maximum values of water quality and primary drinking water standards; i.e., 1.5 and 1.8 mg/L, respectively (84,85).

Table 22 presents some of the water quality criteria, primary and secondary drinking water standards and RCRA's EP Toxicity Maximum Contaminant Limits (MCL's) for the elements studied in this project. Also presented are the

concentrations of elements which approached or exceeded the standards in batch and column eluents. It is important to remember when comparing these values, that the batch studies were not performed in the manner specified by the EP Toxicity Test procedure.

Metal Concentrations in Leachates

The solubility of metals in aqueous solutions is largely dictated by pH. All of the shales produced basic leachates. Water treatment processes generally remove heavy metals from solution through precipitation as a hydroxide. Most heavy metals have very limited solubility at pH values greater than 6.0; however, the minimum solubility may vary according to concentration (88).

Cadmium and iron levels in the batch and column eluents were generally below detection on the AA ($\leq 5 \mu\text{g/L Cd}$ and $\leq 0.02 \text{ mg/L Fe}$). At cadmium levels this low, leachates from raw and spent shales would not present a toxicity threat to man. The water quality and primary drinking water standards for cadmium are both 0.01 mg/L . Cadmium levels in some of the samples from the batch trials did approach this limit (eg., note 0.009 mg/L in Table 23) and present the possibility of toxic effects to aquatic life. However, these concentrations were encountered in very few samples.

TABLE 23

Concentrations of Elements in Batch and Column Eluents Which Approached or Exceeded Standards¹

	As	Cd	F	pH	SO ₄
Water Quality Criteria ²	1.0	0.01	1.5	6.5 - 8.0	250.0
Primary Drinking Water MCL ³	0.05	0.01	1.8	--	--
Secondary Drinking Water MCL	--	--	--	6.5 - 8.5	250.0
RCRA MCL ⁴	5.0	1.0	--	--	--
Anvil					
Batch	0.012	--	11.8	8.7 ⁵	--
Column	0.011	--	6.5	9.0	690
Oxy 6					
Batch	0.012	0.009 ⁶	--	8.6	--
Column	0.106	--	1.1	9.2	500
Antrim					
Batch	0.021	0.011	--	10.6	430
Column	0.038	--	0.98	9.3	4020
Run 16					
Batch	0.007	0.009	5.5	11.5	480
Column	0.026	--	9.4	11.2	2390

1. All concentrations in mg/L.

2. Multiple Use (non-potable) concentration

3. Maximum contaminant limit

4. MCL for characteristic of EP Toxicity

5. pH values reported here are the values at C_{eq}.

6. Maximum level in eluent samples.

Arsenic levels in the batch eluents were less than 21 $\mu\text{g/L}$ for all four shales. This level is less than the primary drinking water standard (50 $\mu\text{g/L}$ As) and water quality criteria (1.0 mg/L As) (Table 23). However, during column elution of Oxy shale, a peak arsenic concentration (C_p) of 106 $\mu\text{g/L}$ was measured (Table 18). The raw shale had the lowest C_p of 11 $\mu\text{g/L}$, followed by Run 16 and Antrim, which yielded 26 and 38 $\mu\text{g/L}$ As, respectively. Oxy spent shale released almost three times as much arsenic as the other shales.

Evidence presented in a study by Peterson and Wagner (18) suggested that trace elements might leach from silicates which were formed during retorting under the extreme temperatures of MIS retorts. It was reported that spent shale containing mostly akermanite-gehlenite released higher levels of trace elements than other silicate forms. It is possible that the Oxy 6 retort, a scaled up version of the 3E, had created temperatures high enough to produce this type of shale.

High levels of iron in water supplies may cause an undesirable taste and staining problems. The 0.3 mg/L drinking water standard is primarily for esthetic reasons. Iron levels in eluents from batch and column trials were all less than 0.18 mg/L. Iron levels in leachates from simulated

in situ spent shales have been reported to range from 0.0004 to 0.042 mg/L (89).

ELUTION BEHAVIOR OF INORGANIC MATERIALS IN SHALE COLUMNS

The column elution results (Appendix C and Table 18) indicated that most of the soluble, inorganic materials were flushed from the shale columns in the first five to eight pore volumes of effluent. Similar results have been documented by Stollenwerk and Runnells (8, 83) and others (22, 23). The first flush of inorganics is due to the solubilization of inorganic salts present on the shale surface. This is followed by the slower dissolution of less soluble materials in and on the shale particles (8, 46). These findings are important in that flushing of spent shale with waters may prove to be a viable treatment method prior to disposal. After an initial flushing treatment, shale would leach lower levels of inorganics, thereby eliminating much of the concern over contamination of ground and surface waters.

ANALYSIS OF SORPTION TRIAL RESULTS

Knowledge of metal behavior in water-shale environments is essential for evaluation of potential hazards associated with co-disposal of spent shale and process waters. In this section, the results of metal addition to water-shale suspensions and columns of shale will be discussed in relation to the shale's effectiveness for removal of these inorganics.

Spent shale can be compared to an adsorbent such as activated carbon. The adsorptive capacity of an adsorbent for a solute is determined through the use of various adsorbate-adsorbent ratios in batch reactors. An attempt was made to plot all of the data in the form of Langmuir and Freundlich isotherms; however, in most cases, the metal ion added was almost completely adsorbed and/or precipitated at all of the liquid-solid ratios considered. Consequently, equilibrium concentrations were not a function of adsorption capacity. This indicates that some mechanism other than adsorption has a significant role in the removal of solute from solution. Because the adsorbate was removed almost completely for all of the liquid-to-solid ratios, the data will not be presented as Langmuir and Freundlich isotherms.

Batch Sorption Results

Metal-ion addition to water-shale suspensions resulted in nearly complete removal of the ions from solution. Cadmium and iron were removed to levels less than 0.01 and 0.03 mg/L, respectively, in the presence of Antrim, Run 16 and Anvil shales. Oxy shale, however, exhibited a lower capacity to remove cadmium. Equilibrium concentrations ranged from 0.30 to 0.45 mg/L, which exceed the water quality and drinking water standards, but not the 1.0 mg/L MCL for EP toxicity.

Control data collected during the sorption trials indicated that Cd and Fe levels, in the absence of an adsorbent, were generally less than the detection limits of the AA by the end of the five-day experiment. It is likely, therefore, that removal was by precipitation at the elevated pH levels of the system (7.7 to 11.4). Cadmium and iron removal from wastewaters may be accomplished by precipitation at an alkaline pH. Nearly complete Cd removal can be accomplished through co-precipitation with iron hydroxide at a pH of 8.5 (Figure 45, 88).

Arsenic levels in the control flasks from the shales indicated that arsenic remained soluble in the leachate. However, arsenic was removed to levels less than 0.60 mg/L in the sorption flasks containing shale. The pH values in

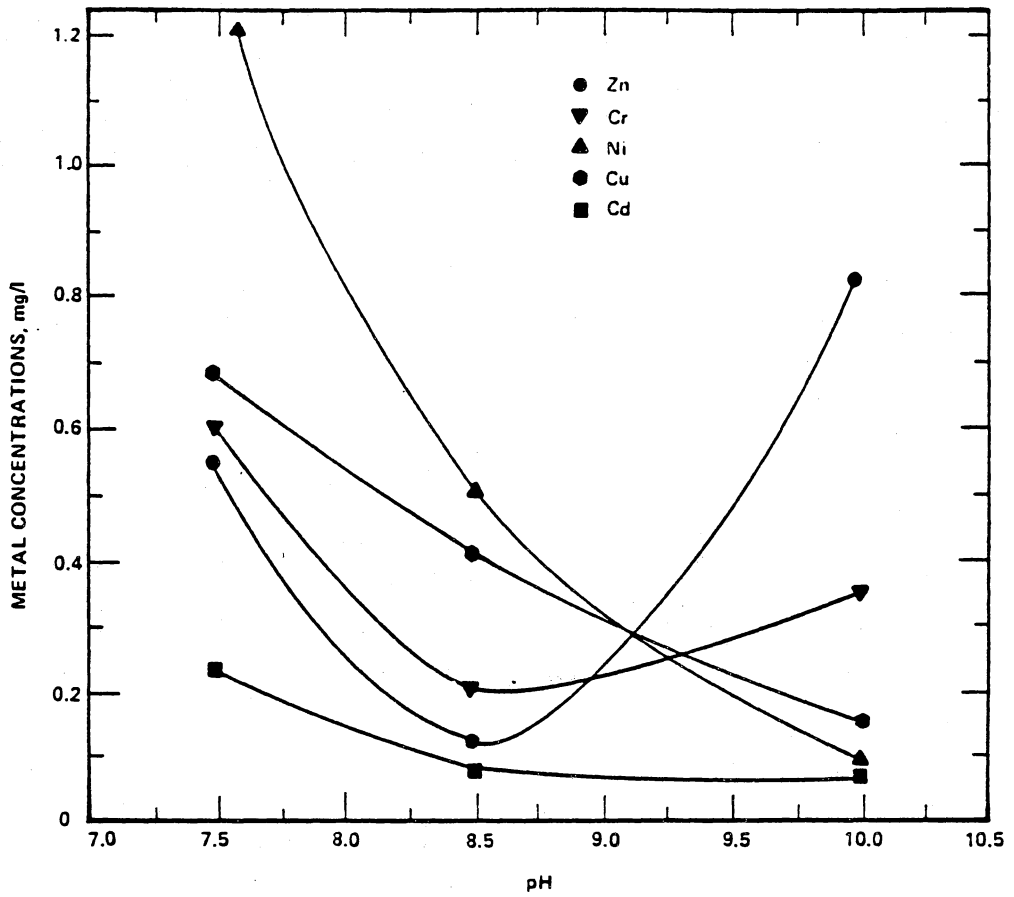


Figure 45. Optimum pH values for metal removal (88).

all of the flasks ranged from 7.7 to 11.4. Although metals generally are precipitated from solution at an alkaline pH, certain metals have minimum solubilities at a specific pH and pH values lower or higher than this will cause the ion to remain in solution (Figure 46). The solubility of various arsenic species at a total concentration of 75 mg/L is illustrated in Figure 47. This Eh-pH diagram represents a conservative estimate for As solubility in the control flasks of this study because the controls contained 10 mg/L As. Figure 47 demonstrates that arsenic was present as various soluble species in the pH range (7.7 to 11.4) in the control and sorption flasks of these experiments. A positive redox potential is assumed to exist in control flasks as a result of agitation and a relatively open system.

Because arsenic was soluble in the control tests in the absence of an adsorbent, arsenic removal in the shale-water slurries was most probably due to adsorption. Livesey and Huang (91) studied the adsorption of low concentrations (0.1 and 2.15 mg/L) of arsenate, AsO_4^{3-} , on soils and discovered that As was removed by adsorption mechanisms and not through precipitation.

Arsenic was removed to levels ranging from 0.1 to 0.90 mg/L at equilibrium in all of the sorption flasks of this

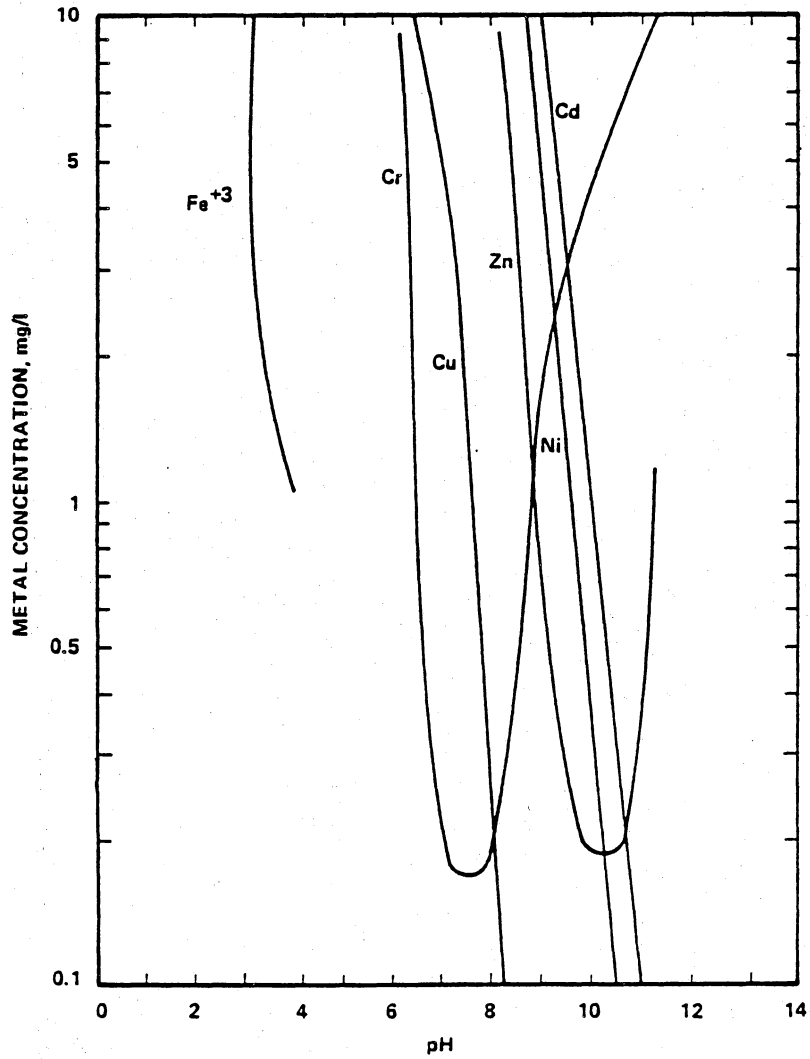


Figure 46. Solubility of metals versus pH (88).

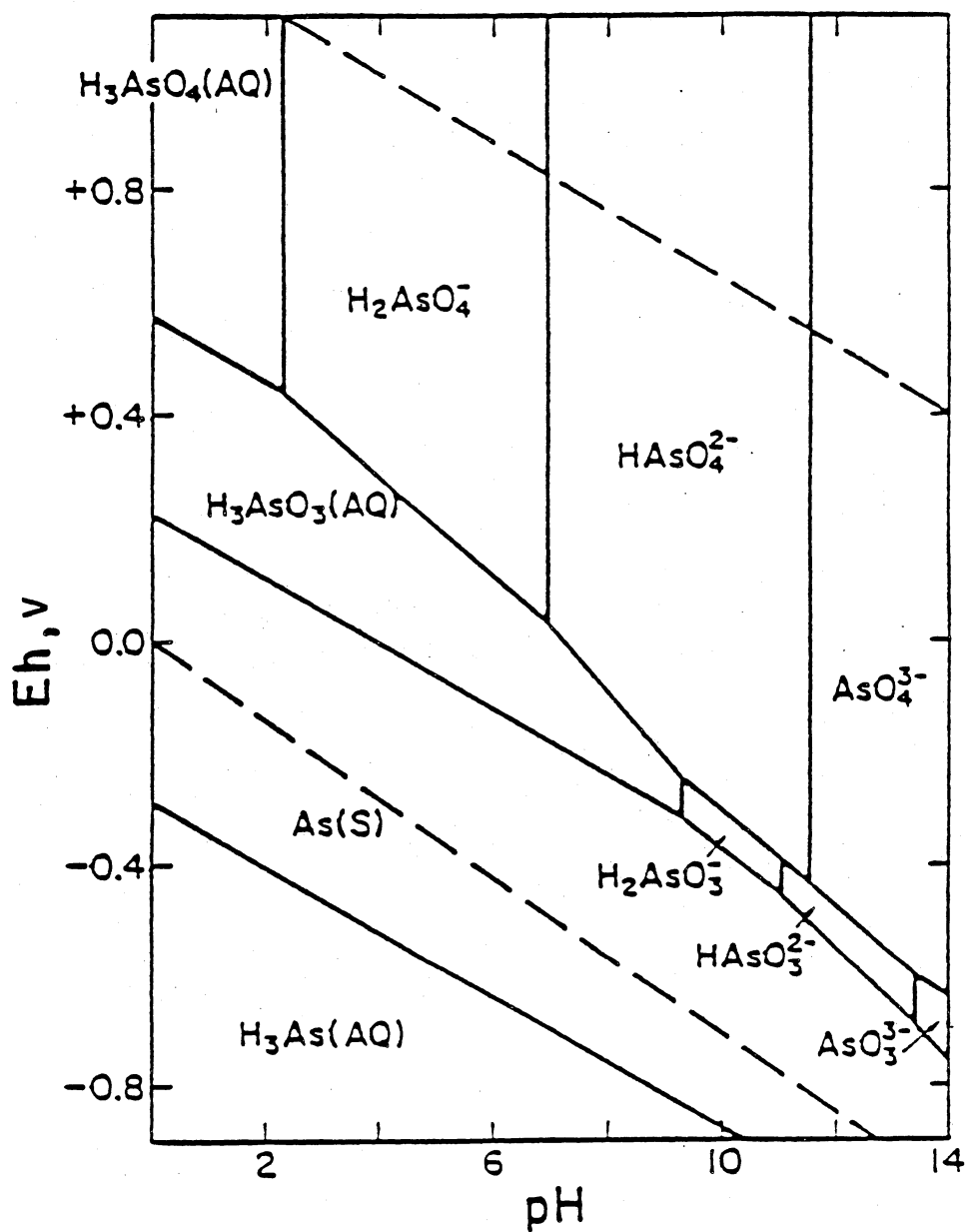


Figure 47. Eh-pH diagram of As-H₂O system at a_{As} (activity of As) = 10^{-3} moles/liter or As = 75 mg/L (90).

study. These values approached the water quality criteria standard, 1.0 mg/L, and exceeded the maximum level prescribed for primary drinking water sources, 0.05 mg/L; however, they are well below the 5.0 mg/L MCL for EP toxicity.

Oxy, Run 16 and Antrim shales exhibited various adsorption capacities for fluoride. Fluoride was not adsorbed by Anvil raw shale. High background levels were eluted from the Anvil shale and these contributed to the amount added for sorption. Evidently, retorting processes caused changes in the shale surface, creating an ability to adsorb fluoride. Fluoride can be precipitated as calcium fluoride; however, the presence of soluble fluoride in the control flasks for Run 16 and Antrim shales indicated that this did not occur (these shales eluted 150 to 250 mg/L Ca in batch elution trials). Calcium levels in the Anvil and Oxy eluents were much lower than the levels in eluents from the other shales. Fluoride levels decreased in the presence of shale; however, these reductions were relatively slight for Run 16 and Oxy shales. Antrim shale had the greatest adsorption capacity for fluoride, however, this removal was in no way as complete as the removal for the metals As, Cd, and Fe in all of the shale-water mixtures. The equilibrium levels of fluoride in the sorption flasks, 4.4 to 9.5 mg/L, were all well over the water quality and primary drinking

water standards (Table 23). It is evident that shale is not a very useful medium for removing fluoride from wastewaters.

DISCUSSION OF SINGLE- AND MULTI-ADSORBATE TRIALS

Throughout the continuous-flow sorption trials Antrim and Run 16 shales exhibited similar sorption capacities. This similarity was probably due to the lower retorting temperatures of these shales. Oxy spent shale, which was retorted under extreme temperatures, had sorption characteristics similar to those of Anvil raw shale. This was not surprising considering the work of Peterson and Wagner (18) and Kuo *et al.* (19) who discovered that shale retorted under extreme temperatures (+800°C), produced a leachate similar to that of raw shale (see previous discussion of retort temperature effects on leachate constituents, this chapter).

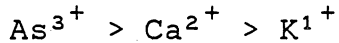
The results from the single- and multi-adsorbate trials are discussed together in the following section because adsorption behavior in the two experiments was basically the same. Differences in the results are pointed out.

Breakthrough curves for arsenic in shale columns illustrated that from highest to lowest adsorption capacity the four shales ranked as follows: Run 16, Antrim, Anvil and Oxy. Anvil raw and Oxy spent shales adsorbed very

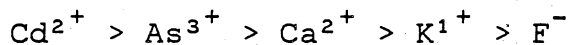
little arsenic compared to Antrim and Run 16 shales. At the end of the single-ion trials, the concentration of As in the Run 16 effluent was 2.5 mg/l, as compared to 1.3 mg/l in the multi-adsorbate trials. It is interesting to note that for both Antrim and Run 16 shales, arsenic adsorption was greater in the multi-adsorbate trials than in the single-ion trials. The solute mixture apparently did not affect the adsorption of As onto Anvil and Oxy shales. The multi-adsorbate arsenic results were very similar to those of the single solute trials for these two shales. Generally, the adsorption of a particular solute in a multi-component solution is less than that exhibited in a pure solution. This behavior has been demonstrated by both organic (74 and Giust74.) and inorganic (92 and 55) agents. It is possible that for Antrim and Run 16 shales, the concentration of other constituents in the feed solution was not sufficient to create interference, or that arsenic was preferentially adsorbed over the other solutes.

The removal processes in the shale columns may be a combination of several mechanisms such as precipitation, adsorption and ion exchange. In ion exchange, the magnitude of charge on the ion is an important factor in the extent and preference of ion exchange. Generally, exchange materials prefer counter-ions of high valence (76). Based

on valence one would therefore anticipate that preference for exchange of As, Ca, and K would be as follows:



Another factor which might affect exchange preference is the hydrated radius of an ion. Generally, multivalent hydrated ions are smaller than ions having a lower valence and are preferably exchanged and held tighter (76). Ions of larger ionic radius (increasing atomic number) have smaller a hydrated radius. Thus, based on consideration of valence and periodic functions, one might anticipate that ion exchange preference for the ions considered in this study may be ordered as follows:



However, it is important to note that arsenic may also occur as As^{5+} .

The presence of anions in a solvent may increase the adsorption of particular metal ions (51 - 53,93 and 94). Anions accumulate in the double layer of a positively charged particle, enhancing the approach of metal ions to a solid surface. The heavy metal ions form complexes or chelates with the anionic ligands that are already attached to the adsorbent (94). This type of behavior becomes particularly significant when considering the case of increased adsorption of arsenic in the multi-adsorbate

trials with Antrim and Run 16 spent shales. The presence of the anion, F, in the feed solution might have influenced the adsorption of As in the multi-adsorbate trials. Antrim and Run 16 shales exhibited a capacity to adsorb fluoride. The fluoride ion may have adsorbed to the Antrim and Run 16 shale surfaces, thereby creating additional sites for adsorption of cations. Huang et al. (93) interpreted increasing adsorption in the presence of anions as the formation of a metal ligand which is adsorbed by the hydrous solid through chemical bonds. This may be a potential mechanism for the increased arsenic adsorption noted in the multiadsorbate trials.

Calcium and potassium adsorption was not observed with Run 16 and Antrim shales because elution levels of these ions from the shales were much greater than that of the feed solution (10 mg/l). The Ca and K adsorption capacities of Anvil and Oxy shales were less in the multi-adsorbate trials than in the single-ion trials. These results (i.e., adsorption of solute was less from a mixture than from a pure solution) are supported by the results obtained by other investigators with Mg, Ca, Cd, Co, Zn, Cu and Pb (92 and 55).

The capacities of Antrim and Run 16 shales for F⁻ were basically the same in both the single- and multi-adsorbate

experiments. Adsorption of fluoride by these two shales in columns verified the results of the batch sorption experiments. Antrim had the greatest capacity for the adsorption of fluoride, followed by Run 16 shale. Oxy shale, however, did not exhibit the same ability for fluoride removal in the column trials, as it did in the batch experiments. A small amount of fluoride was adsorbed in the batch trials, while there was no apparent removal of fluoride in the columns. This may be explained by film and pore diffusion transfer processes. In batch reactors, the degree of agitation probably reduced the influence of the rate-controlling factor of film diffusion. In a continuous-flow column, however, film diffusion must be overcome before pore diffusion can take place (76). Therefore, adsorption could not occur until these factors were overcome.

In the single- and multi-adsorbate trials Anvil and Oxy shales exhibited a difference in the amount of fluoride contained in initial pore volumes of effluent. The fluoride concentration in the initial effluents was greater in the single solute experiments than in the mixed solute trials. Apparently, the mixture of agents decreased the solubility of fluoride containing materials in the shale.

Generally, all of the shales removed cadmium from solution to levels below detection on the AA in both the

single- and multi-sorbate column experiments. Whether this removal was due to precipitation, as in the batch sorption trials, or adsorption, cannot be firmly stated. However, the batch control flasks, which contained leachate and ions, but no shale, provided an indication of the extent of precipitation. Recall that cadmium and iron levels in these control flasks were generally below detection limits, indicating that removal was by some other mechanism than adsorption. In this case, removal was probably due to precipitation at the alkaline pH of the solvent.

Iron was not included in the multi-adsorbate trials because it created a floc in the feed solution. Single-ion trials were conducted with Fe, however, and the results obtained with all four shales indicated that Fe was removed to levels below detection. As with Cd, it is likely that due to the alkaline pH of the eluents, precipitation was the major removal mechanism.

Desorption Trials

Desorption of columns with distilled water after the sorption trials yielded the same results for both the single- and multi-adsorbate experiments. Generally, all ions considered were flushed from the columns in the first two or three pore volumes to an equilibrium concentration.

The initial levels of ions in the effluent were probably due to the elution of ions in the pore space of the shale columns, rather than the elution of adsorbed species.

Desorption of calcium from Anvil and Oxy shales paralleled the results of the elution experiments. In the multi-sorbate trials, calcium was initially flushed from the column to less than 1 mg/L, then Ca levels increased in the effluent. This is most likely the result of slow dissolution of calcium-containing minerals in the shale. Antrim shale also exhibited this behavior in the desorption experiments, although it did not in the elution trials. In the Antrim elution trials, the Ca levels were very high initially, 600 mg/L, and were eluted to approximately 10 mg/L in the final effluents. However, Ca had been eluted from this shale to about 20 mg/L in first phase of the sorption/desorption trials when the desorption trial was begun. It is likely that if the elution trials had been extended in time, Ca would have been dissolved from the shale matrix as in the desorption trials.

Potassium levels in the effluents of the multi-sorbate trials with all of the shales indicated that K minimally desorbed from the shales. Effluent K concentrations were less than 1 mg/L after five pore volumes of effluent. Similar values were obtained in desorption of the single-ion

sorption columns. In a K sorption/desorption study of soils, Sparks (95) found that K desorption was rapid initially due to desorption from the surface and then more slowly as K diffused through pore spaces.

Cadmium and iron did not desorb from the shales when eluted with distilled water. Precipitates of these ions may have been strongly adsorbed, sedimented and/or filtered from the feed stream. This is consistent with the findings of Dudas (46) who reported that Cd was sparingly dissolved and removed in the leachates from columns of fly ash.

Arsenic appeared in eluents from all of the columns. Some of the ion was derived from feed solution left in the shale columns. However, the levels of As in the initial eluents of Anvil (10 to 12 mg/L) and Antrim (14 to 18 mg/L) indicated that some desorption took place. Initial levels of As from Run 16 and Anvil columns contained lower As concentrations, approximately 5.0 to 6.5 mg/L and less than 1.8 mg/L, respectively.

Run 16 and Anvil shales exhibited some desorption of fluoride. Fluoride levels in effluents ranged from 2 to 3 mg/L in approximately the tenth pore volume of eluent to the end of the 48 hour desorption period. Fluoride in Anvil eluents was most likely derived from a solid source in the shale. Several investigators have reported that the

fluoride in leachates from raw shales was probably due to the dissolution of a fluoride containing mineral in the shale. Antrim and Oxy desorbed much less fluoride, but Oxy shale apparently did not adsorb fluoride, so the desorption levels noted were predominantly due to elution of pore volume fluoride levels. Antrim shale apparently had the capacity to bind fluoride strongly enough to prevent its elution.

Summarizing the desorption phase of the column sorption trials, it was found that very little cadmium and iron desorbed from the shales, and arsenic desorbed more from Anvil and Antrim shales than Oxy and Rn 16 spent shales. Calcium increases in column eluents were most likely due to dissolution of minerals in the shale. Fluoride desorbed from Anvil and Run 16 shales to a greater degree than with Oxy and Antrim shales.

Factors Which May Affect Adsorption Capacity

Adsorption processes are known to be pH dependent. This dependence is directly related to the solubility of the adsorbate. Generally, increasing pH values decrease the solubility of a solute, thereby driving the solute towards the solid phase. Many investigators have reported that at higher pH levels, there is increased removal of ions such as

Cd, Pb, Zn, Cu and Co (52,92, and 93). The pH values of the eluents in these sorption experiments were all greater than 7.5. As mentioned earlier, precipitation processes cannot be differentiated from adsorption in the column trials. However, the control, batch experiments did indicate that precipitation of Cd and Fe was extensive under the conditions of the trials.

It is well known that adsorption increases with increases in surface area or porosity (88). Highly porous adsorbents have a large surface area and, therefore, have many sites available for adsorption. This concept relates directly to the results of this study. Recall that based on porosity, the shales may be ordered from most to least porous as follows: Run 16, Antrim, Anvil and Oxy. This evidence supports the high adsorption capacities noted for Run 16 and Antrim shales, as compared to the other shales, which had much lower porosities.

ASSESSMENT OF BATCH AND COLUMN EXPERIMENTS

Batch elution trials were easier to set up and yielded results which accurately depicted the constituents in leachates from shales. Column trials provided the same results with respect to the amounts of inorganics leached, and also showed that most materials were flushed from the

columns in the first two to eight pore volumes. However, the choice of one type of experimental configuration over the other would depend upon the purposes of the study; i.e., whether to simulate natural leaching conditions or to quantify the constituents released until an equilibrium state is reached. The results from both types of experiments can be compared to water quality standards.

Batch sorption trials, as performed in this study, proved to be ineffective for evaluating shale adsorption capacity. This was because most of the ions added were completely adsorbed and/or precipitated within 24 hours of the experiment. A larger liquid-to-solid ratio might correct this problem. The experiment would also need to be developed with respect to pH and ligand effects on adsorption.

Column sorption trials were useful for determining the breakthrough of ions in the columns and also illustrated nicely the different adsorption capacities of the various shales. The extent of desorption of adsorbed ions could be examined in these experiments. However, column experiments require more time and equipment, and are therefore more expensive to perform than batch trials. Thus, application of the results of a study should be taken into consideration when deciding which experiments to utilize.

Chapter VI

SUMMARY AND CONCLUSIONS

Elution and sorption characteristics of a raw and three spent shales were examined in batch and continuous-flow column experiments. Elution experiments consisted of leaching shale samples with distilled water and quantifying the constituents released. Batch sorption experiments involved the addition of As, Cd, F and Fe to water-shale suspensions. The adsorption capacities of the four shales were also examined in continuous-flow column experiments.

Batch elution trials with spent shales produced eluents having a characteristic pH in the range 8.5 to 11.5. The shales retorted at low temperatures (660°C and 793°C) released, in batch elution trials, higher levels of Ca (150 to 250 mg/L), K (125 to 225 mg/L), and SO₄ (350 to 475 mg/L) than did a higher temperature, retorted shale (800 to 1000°C) and raw shale (Ca, 5 to 18 mg/L); K, 2 to 6 mg/L; SO₄, 5 to 55 mg/L).

The shales retorted at lower temperatures also had higher porosity values than the raw shale and higher temperature retorted shale. These shales also exhibited greater sorption capacity for As, Cd and F in column trials. Column sorption experiments with single and mixed solutes

indicated that some ions were sorbed to a lesser or greater extent in the multi-adsorbate trials while other ions were apparently not affected. Cadmium and iron desorption from shale columns was minimal while other ions desorbed to different extents.

The conclusions derived from this study are as follows:

1. Retort temperatures and porosity values of the various shales had a significant effect on the quantity of inorganic constituents leached from the spent shales. Most of these constituents were flushed from the columns during elution trials in the first two to eight pore volumes of effluent.
2. Shales retorted at lower temperatures, which also had higher porosity values, exhibited greater sorption capacity for As, Cd and F. As, Cd, and Fe were removed to below detection limits for most of sorption trials. High pH values of the eluents were most likely responsible for the removal of Cd and Fe through precipitation.
3. Although there was almost complete adsorption and/or precipitation of many of the ions considered in the batch sorption trials, these experiments did give an indication of how the agents would behave in the presence of shale. The continuous-flow column

experiments provided for a more accurate analysis of the sorption/desorption capacity and elution properties of the shales.

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Appendix A

EQUILIBRIUM ISOTHERMS FOR BATCH ELUTION TRIALS

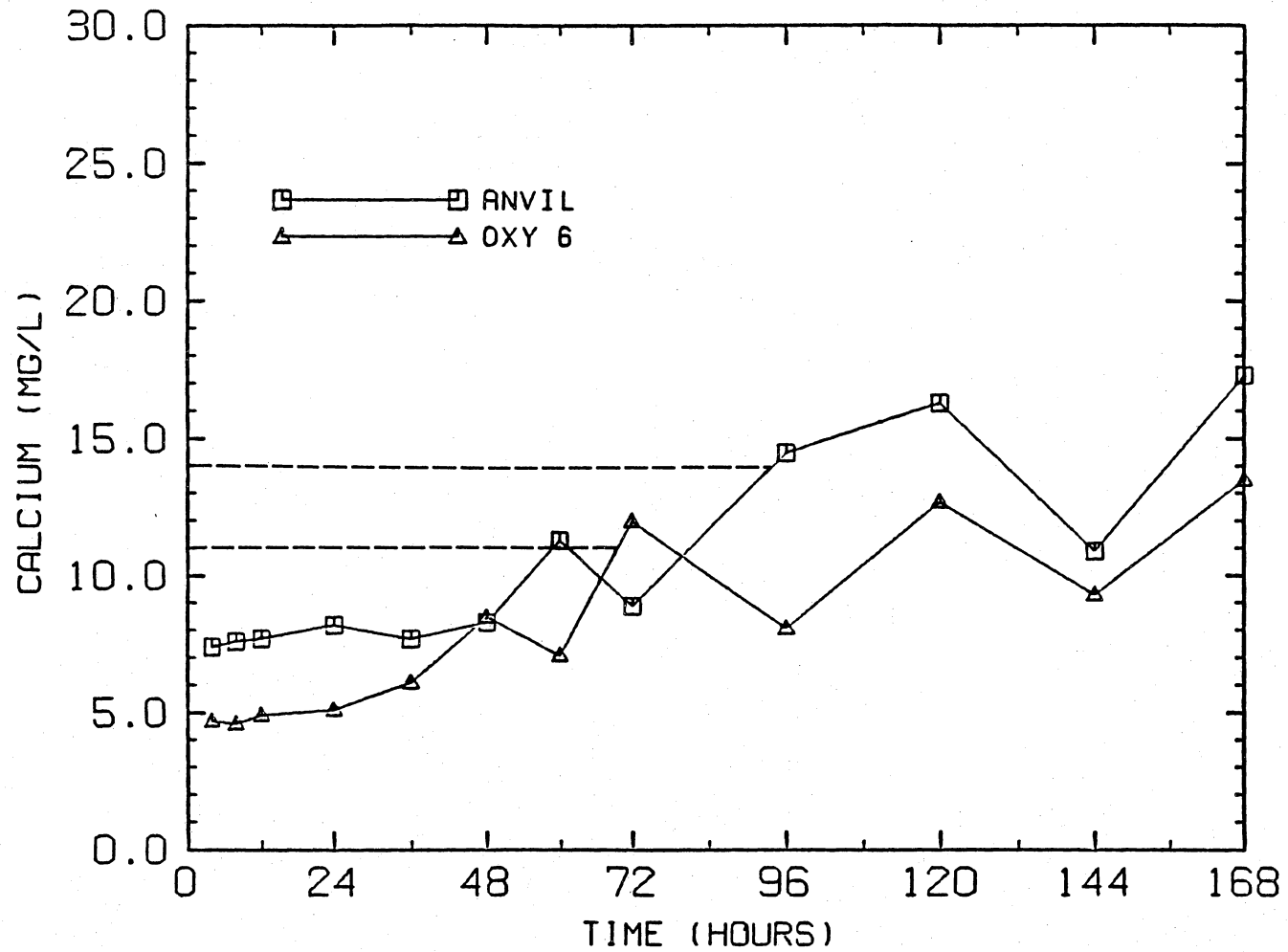


Figure A1. Variation in calcium of batch eluents for Anvil raw and Oxy spent shales. Dashed line represents concentration at equilibrium.

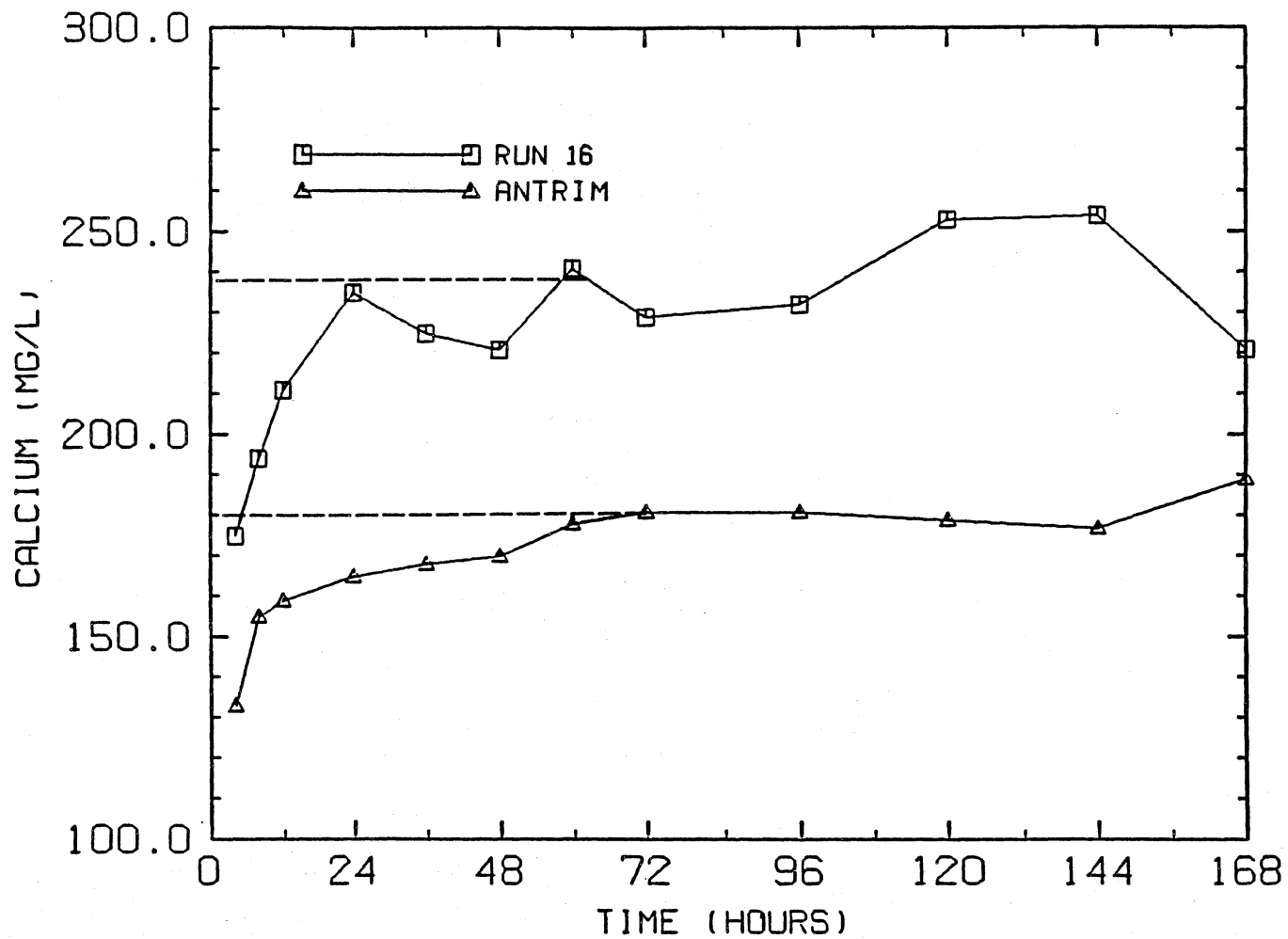


Figure A2. Variation in calcium of batch eluents for Antrim and Run 16 spent shales. Dashed line represents concentration at equilibrium.

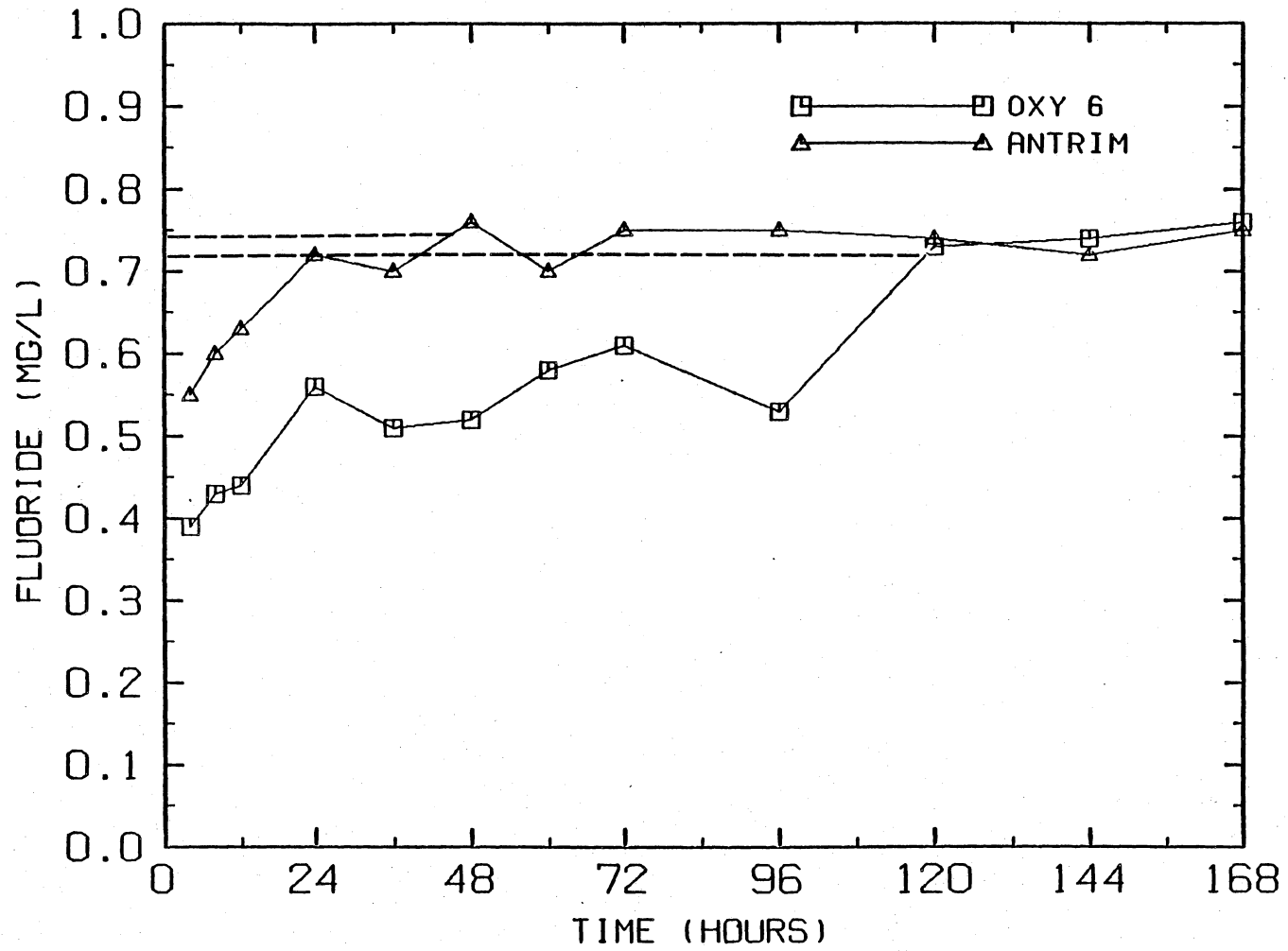


Figure A3. Variation in fluoride of batch eluents for Oxy and Antrim spent shales. Dashed line represents concentration at equilibrium.

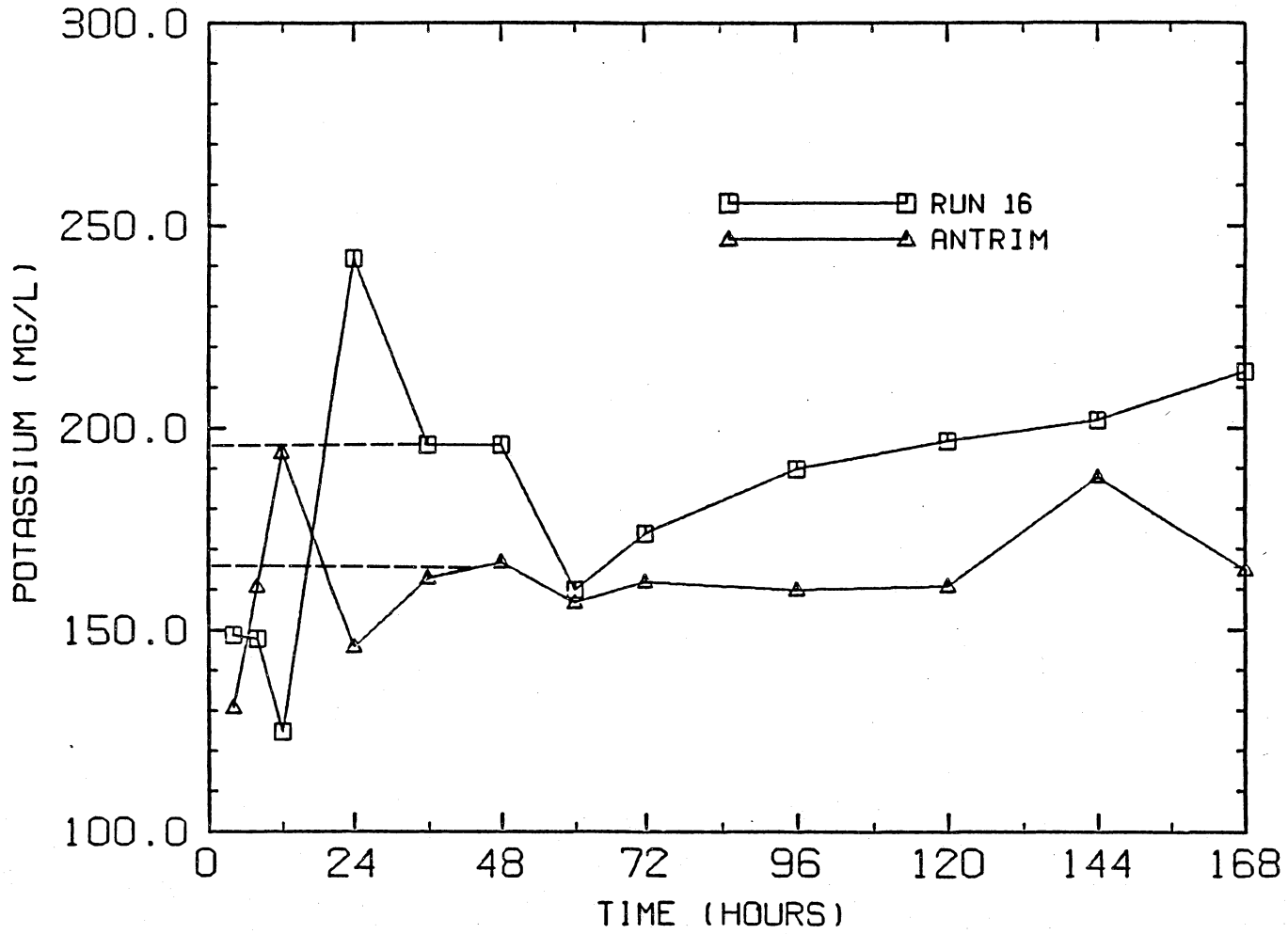


Figure A4. Variation in potassium of batch eluents for Run 16 and Antrim spent shales. Dashed line represents concentration at equilibrium.

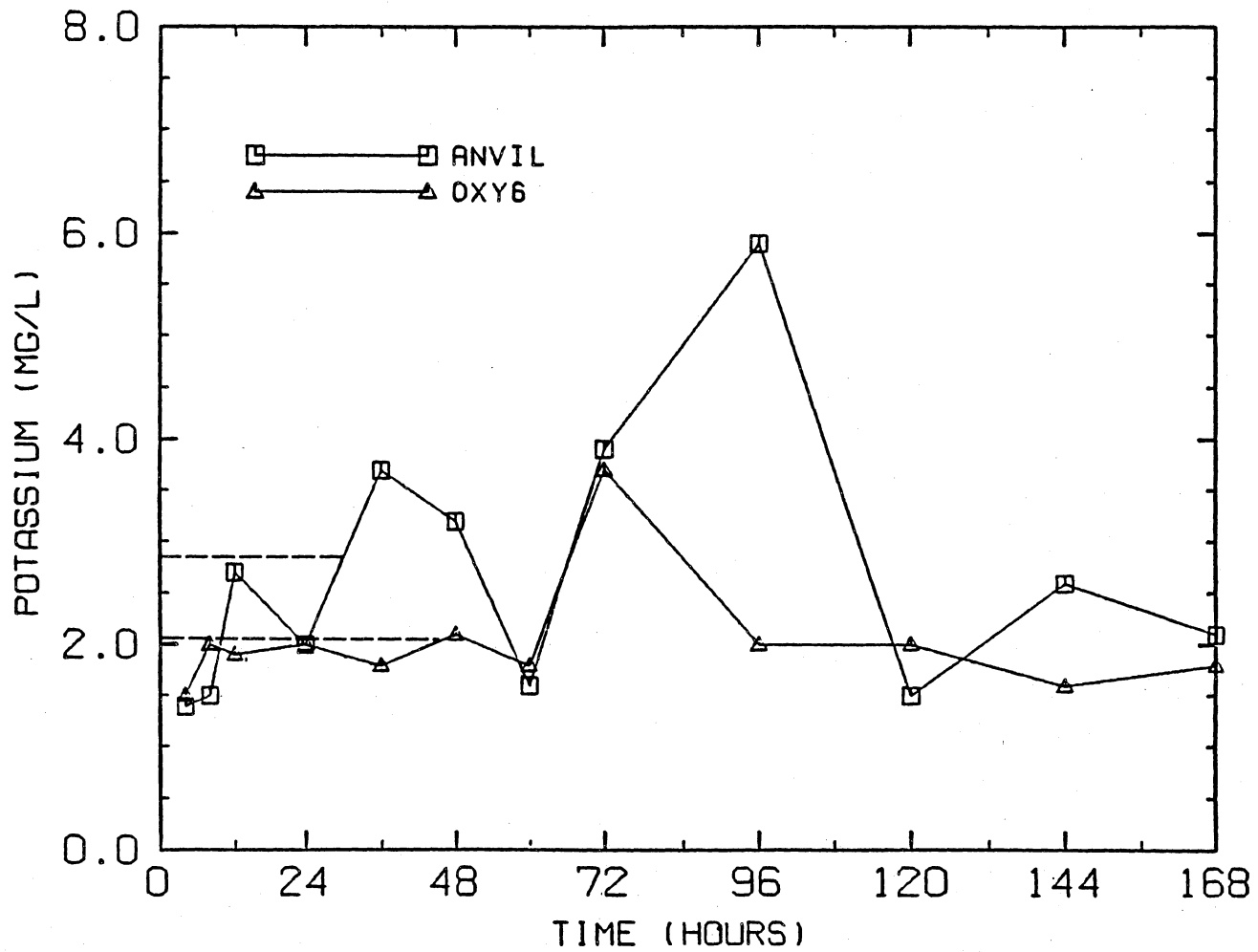


Figure A5. Variation in potassium of batch eluents for Anvil raw and Oxy spent shales. Dashed line represents concentration at equilibrium.

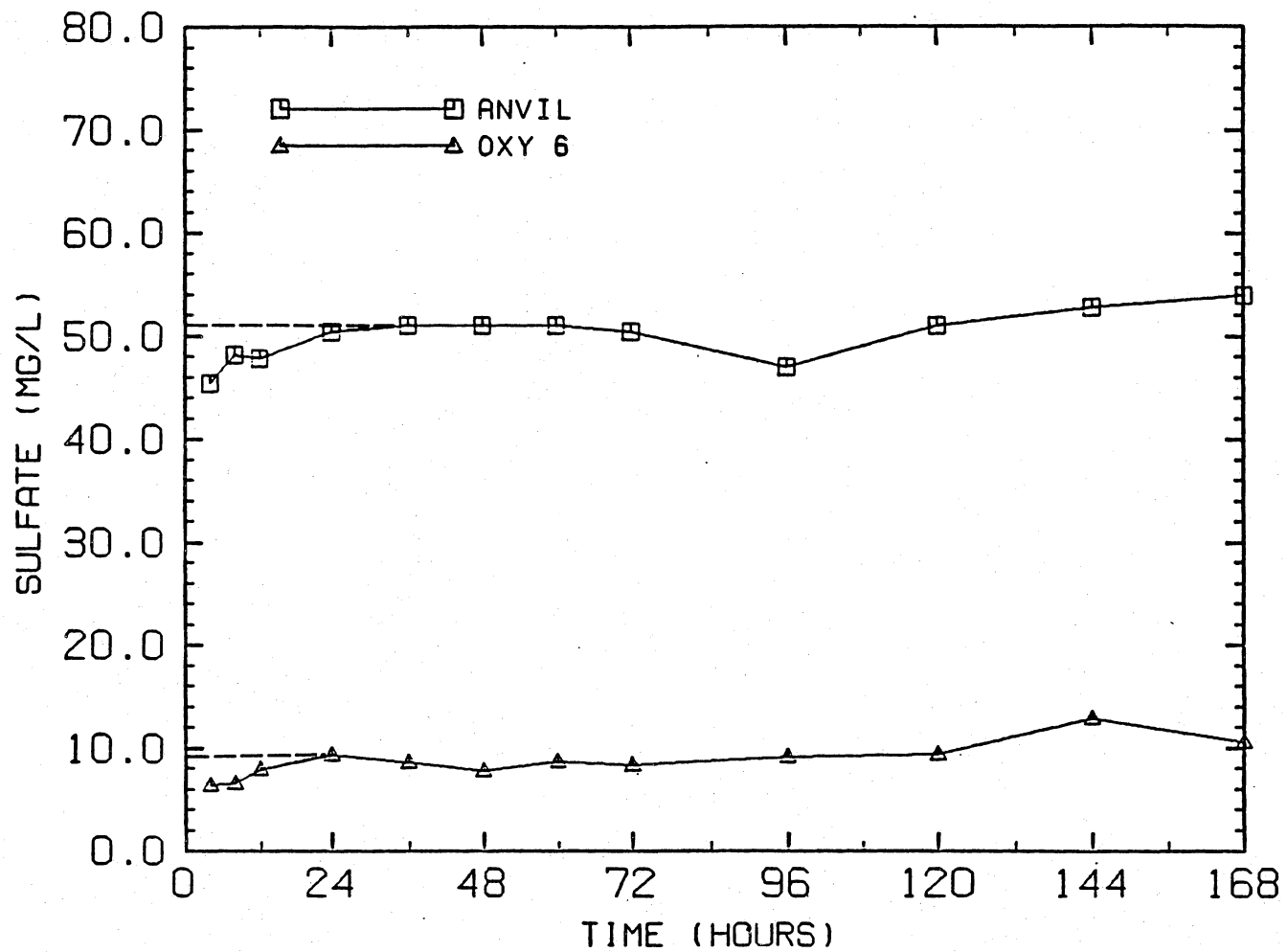


Figure A6. Variation in sulfate of batch eluents for Anvil raw and Oxy spent shales. Dashed line represents concentration at equilibrium.

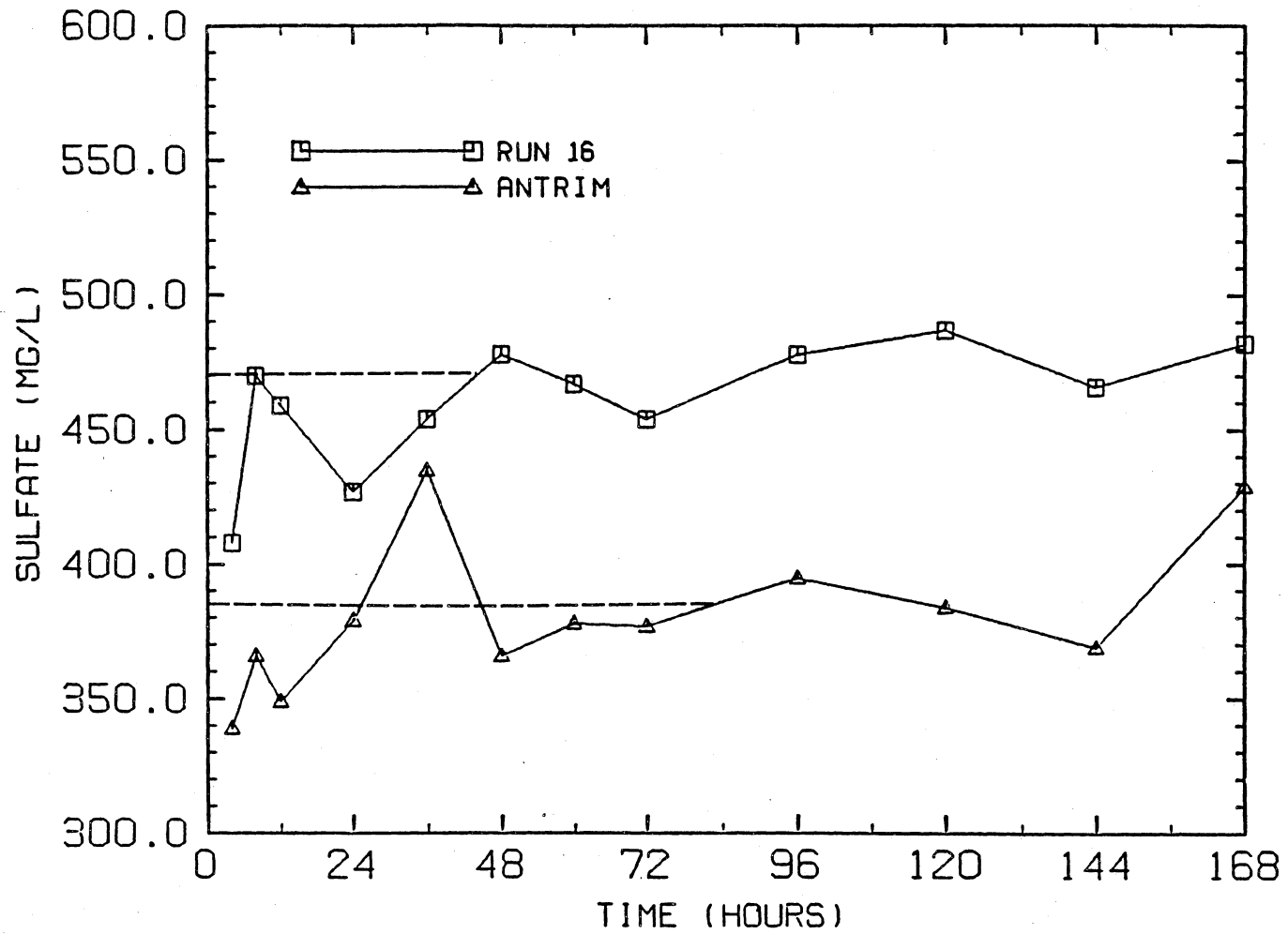


Figure A7. Variation in sulfate of batch eluents for Run 16 and Antrim spent shales. Dashed line represents concentration at equilibrium.

Appendix B

BATCH SORPTION ISOTHERMS

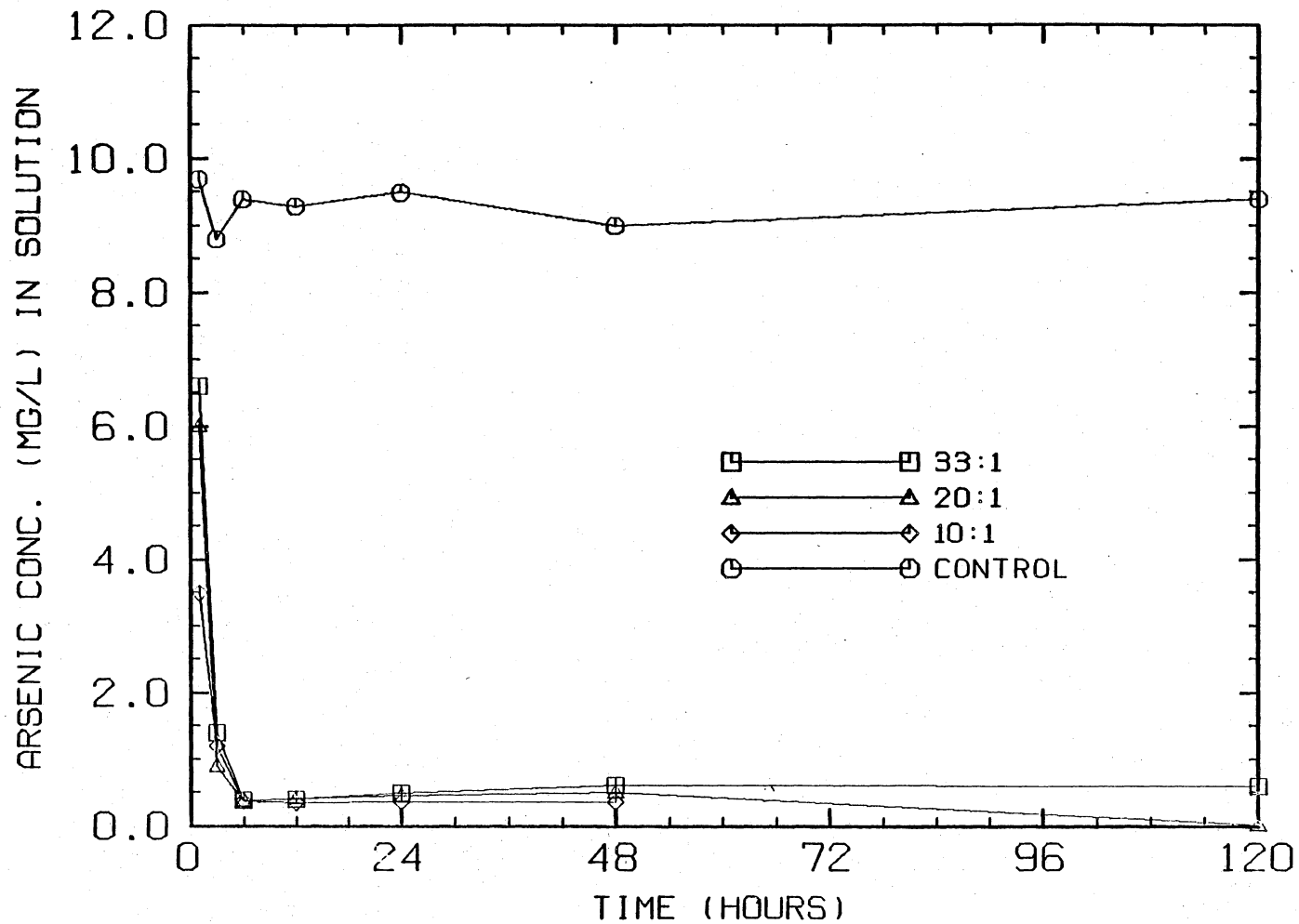


Figure B1. Comparison of arsenic concentrations remaining in solution during the batch sorption and control experiments with Anvil raw shale.

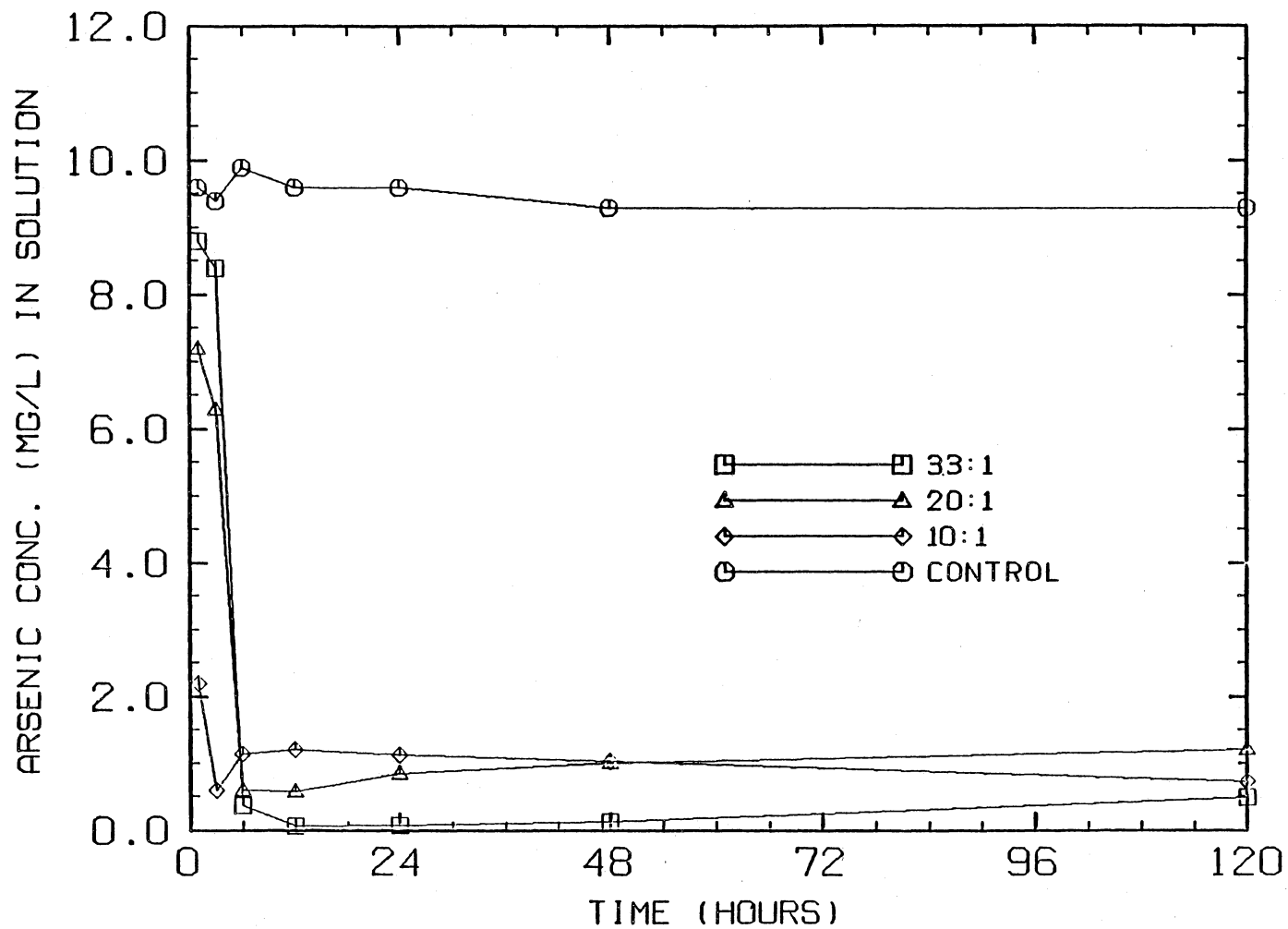


Figure B2. Comparison of arsenic concentrations remaining in solution during the batch sorption and control experiments with Antrim spent shale.

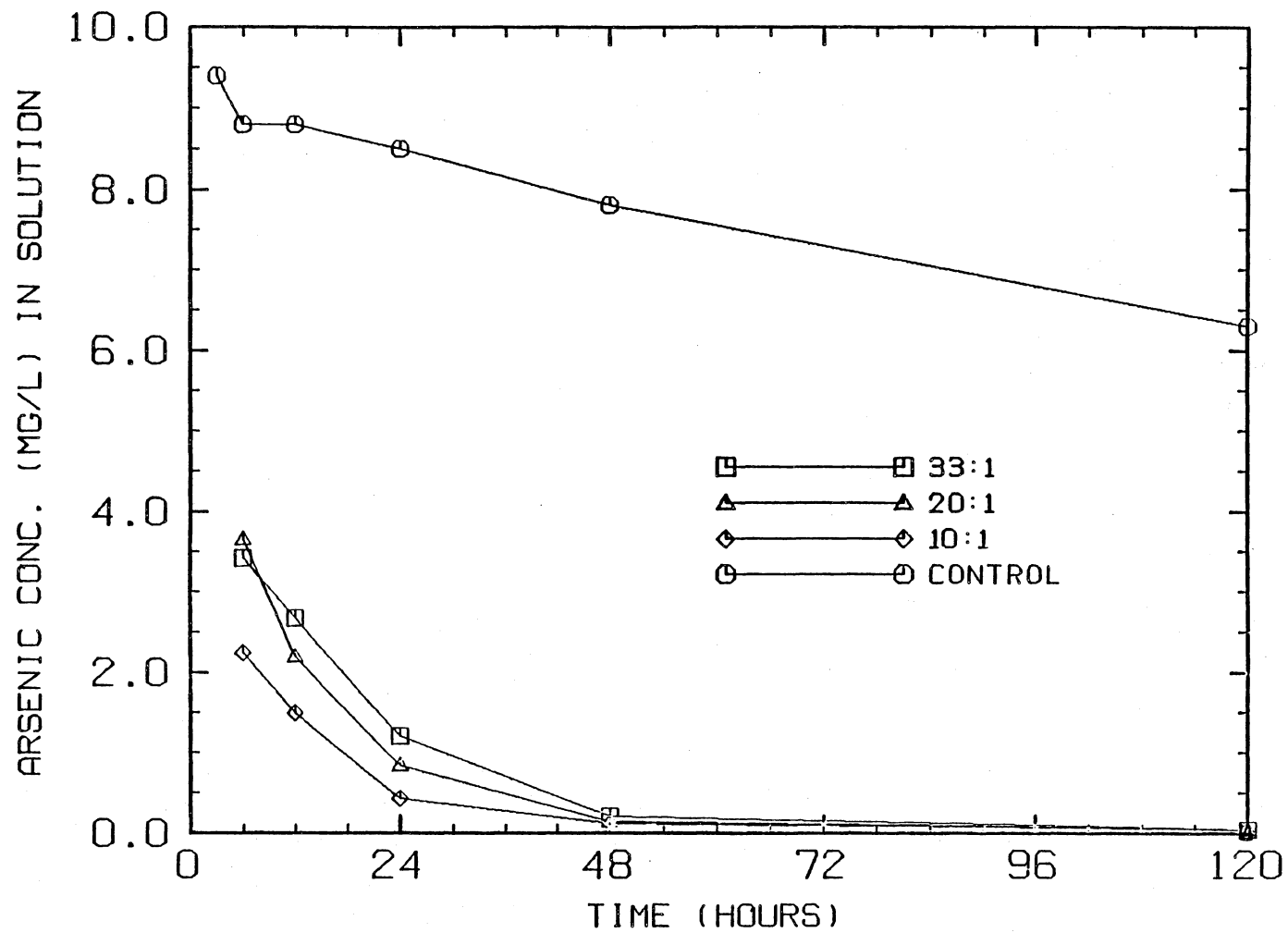


Figure B3. Comparison of arsenic concentrations remaining in solution during the batch sorption and control experiments with Run 16 spent shale.

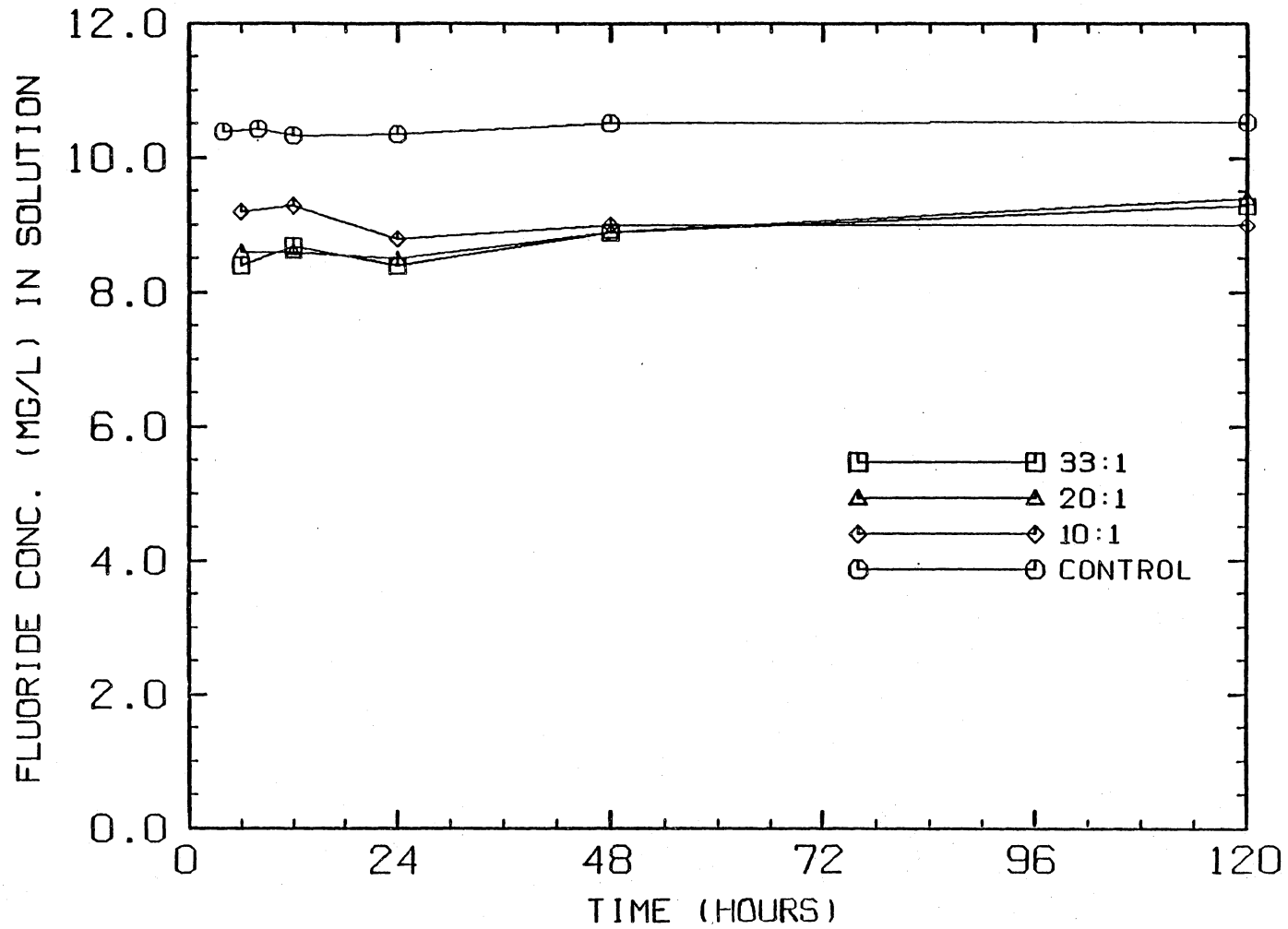


Figure B4. Comparison of fluoride concentrations remaining in solution during the batch sorption and control experiments with Oxy spent shale.

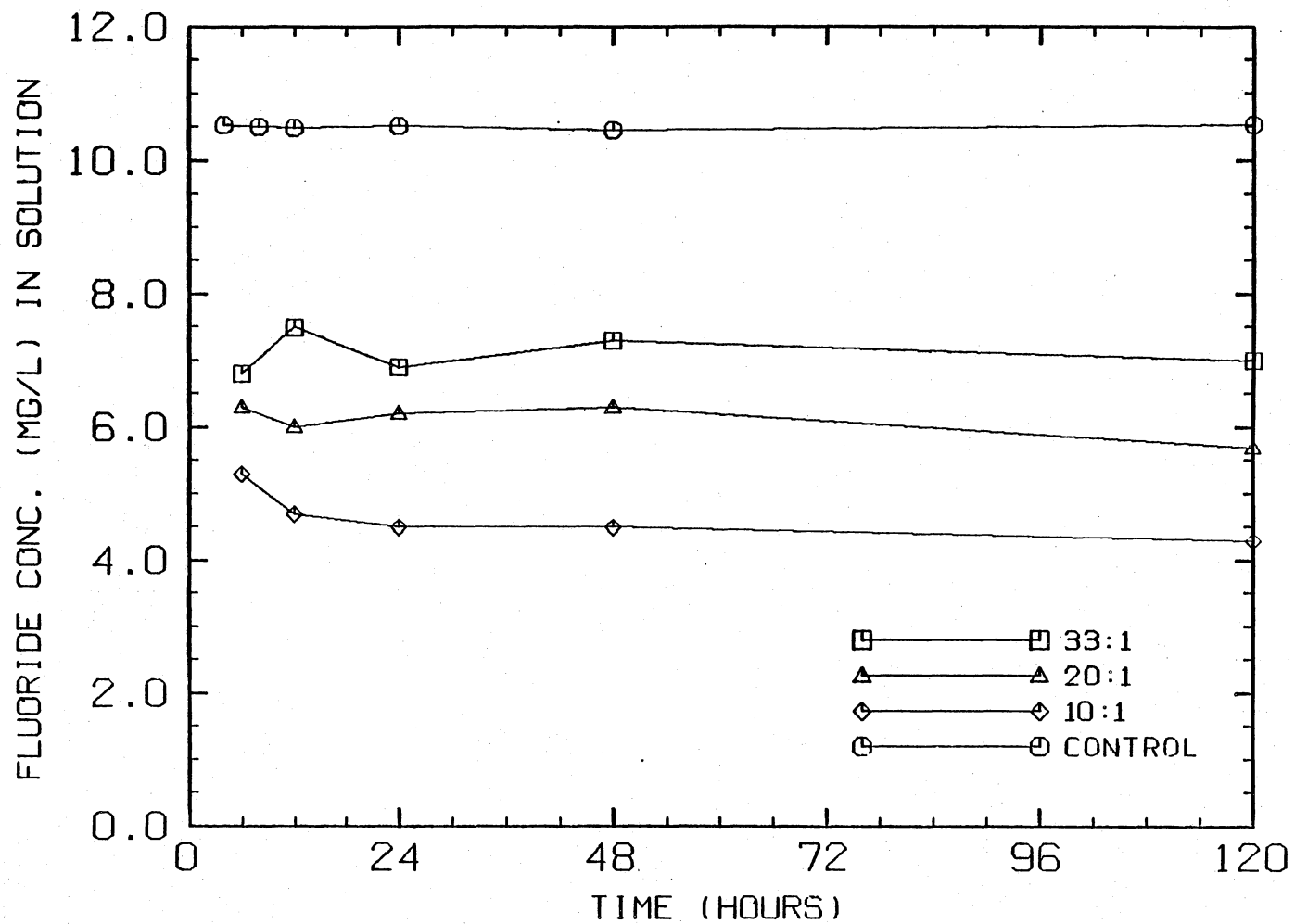


Figure B5. Comparison of fluoride concentrations remaining in solution during the batch sorption and control experiments with Antrim spent shale.

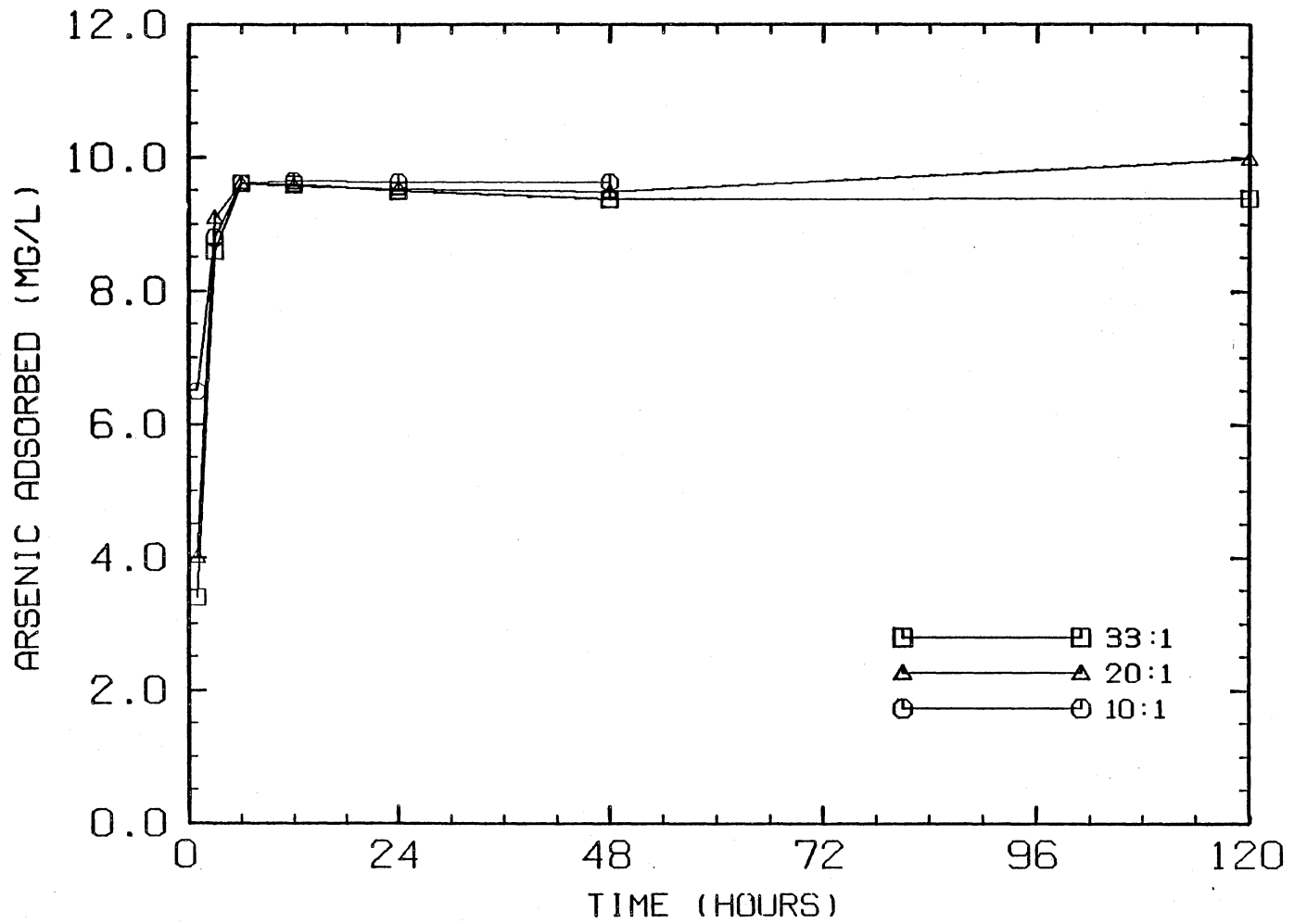


Figure B.6. Arsenic adsorbed as a function of time for three liquid-to-solid ratios of water to Anvil raw shale.

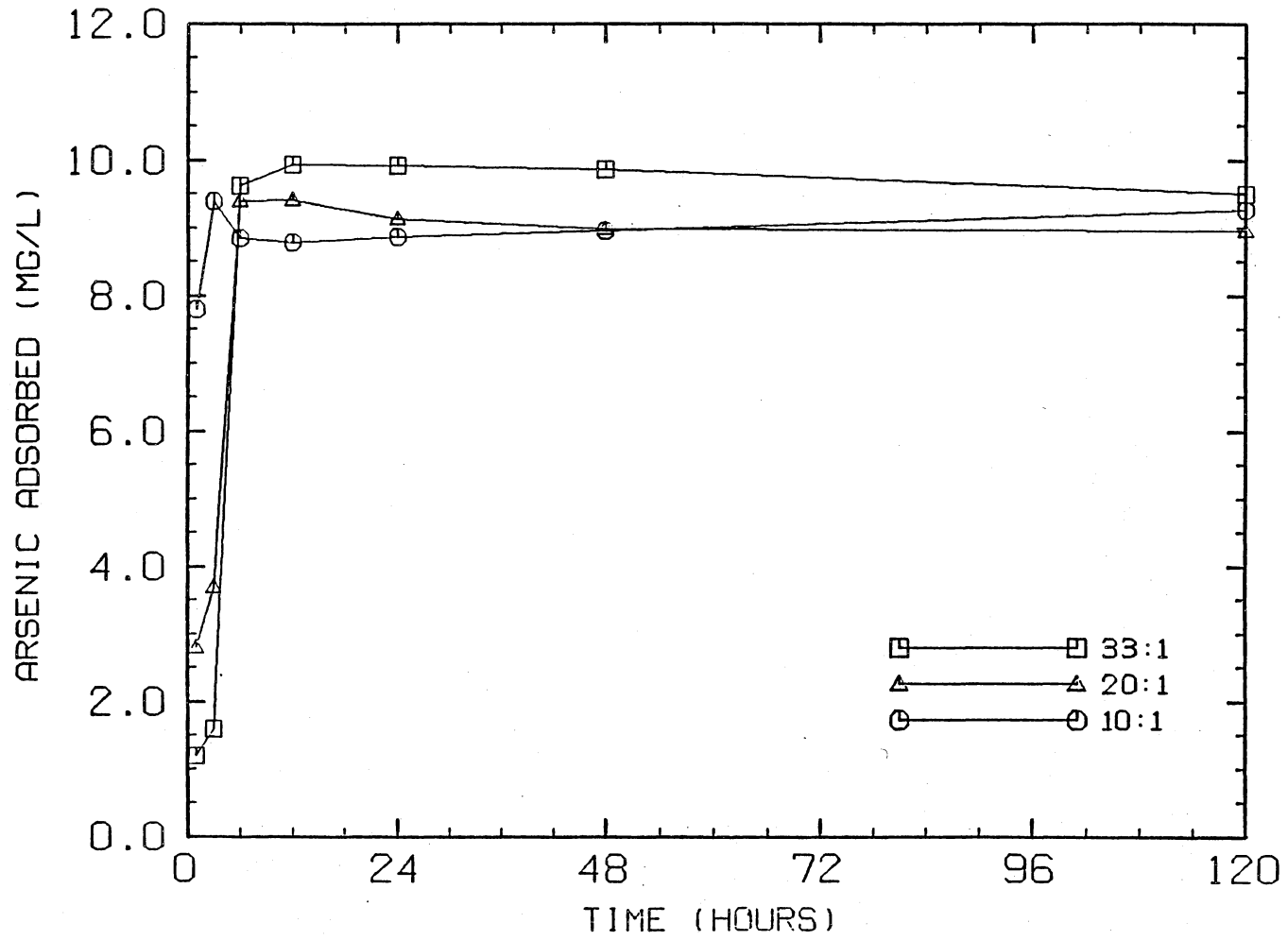


Figure B 7. Arsenic adsorbed as a function of time for three liquid-to-solid ratios of water to Antrim spent shale.

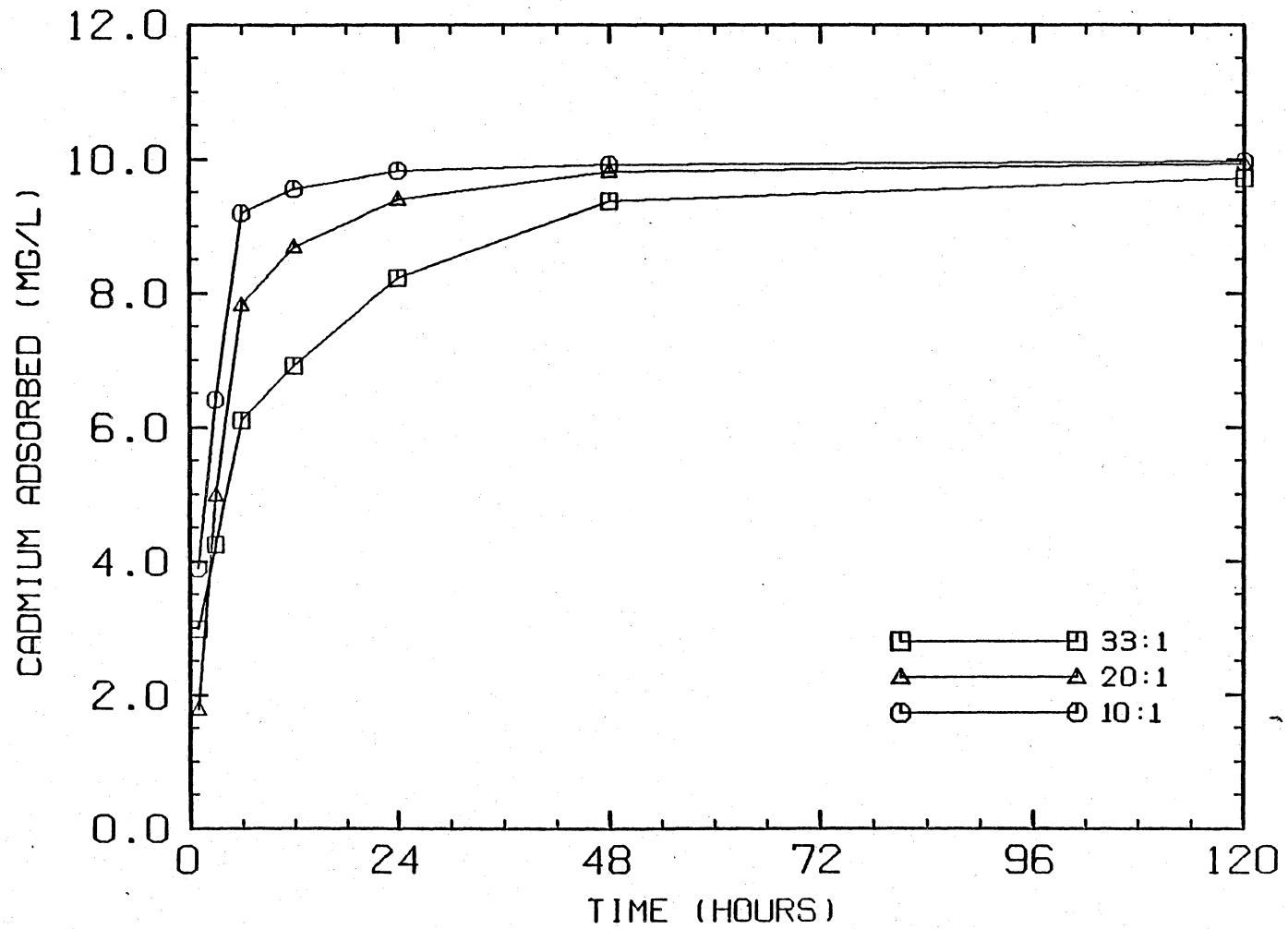


Figure B8. Cadmium adsorbed as a function of time for three liquid-to-solid ratios of water to Oxy spent shale.

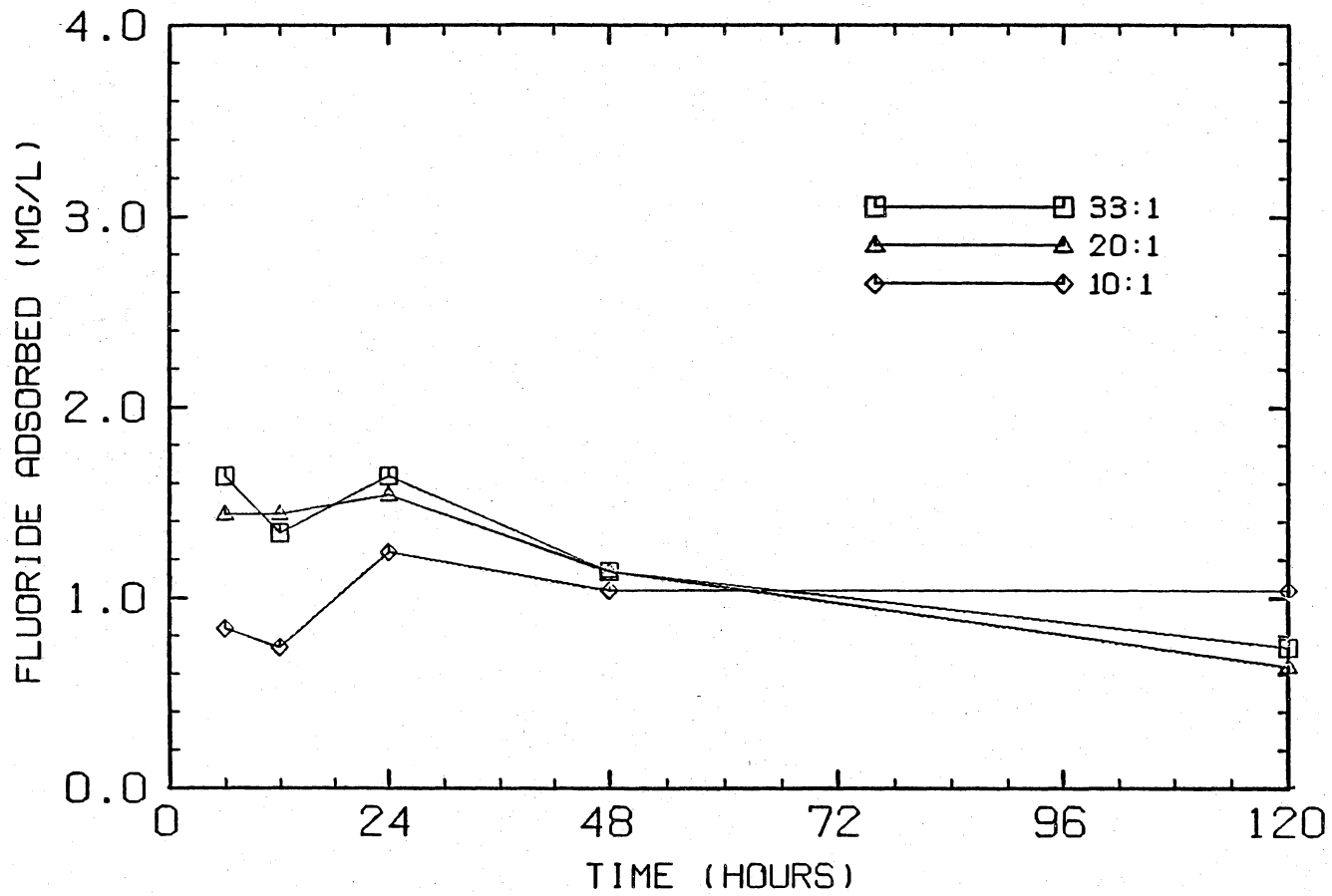


Figure B9. Fluoride adsorbed as a function of time for three liquid-to-solid ratios of water to Oxy spent shale.

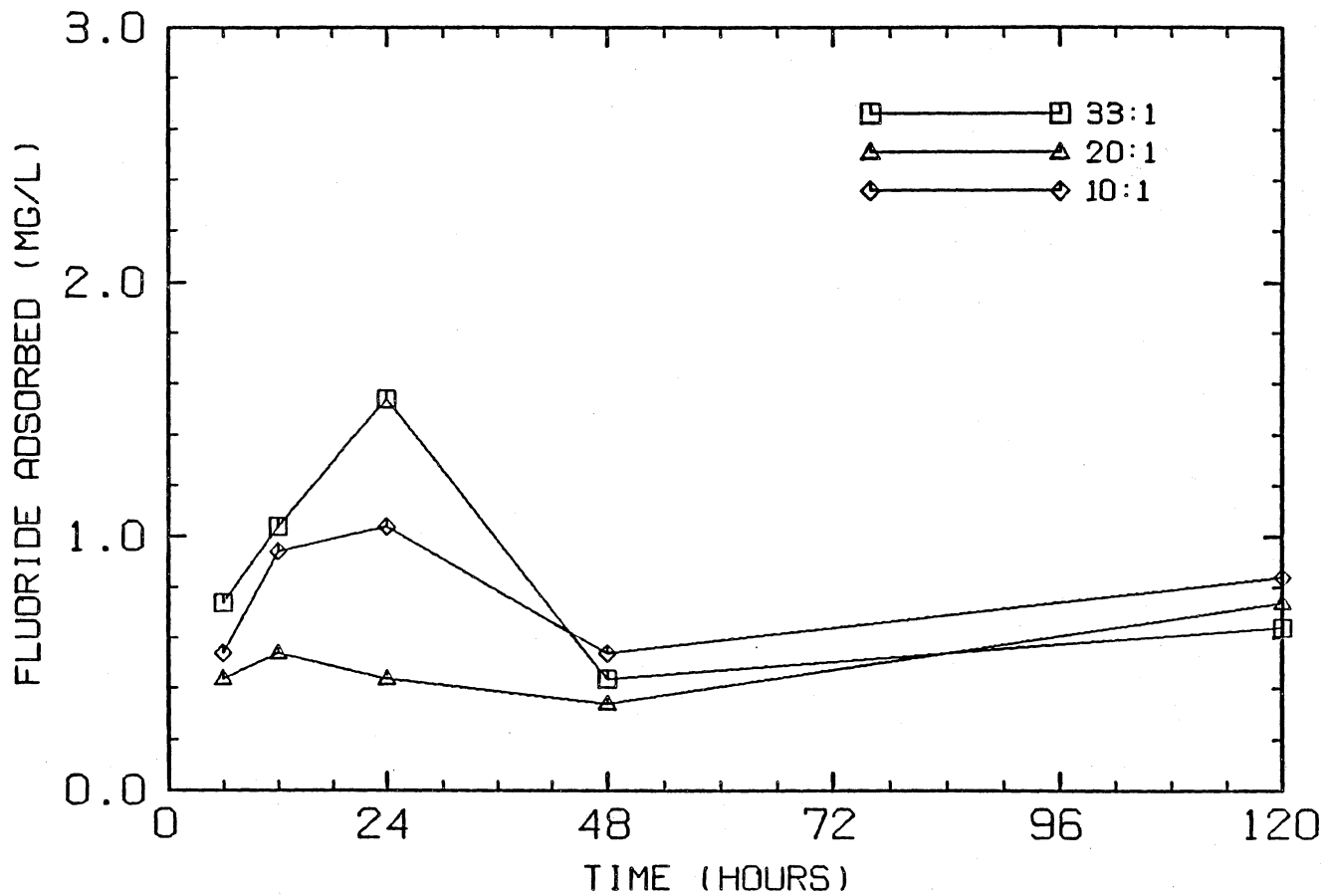


Figure B10. Fluoride adsorbed as a function of time for three liquid-to-solid ratios of water to Run 16 spent shale.

Appendix C
COLUMN ELUTION TRIALS

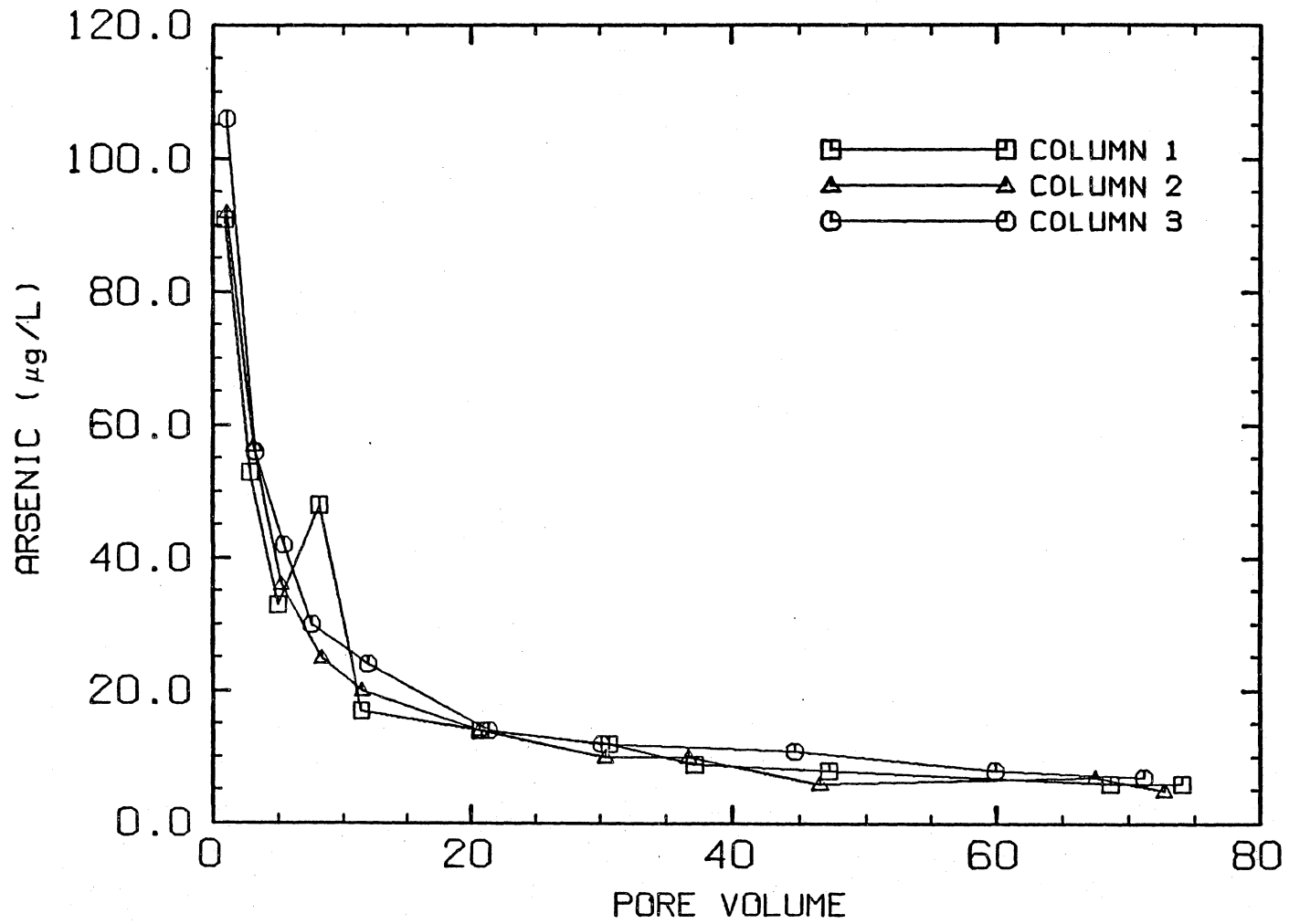


Figure C1. Variation in arsenic during column elution of Oxy spent shale.

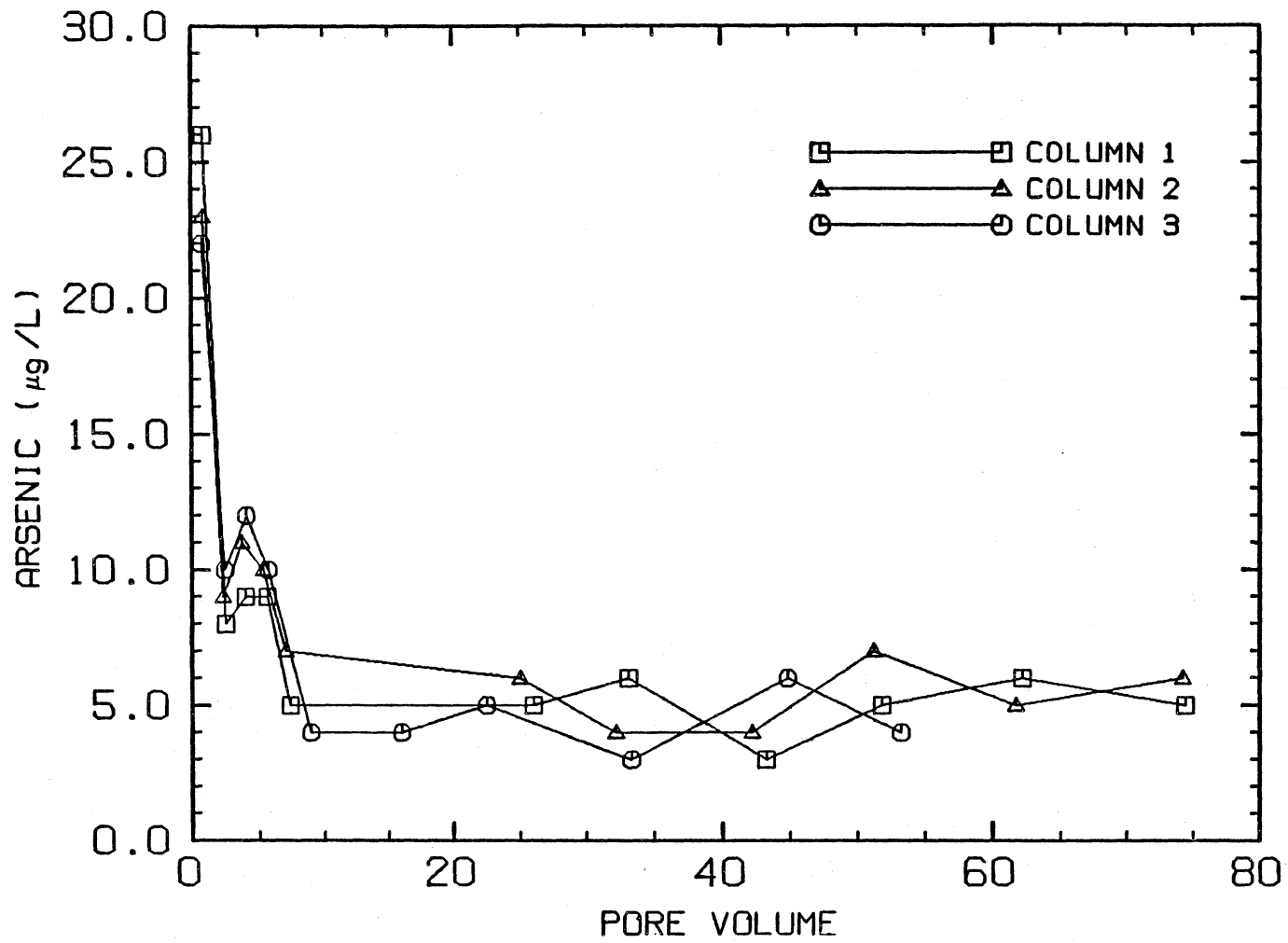


Figure C2. Variation in arsenic during column elution of Run 16 spent shale.

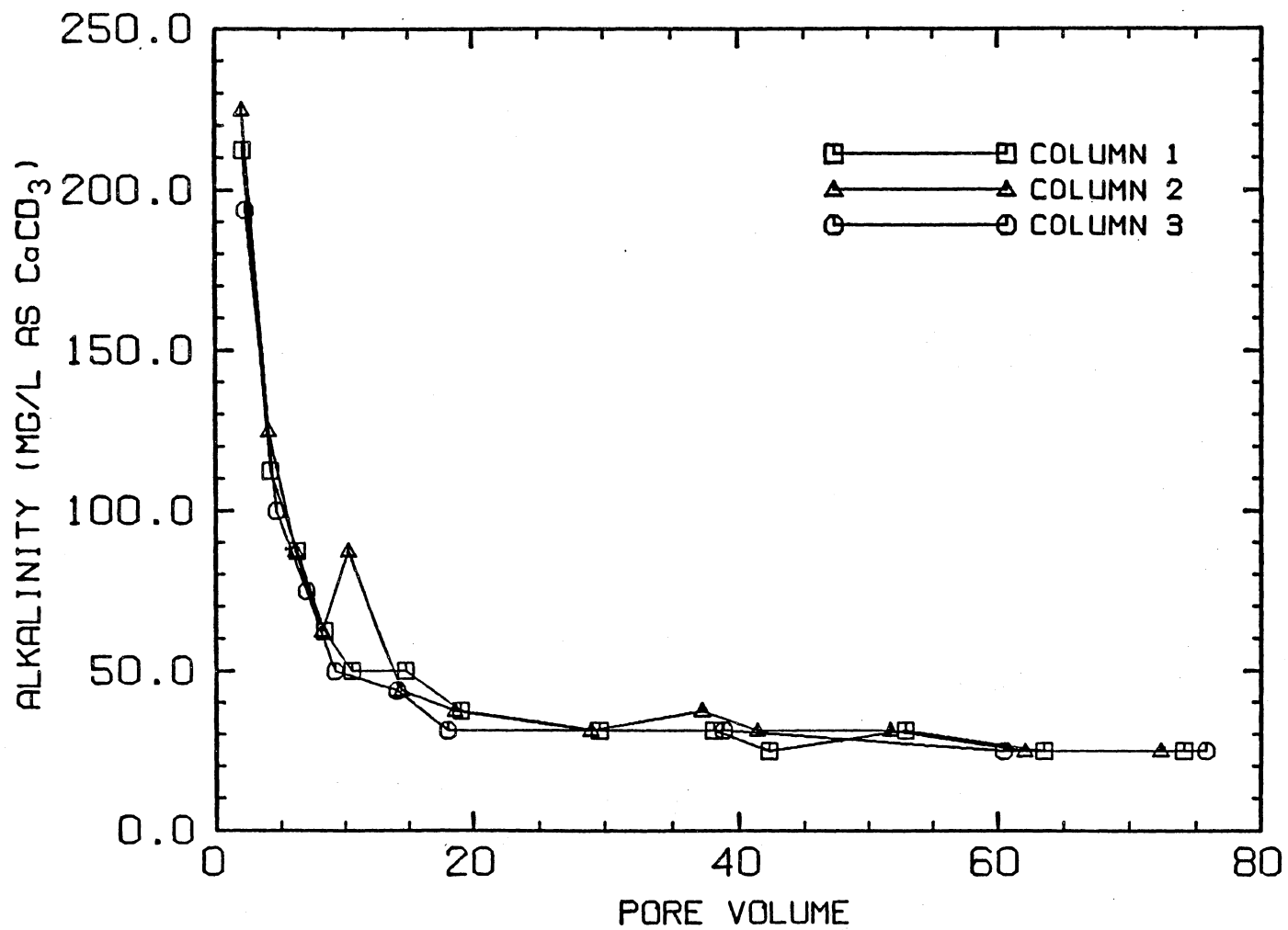


Figure C3. Variation in alkalinity during column elution of Anvil raw shale.

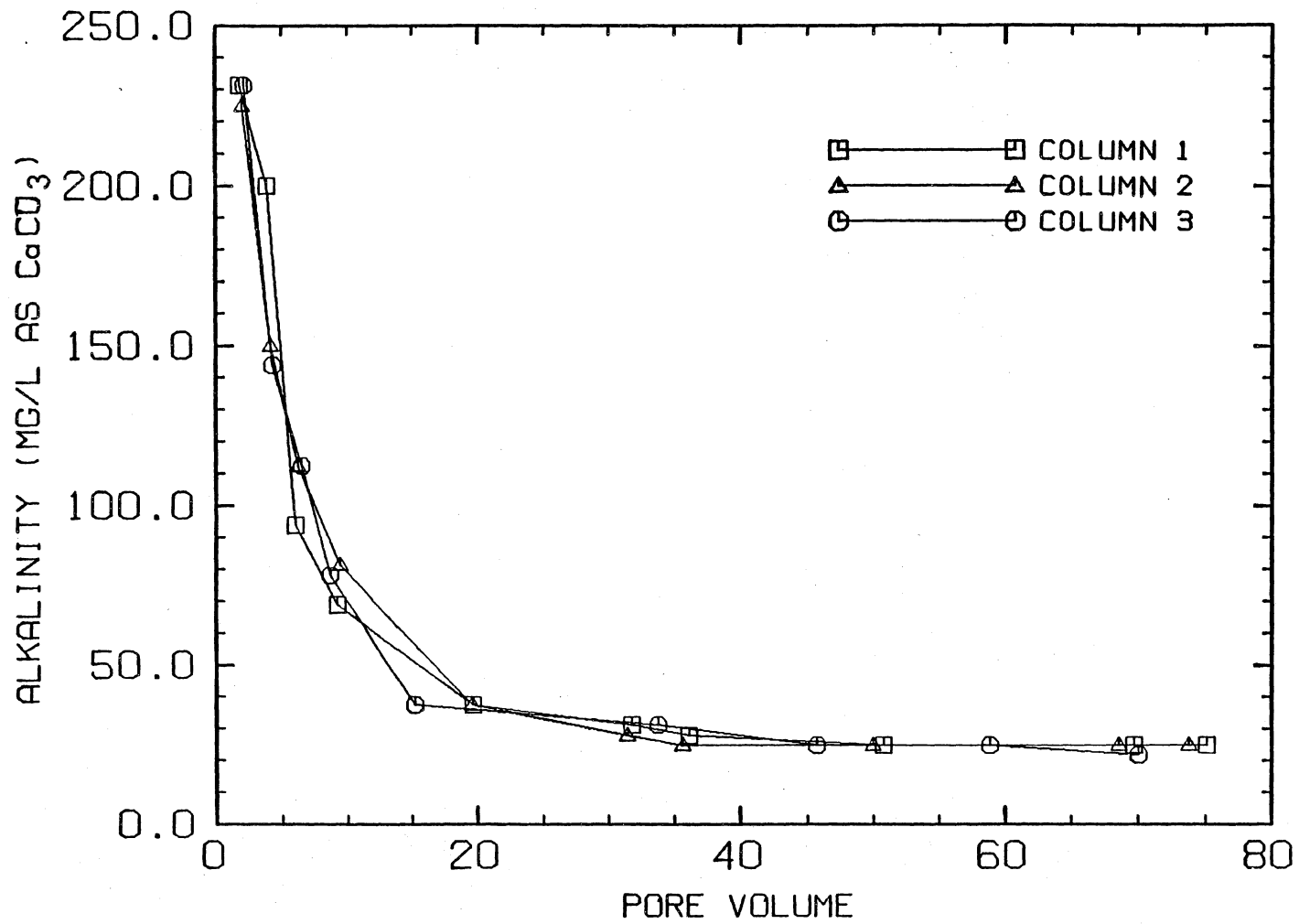


Figure C4. Variation in alkalinity during column elution of Oxy spent shale.

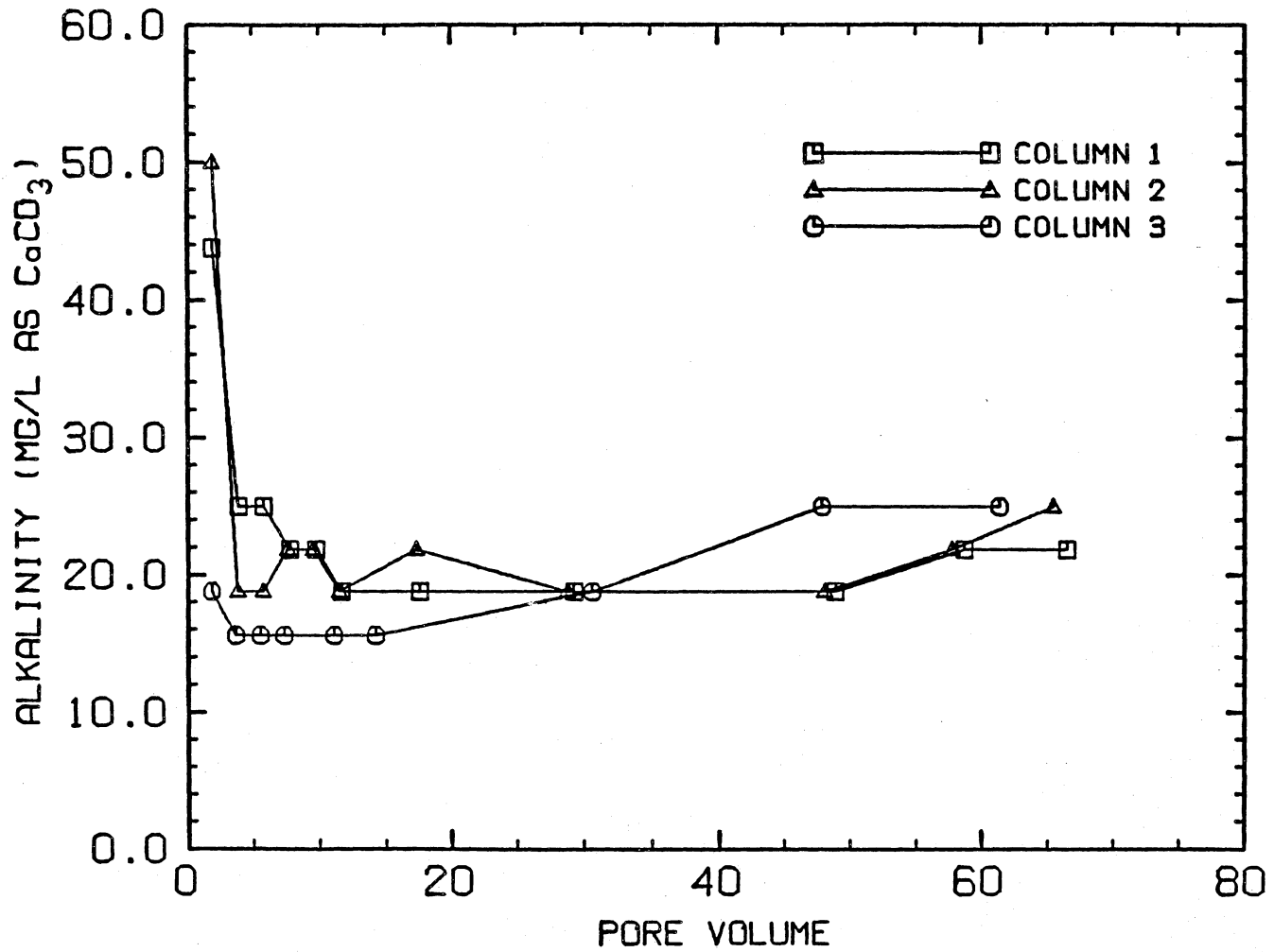


Figure C5. Variation in alkalinity during column elution of Antrim spent shale.

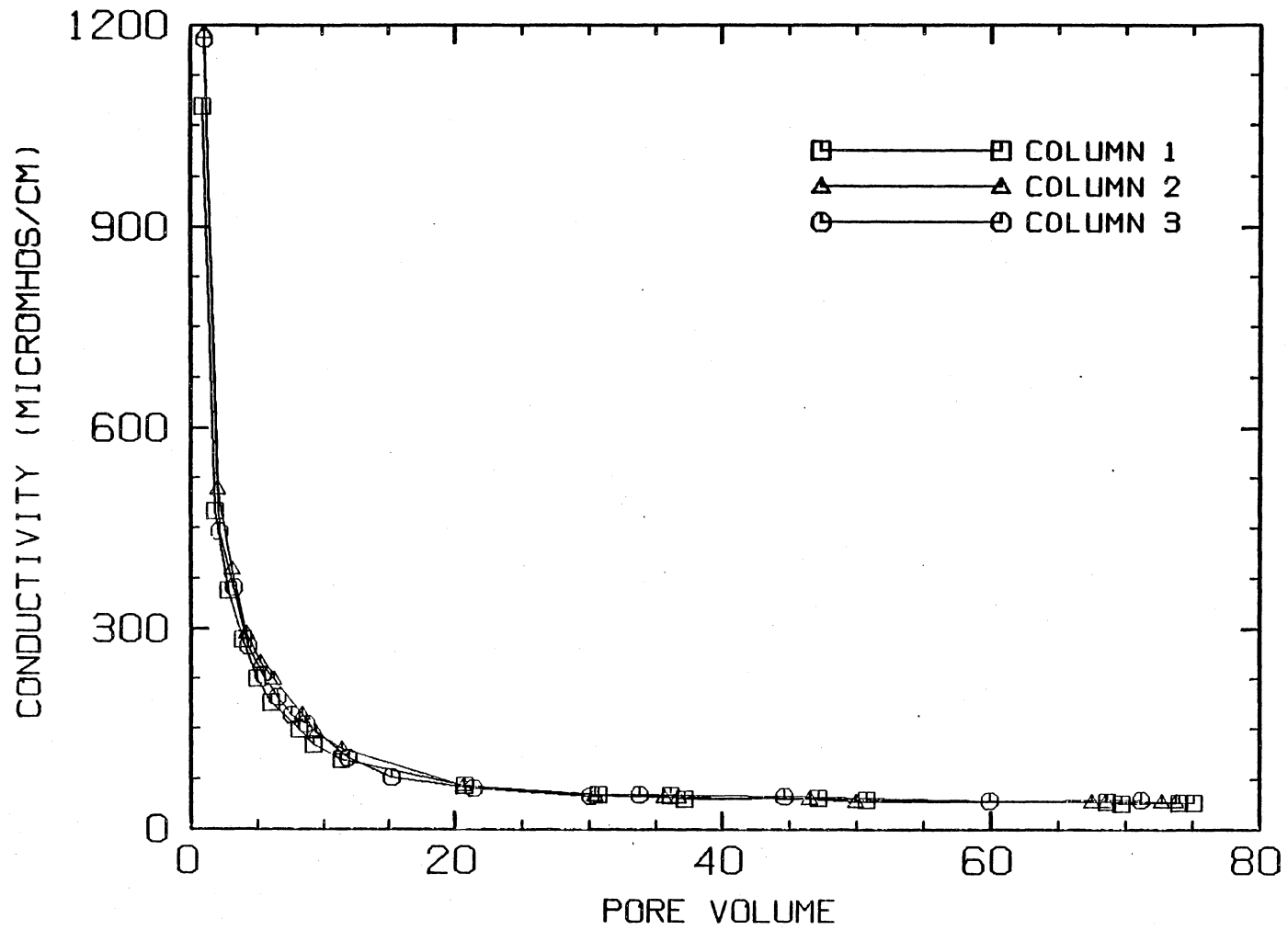


Figure C6. Variation in conductivity during column elution of Anvil raw shale.

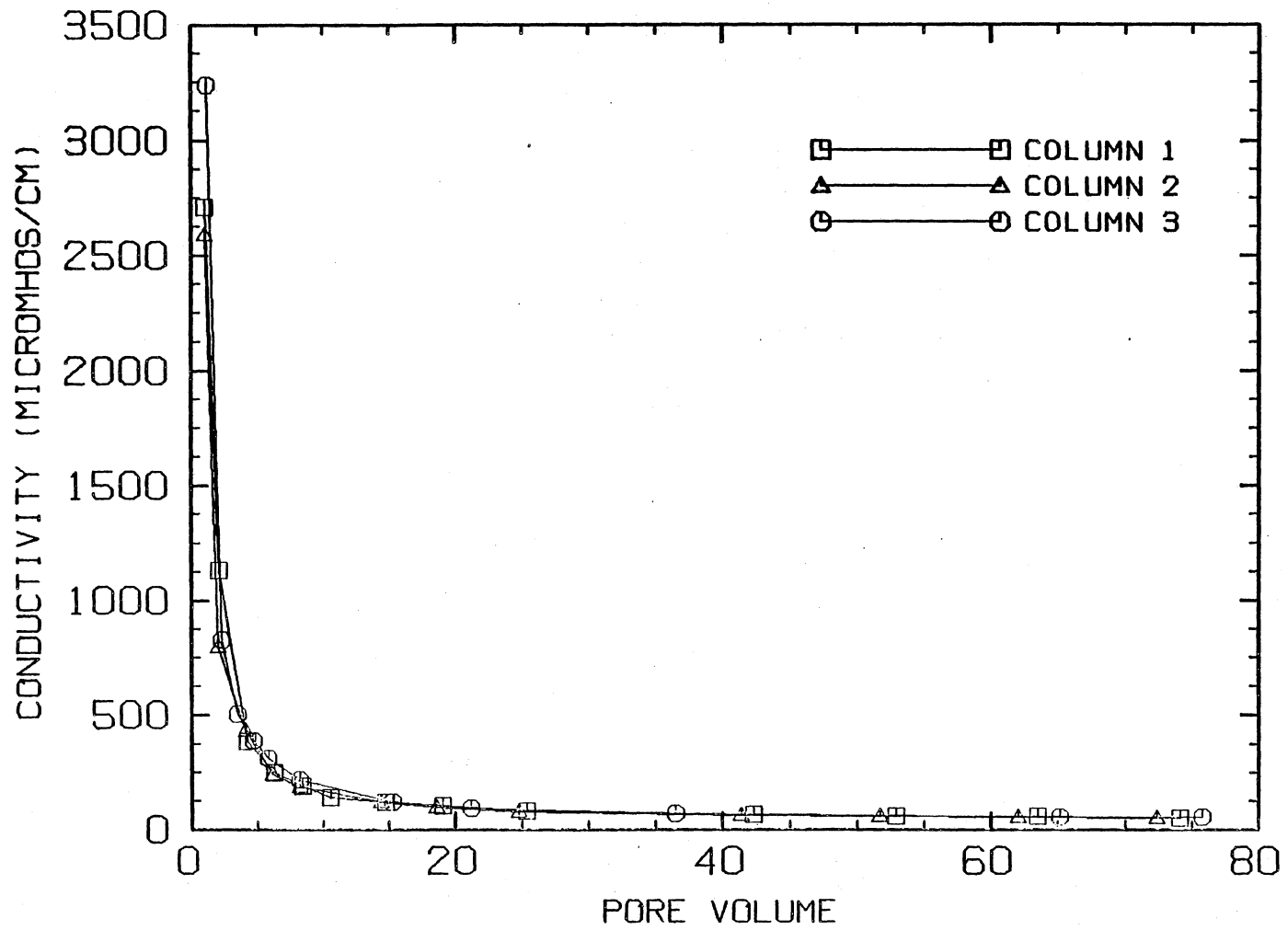


Figure C7. Variation in conductivity during column elution of Oxy spent shale.

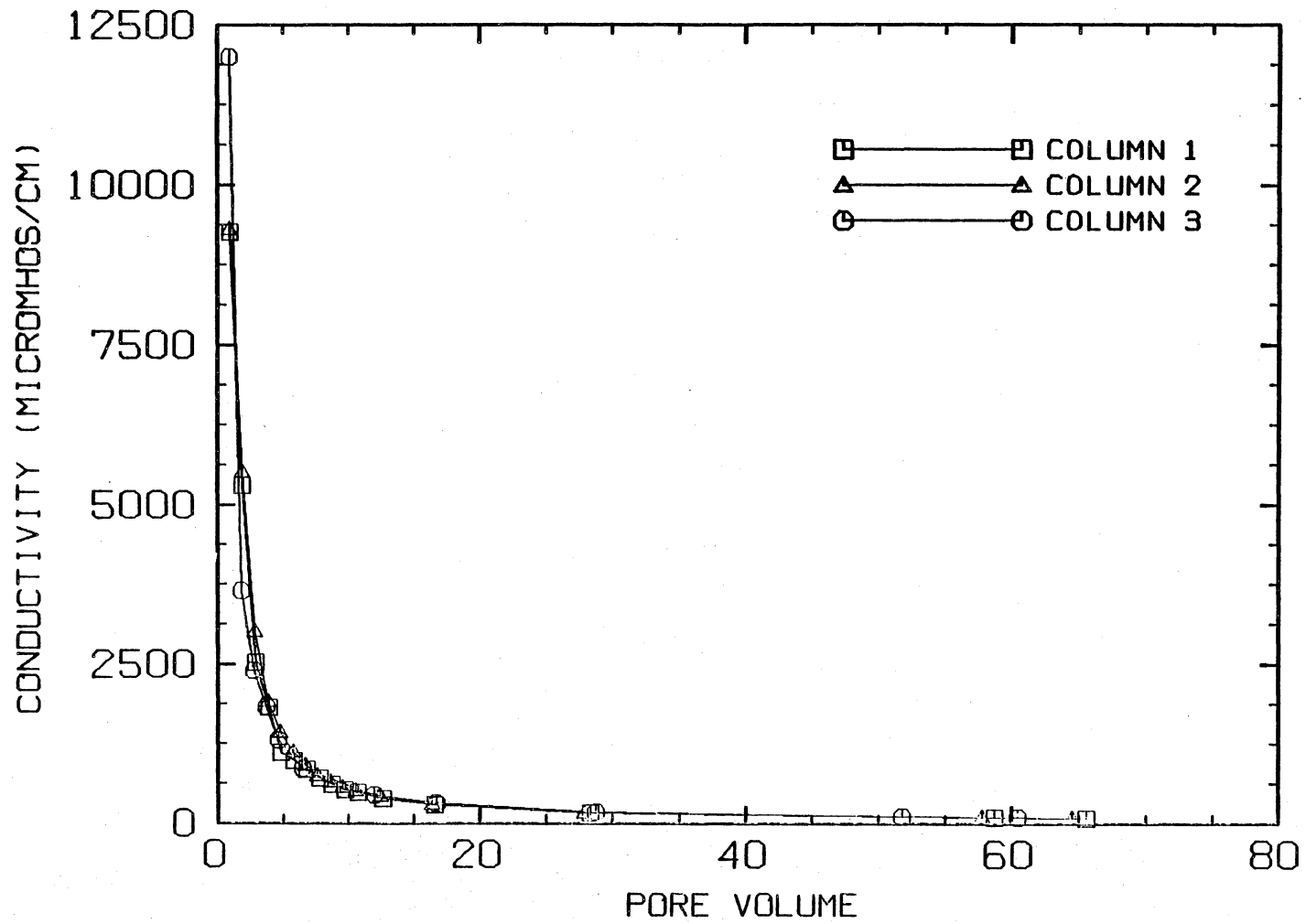


Figure C8. Variation in conductivity during column elution of Antrim spent shale.

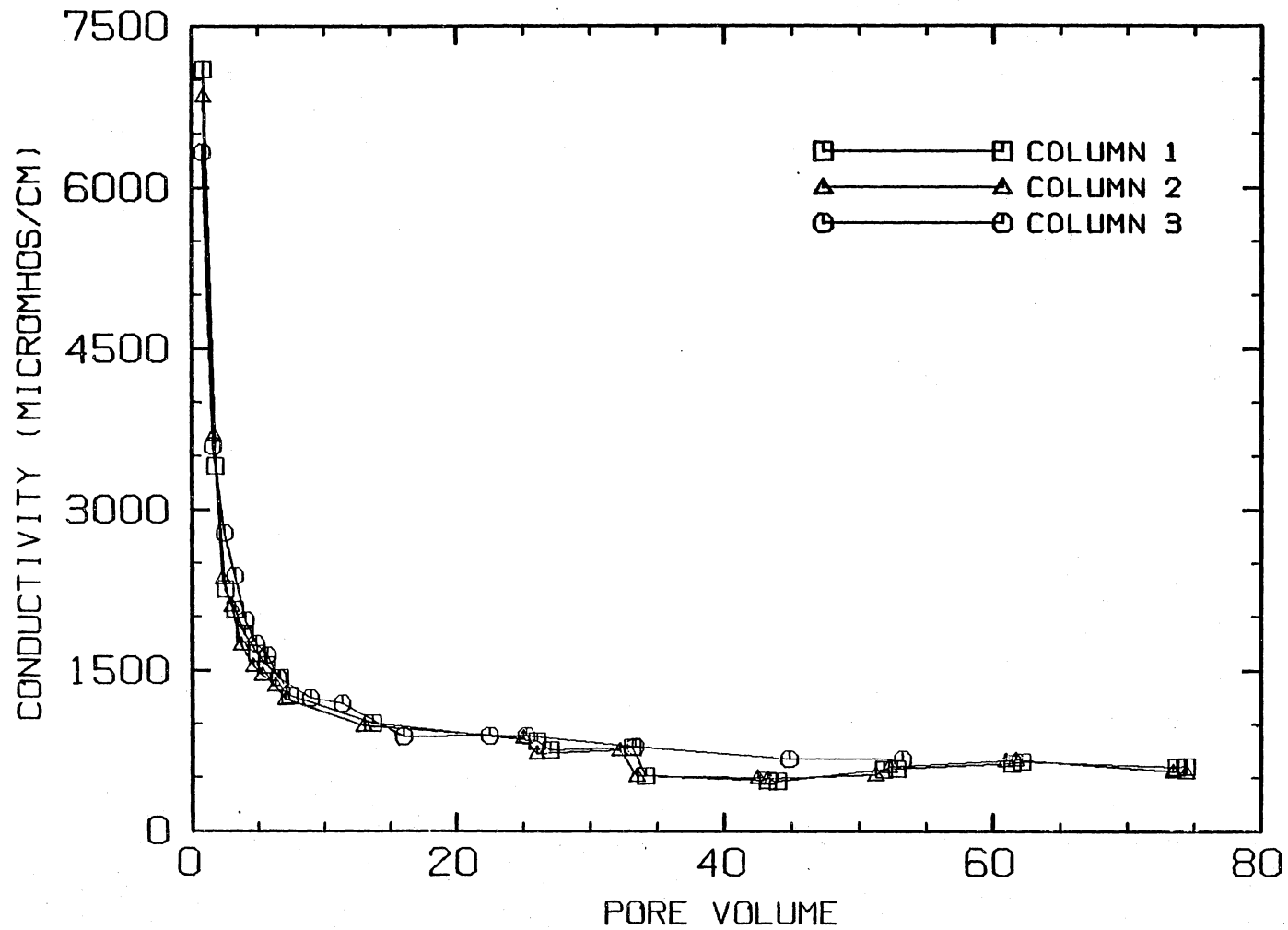


Figure c9. Variation in conductivity during column elution of Run 16 spent shale.

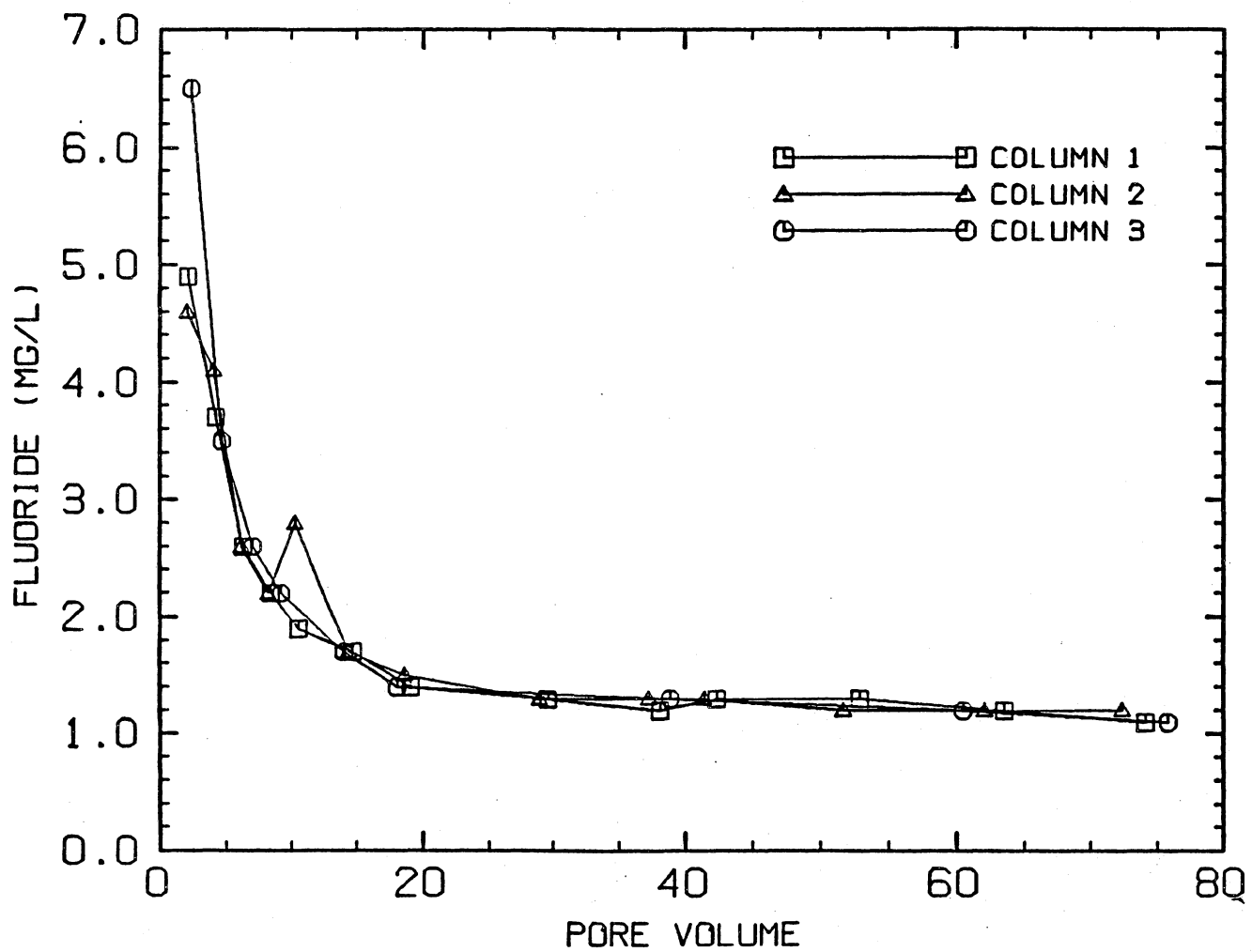


Figure C10. Variation in fluoride during column elution of Anvil raw shale.

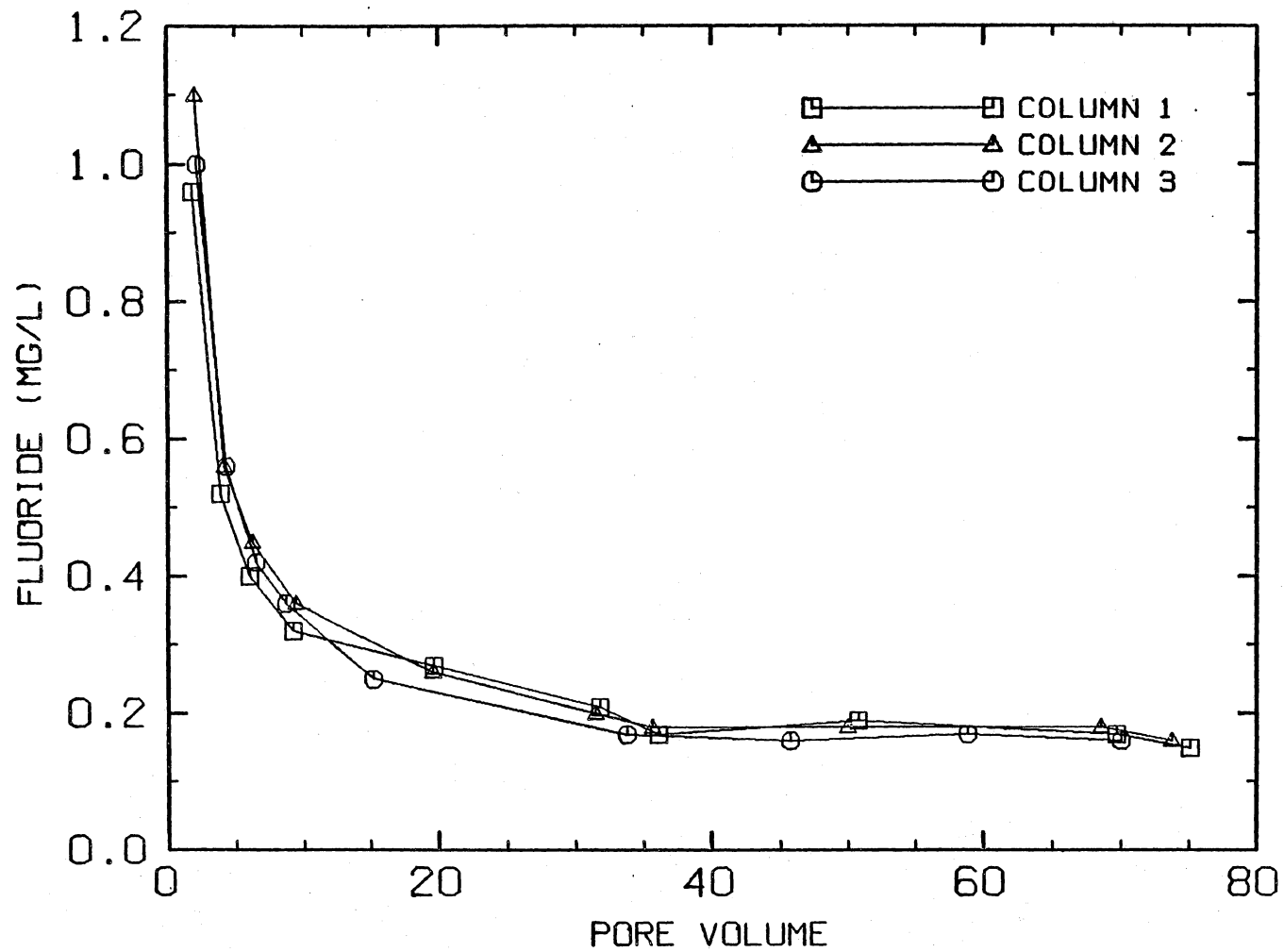


Figure C11. Variation in fluoride during column elution of Oxy spent shale.

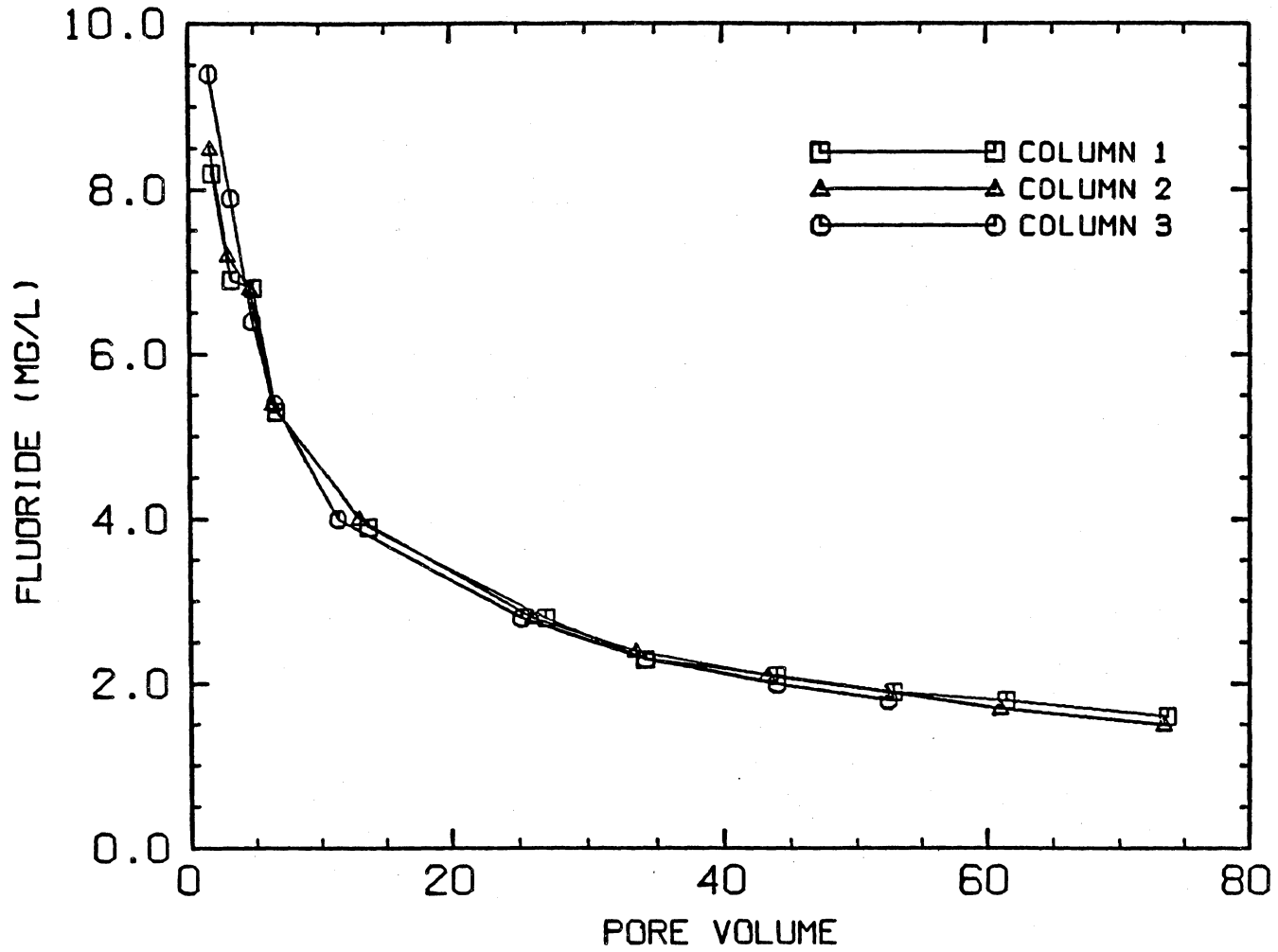


Figure C12. Variation in fluoride during column elution of Run 16 spent shale.

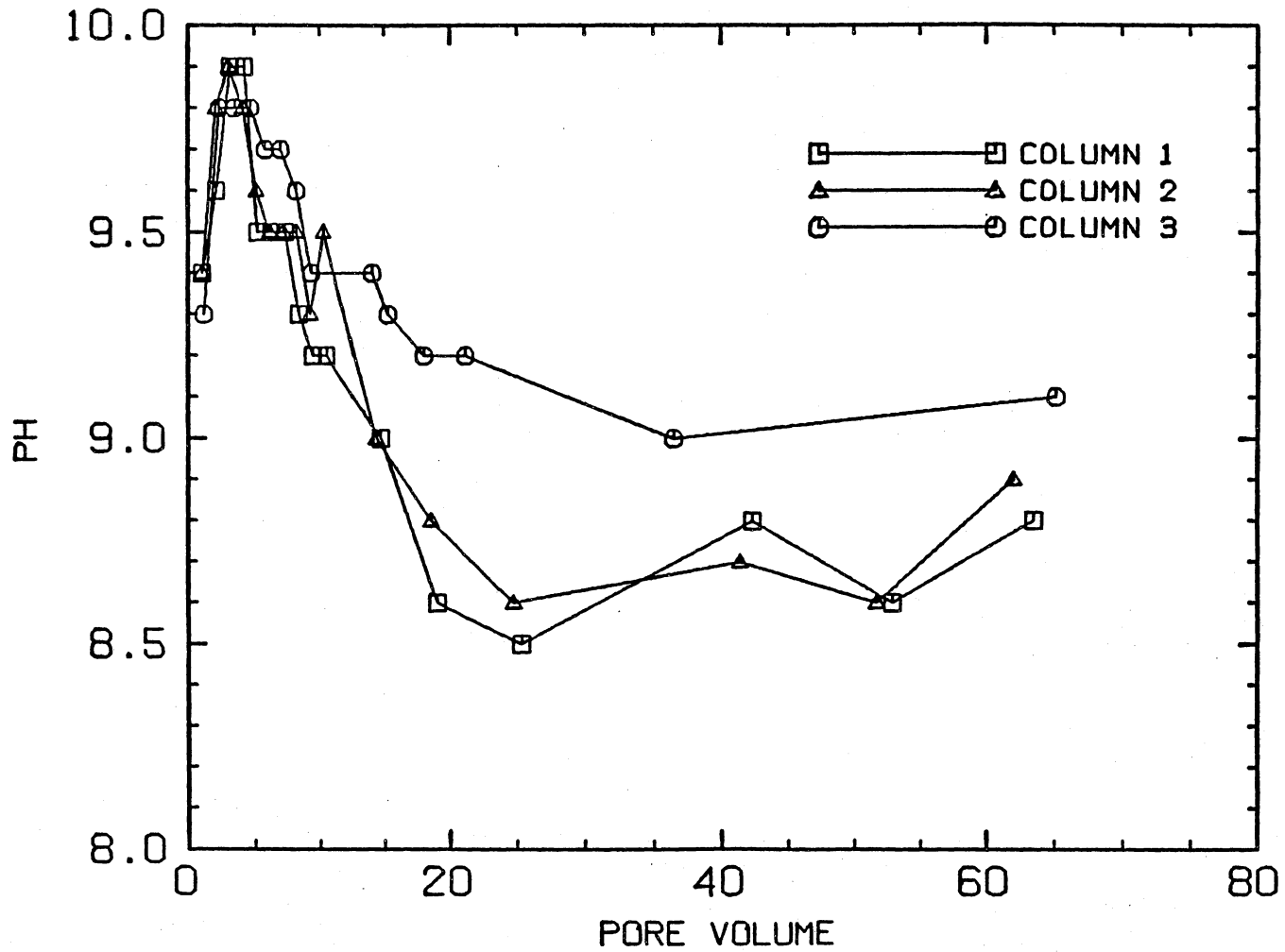


Figure C13. Variation in pH during column elution of Anvil raw shale.

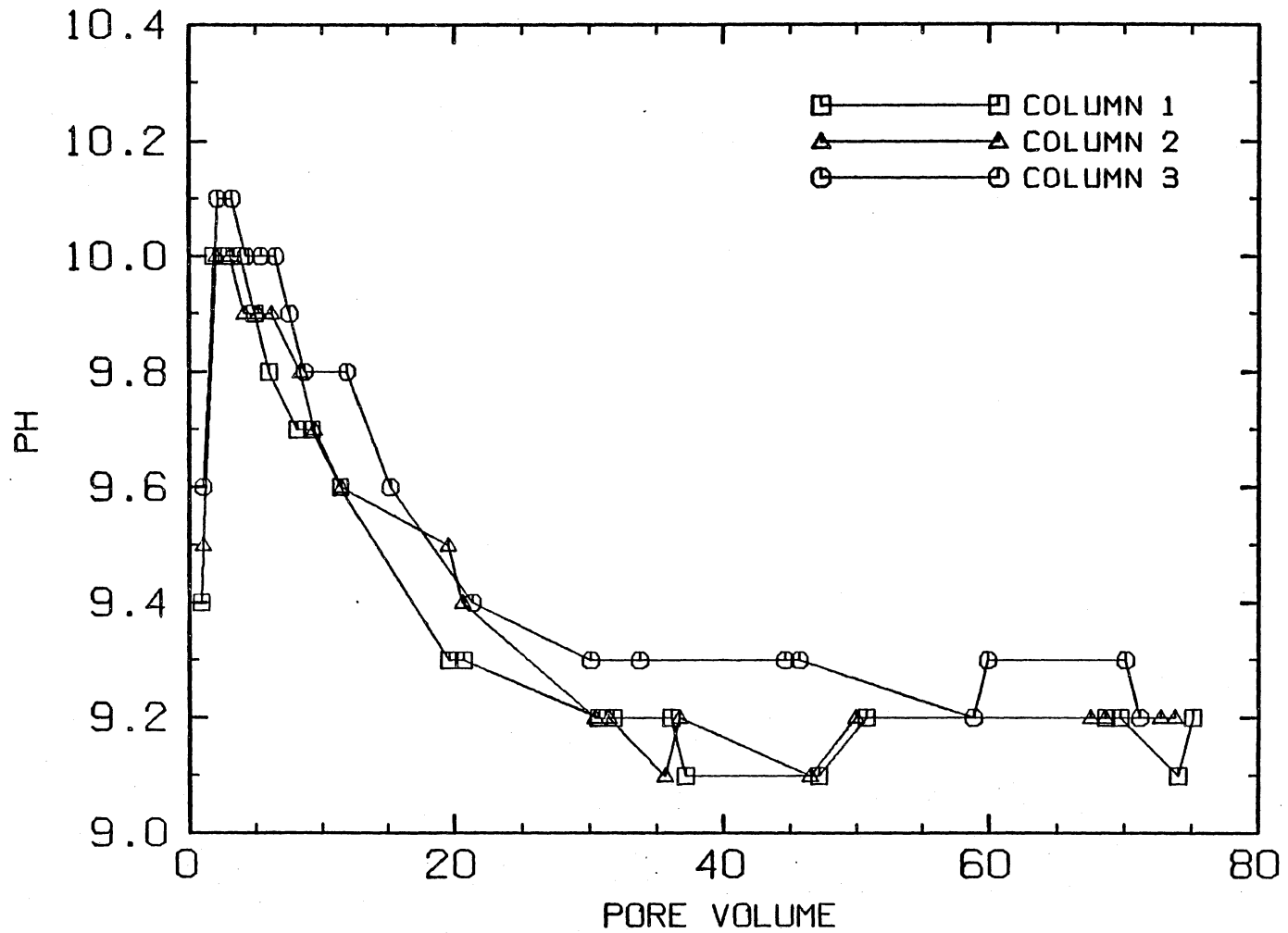


Figure C14. Variation in pH during column elution of Oxy spent shale.

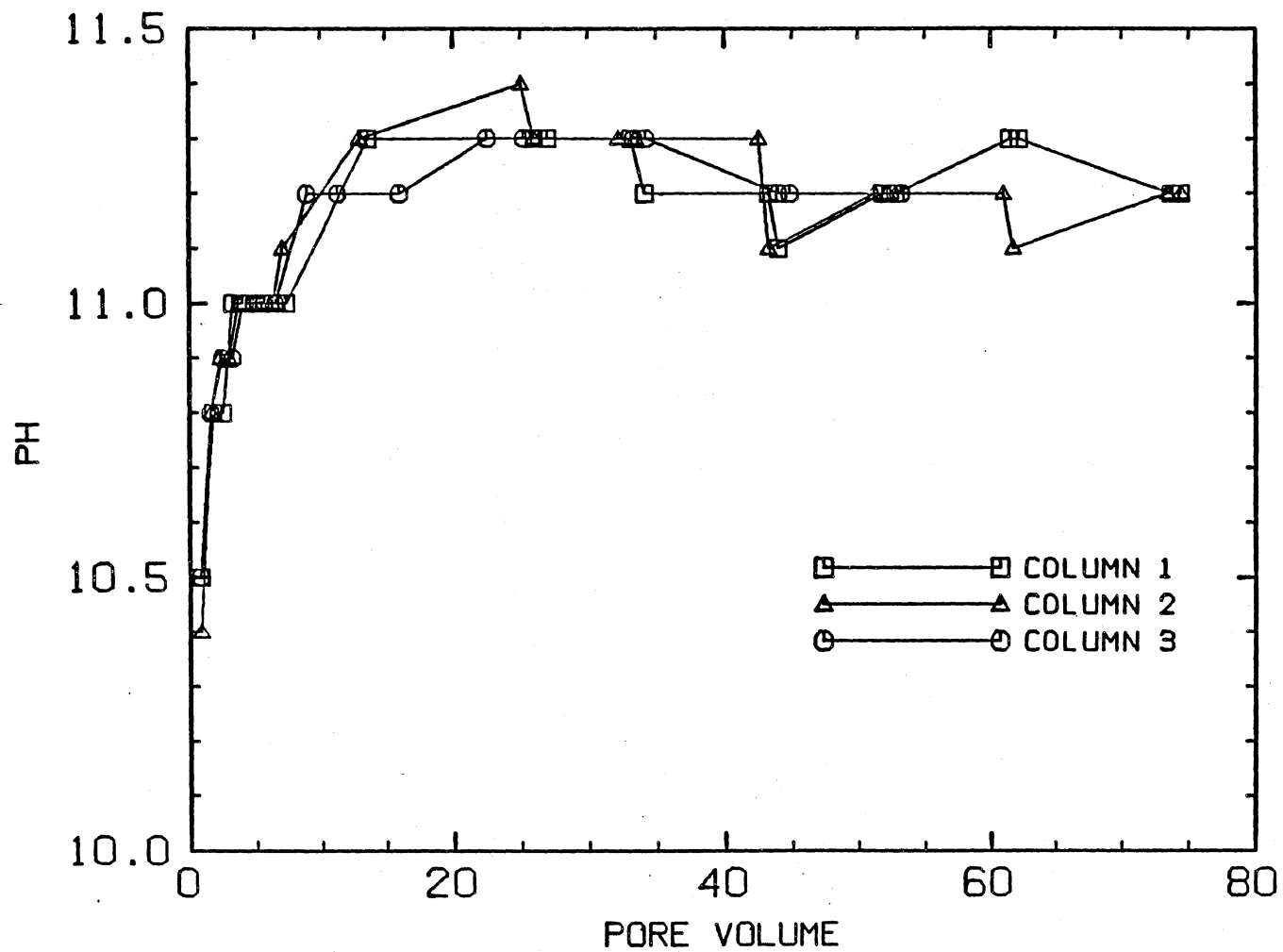


Figure C15. Variation in pH during column elution of Run 16 spent shale.

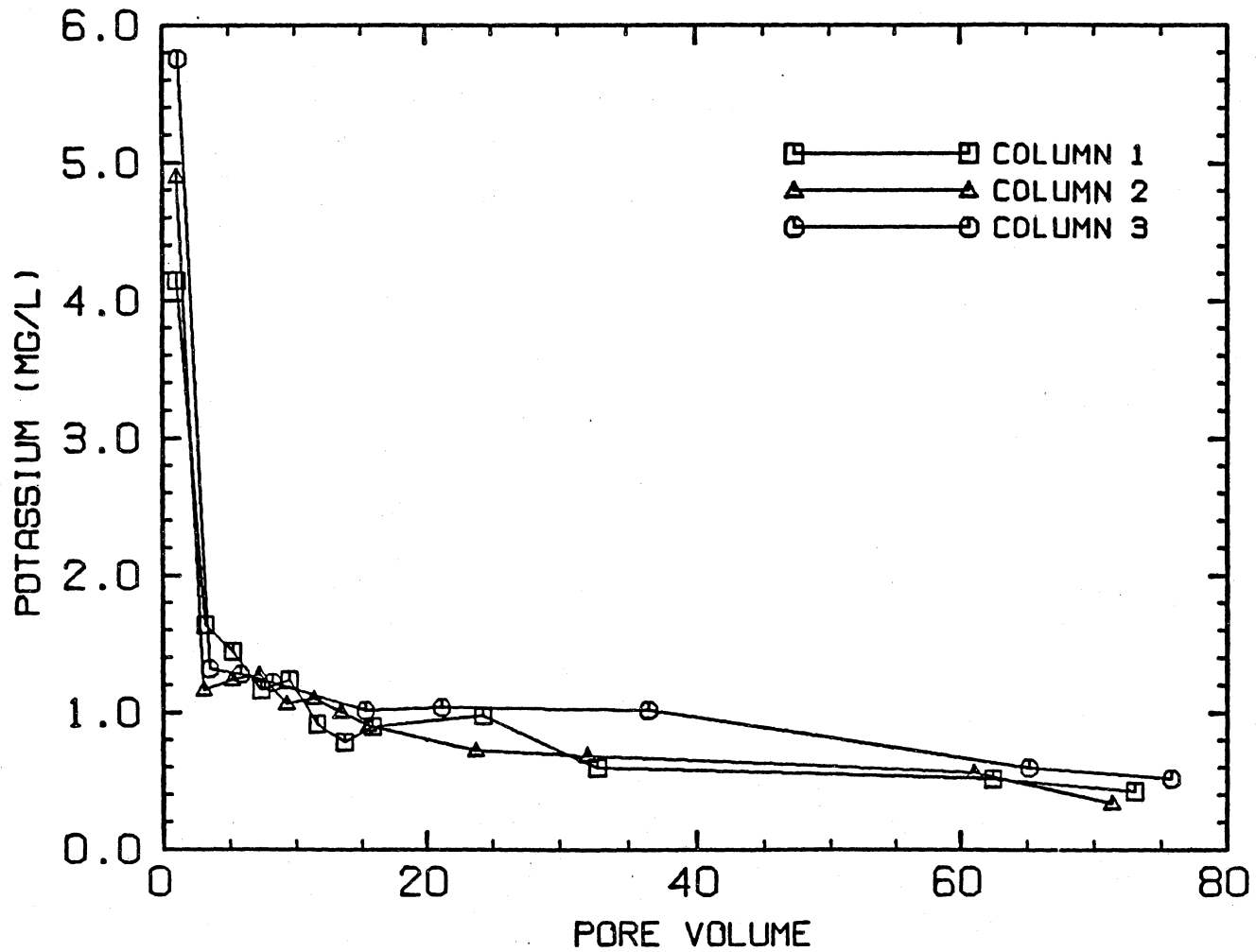


Figure C16. Variation in potassium during column elution of Anvil raw shale.

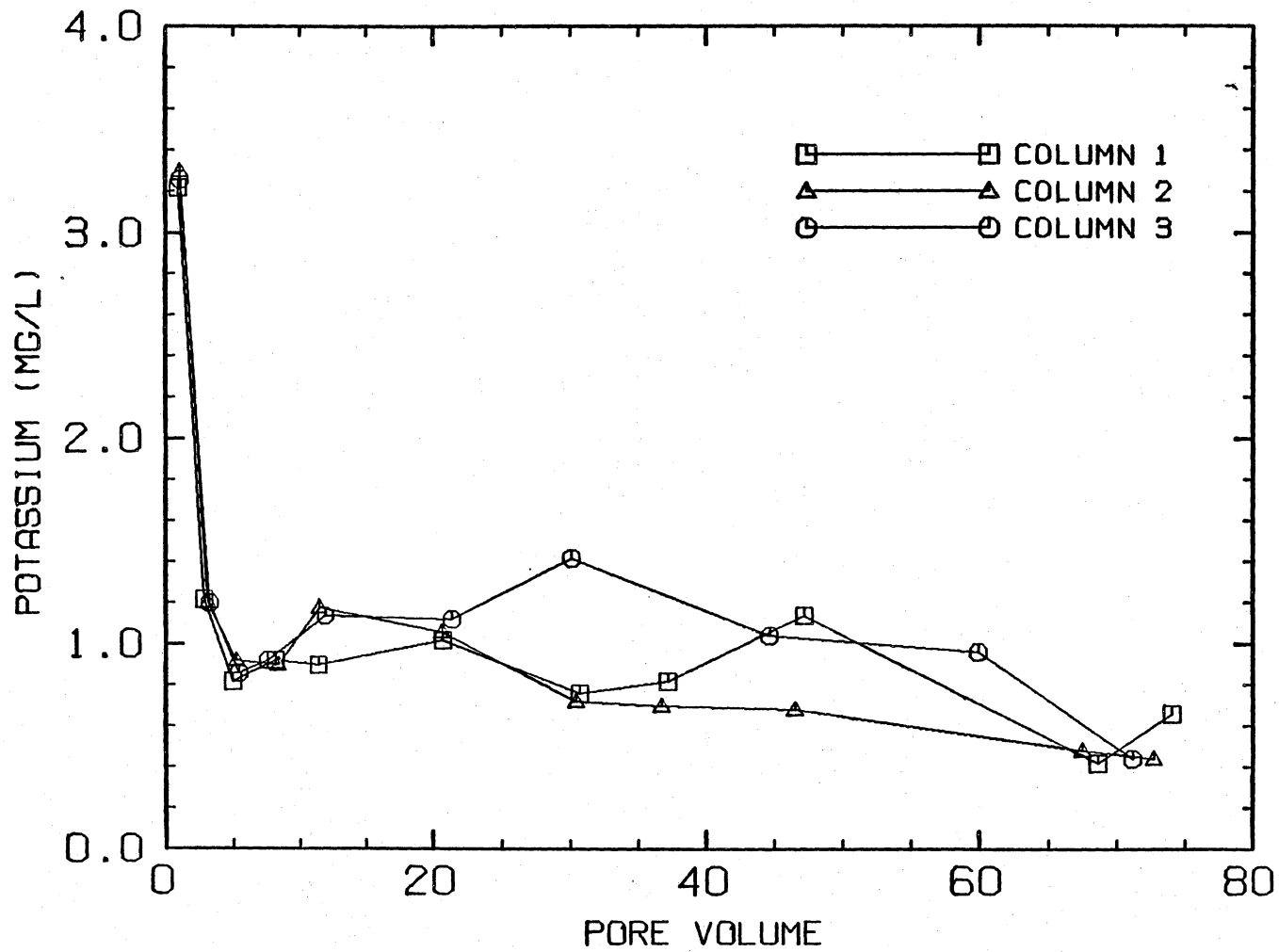


Figure C17. Variation in potassium during column elution of Oxy spent shale.

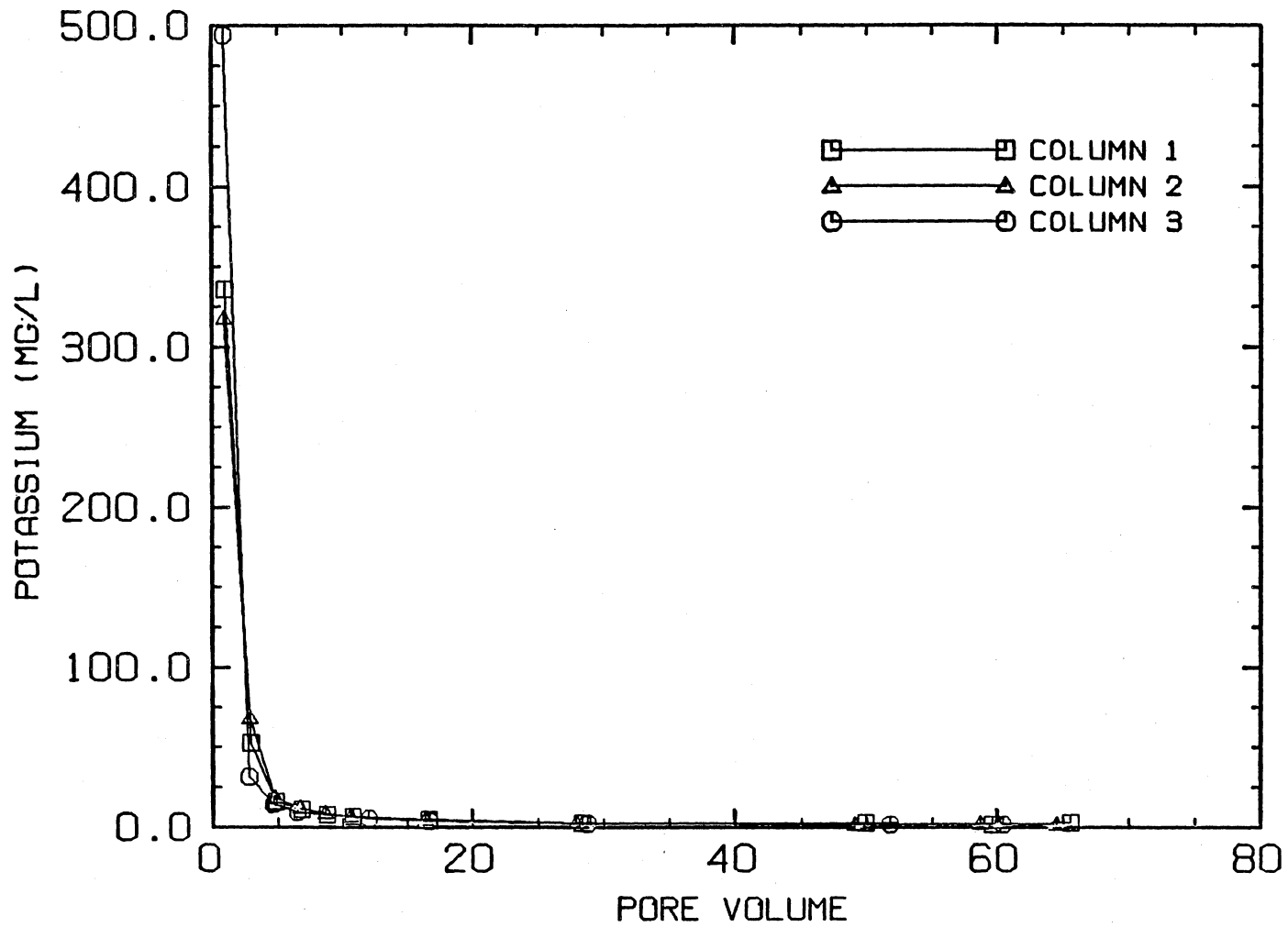


Figure C18. Variation in potassium during column elution of Antrim spent shale.

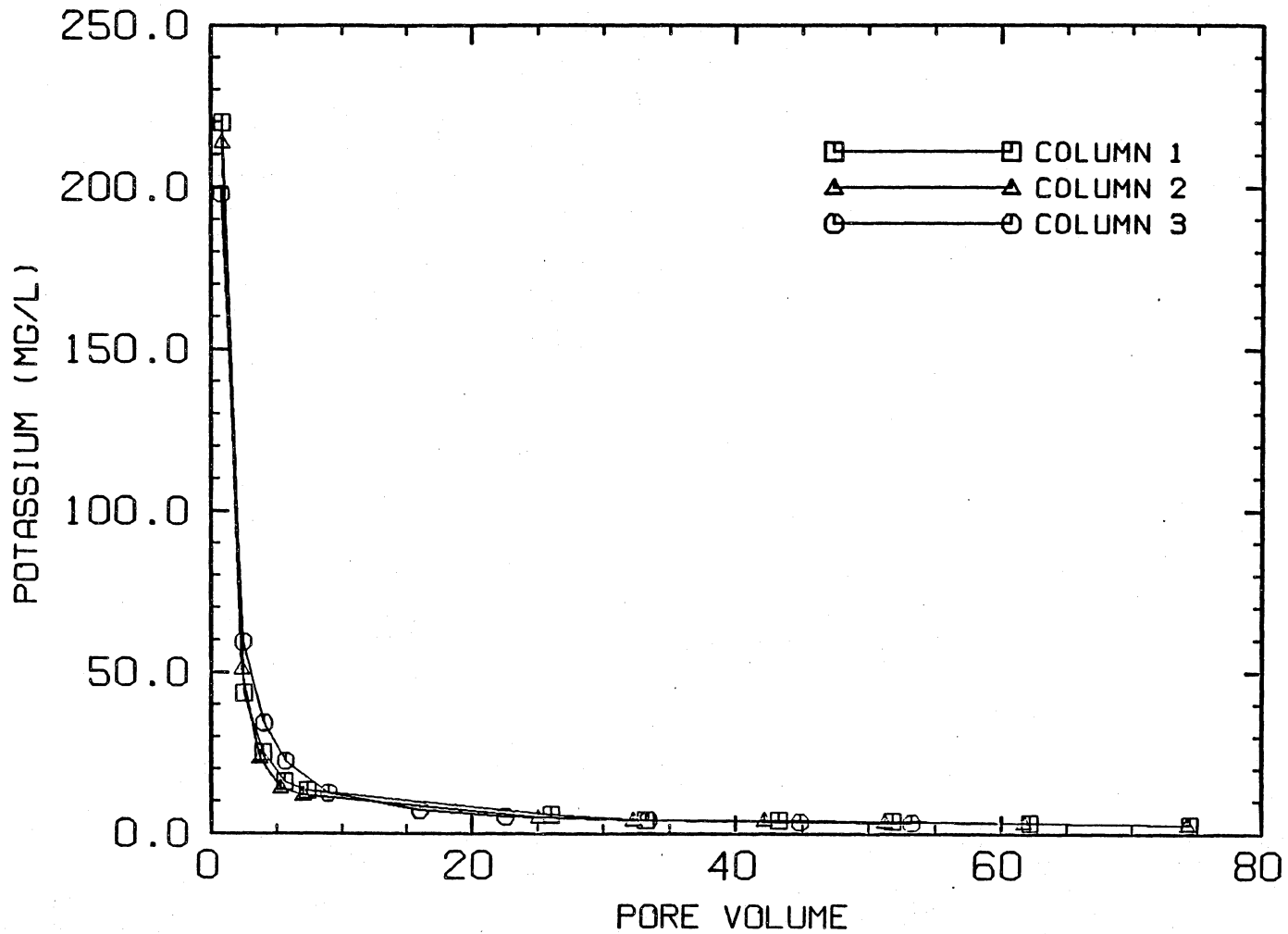


Figure C19. Variation in potassium during column elution of Run 16 spent shale.

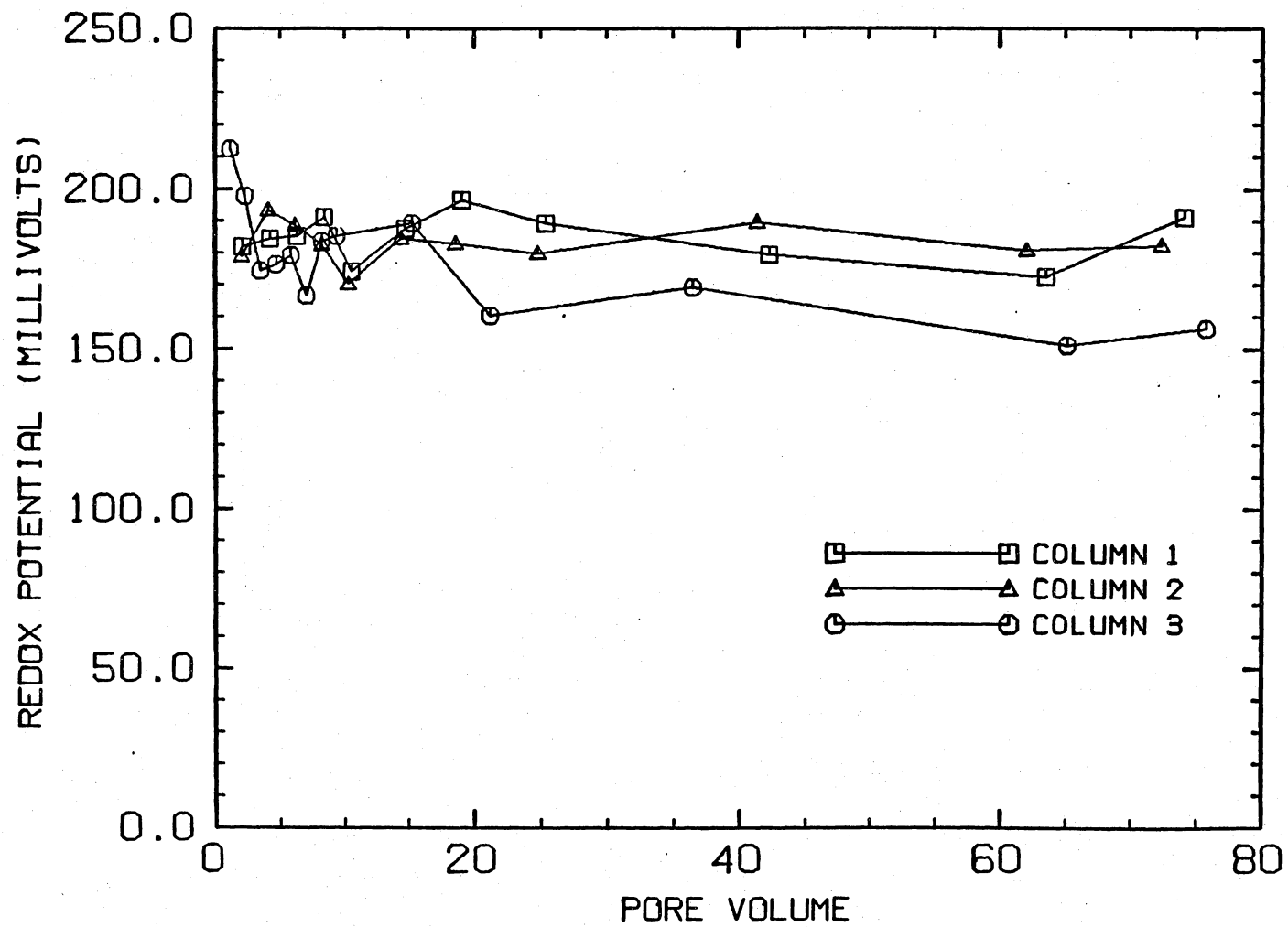


Figure C20. Variation in redox potential during column elution of Anvil raw shale.

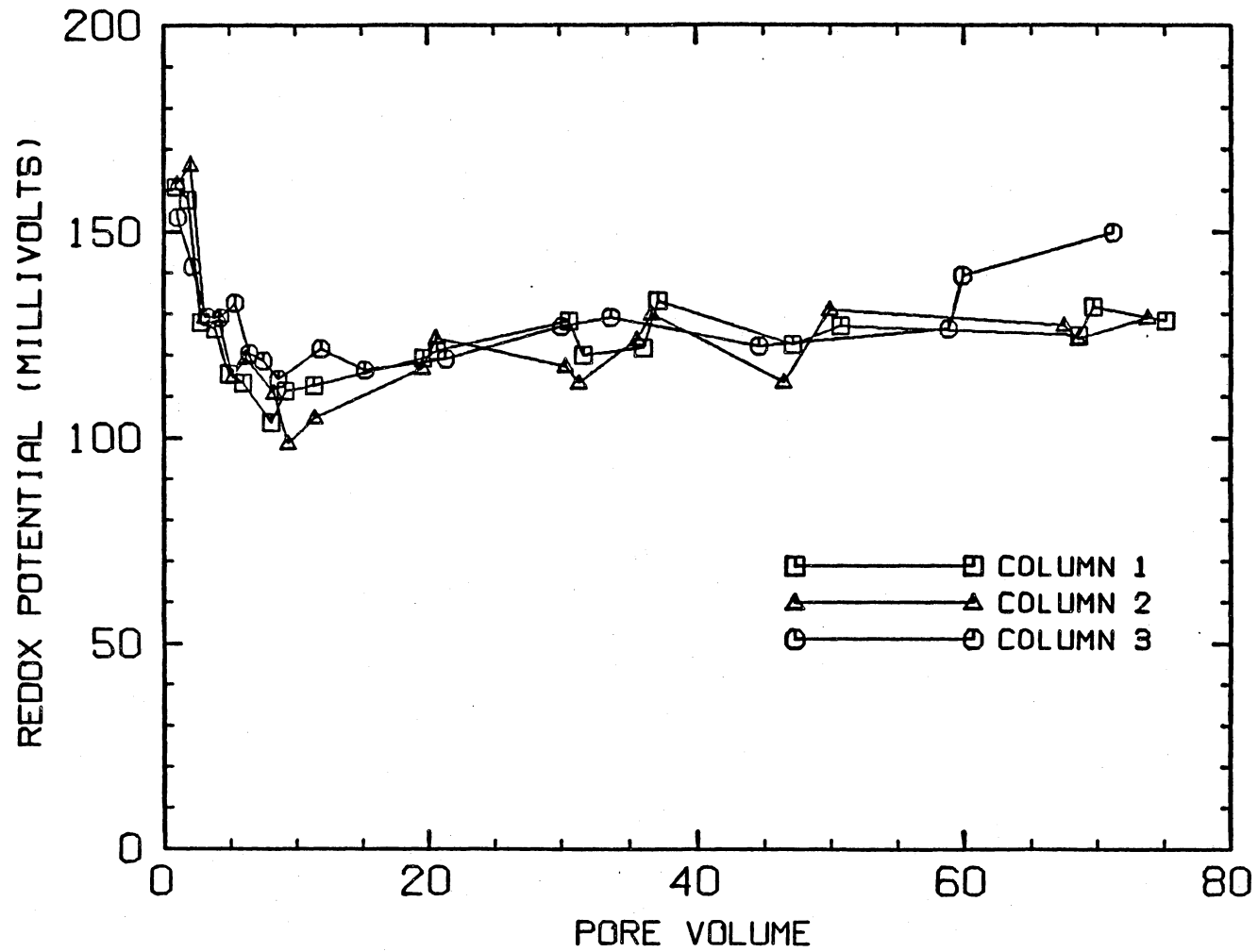


Figure C21. Variation in redox potential during column elution of Oxy spent shale.

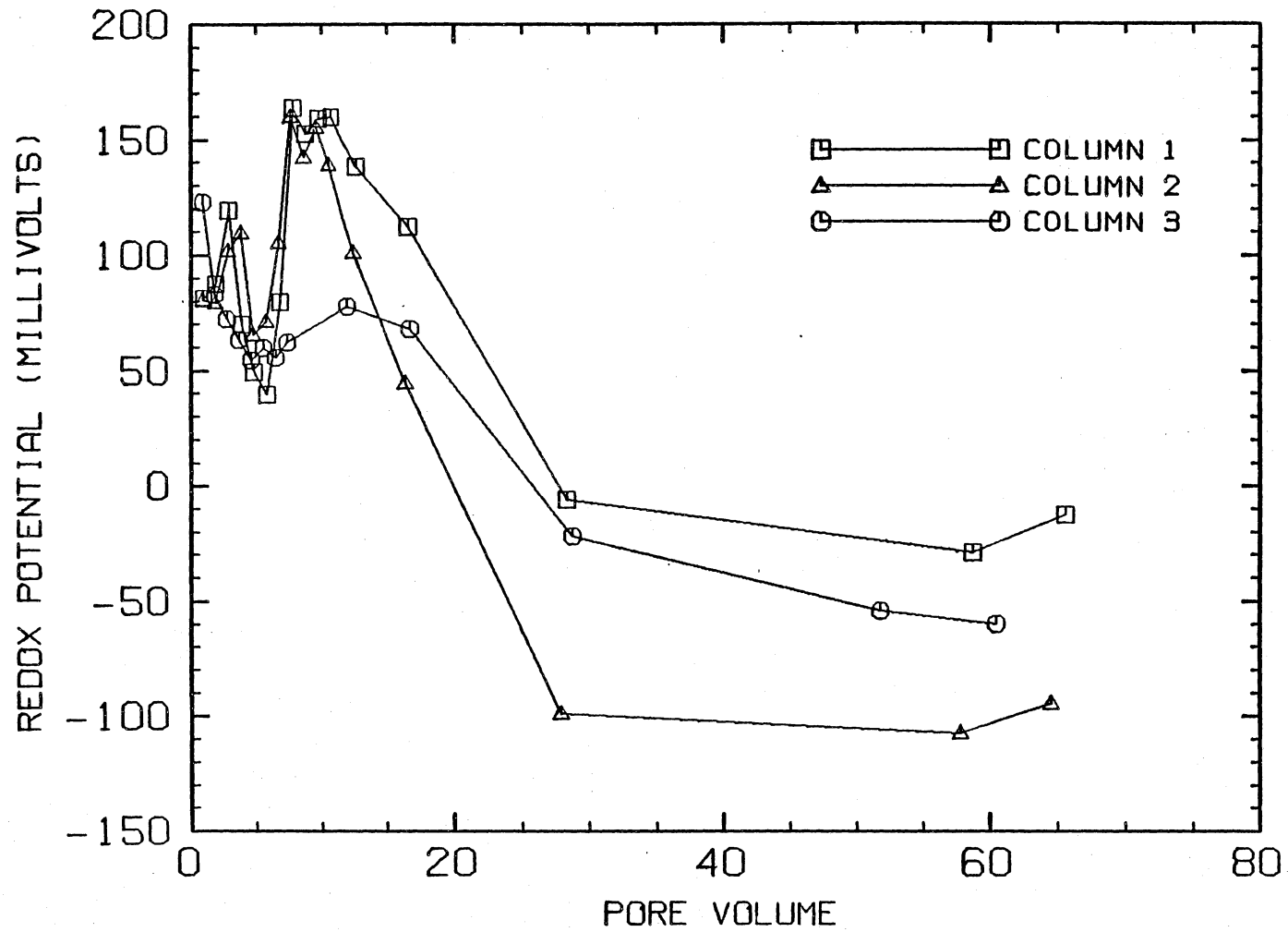


Figure C 22. Variation in redox potential during column elution of Antrim spent shale.

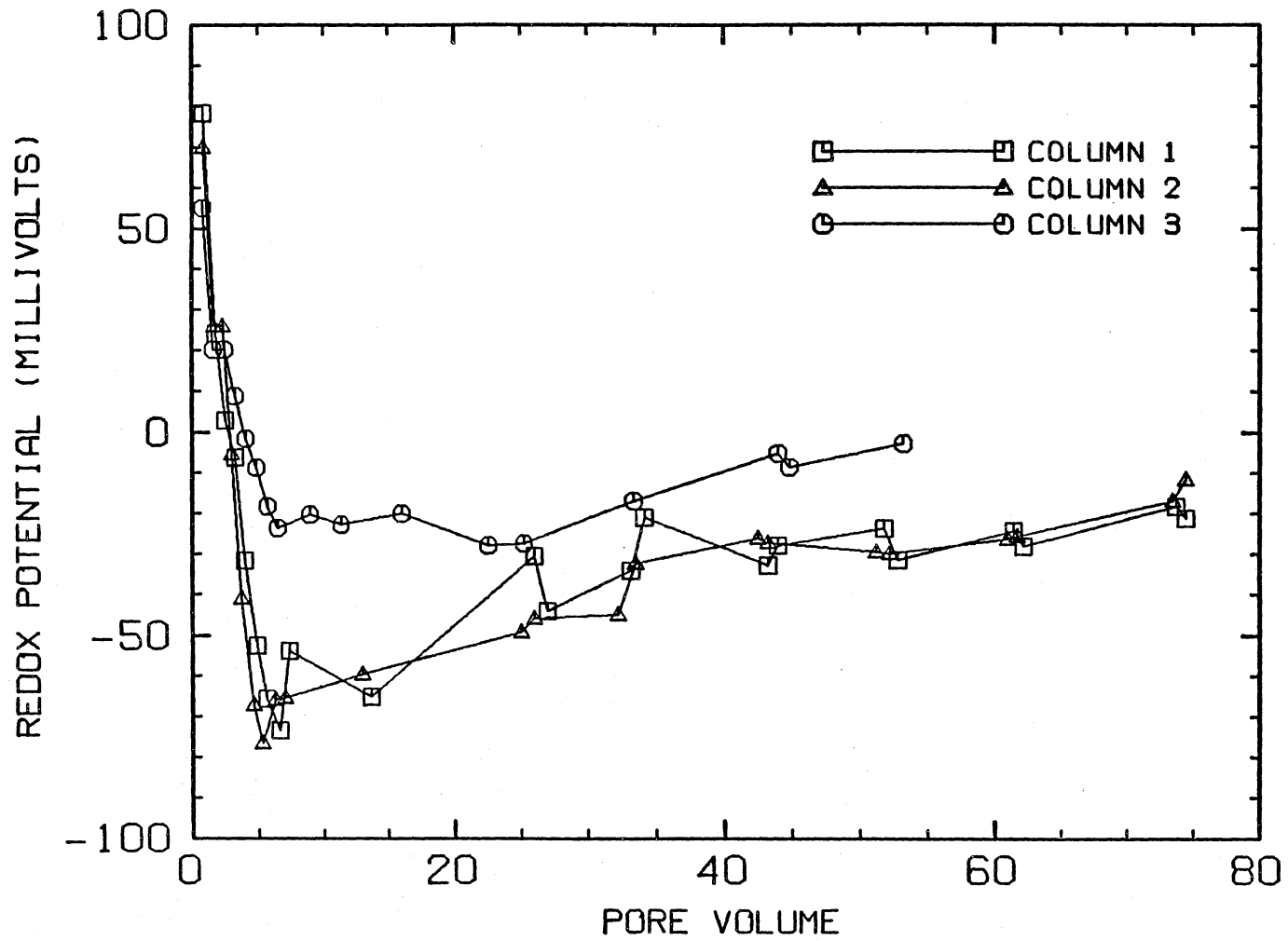


Figure C 23. Variation in redox potential during batch elution of Run 16 spent shale.

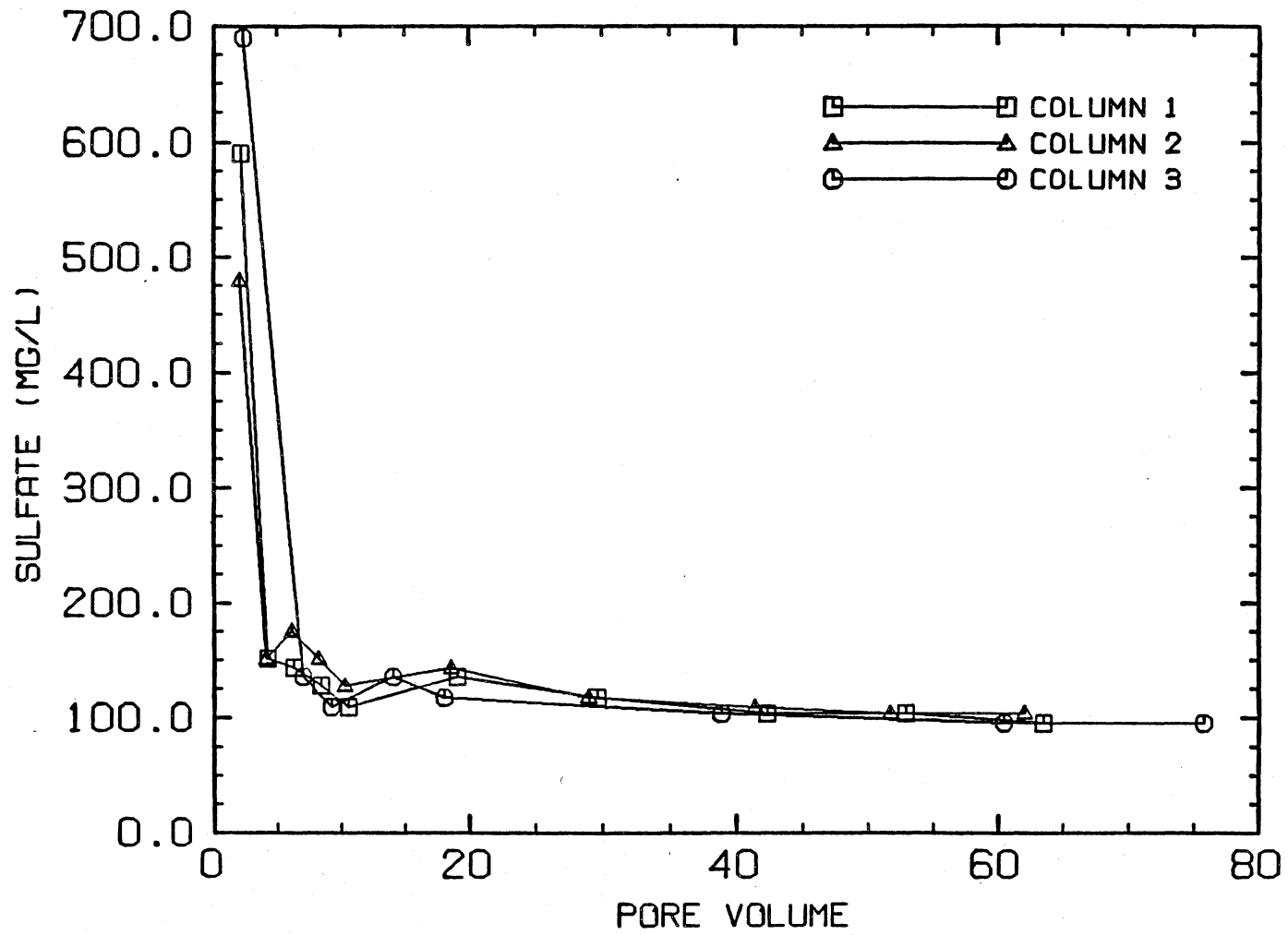


Figure C24. Variation in sulfate during column elution of Anvil raw shale.

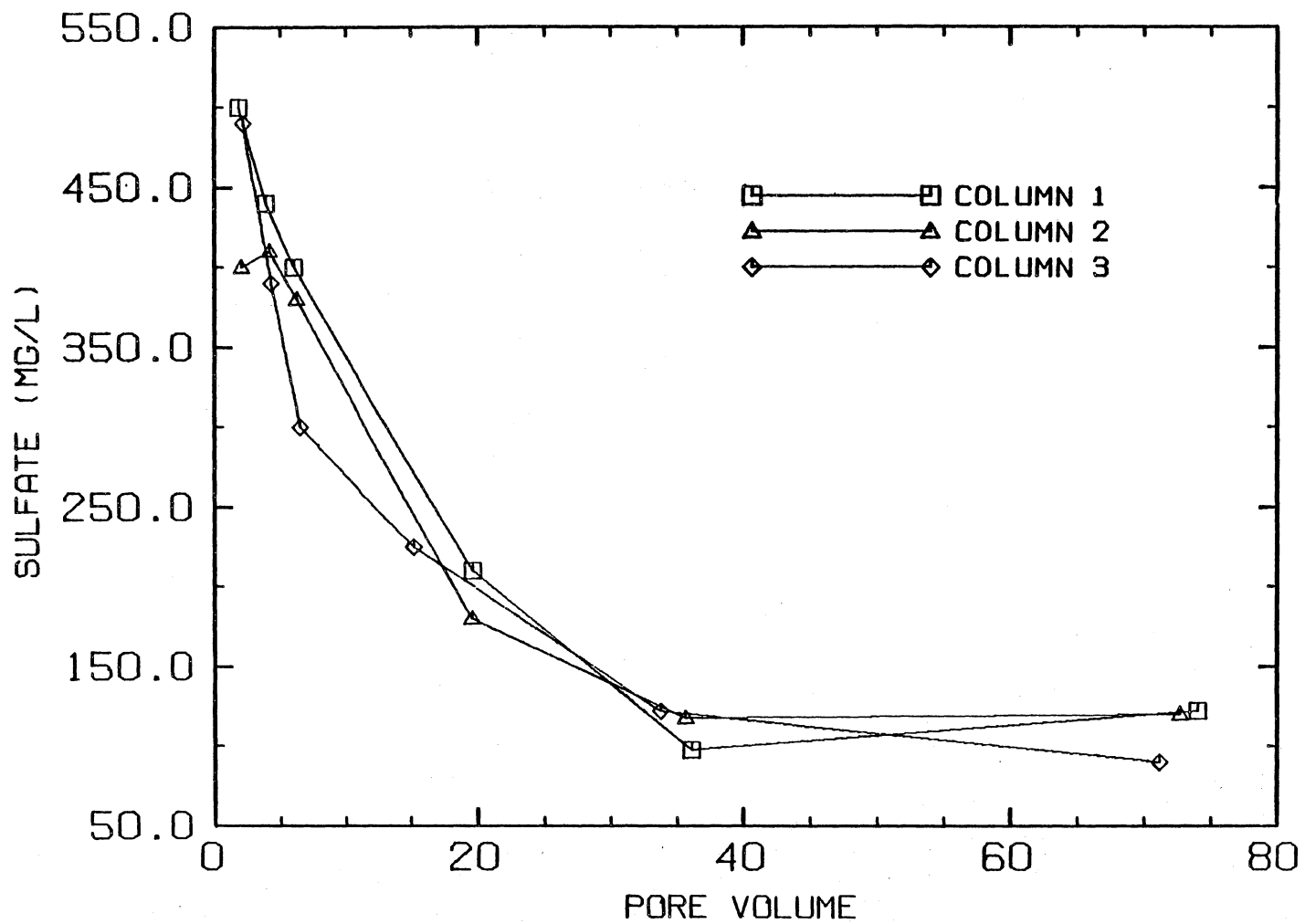


Figure C25. Variation in sulfate during column elution of Oxy spent shale.

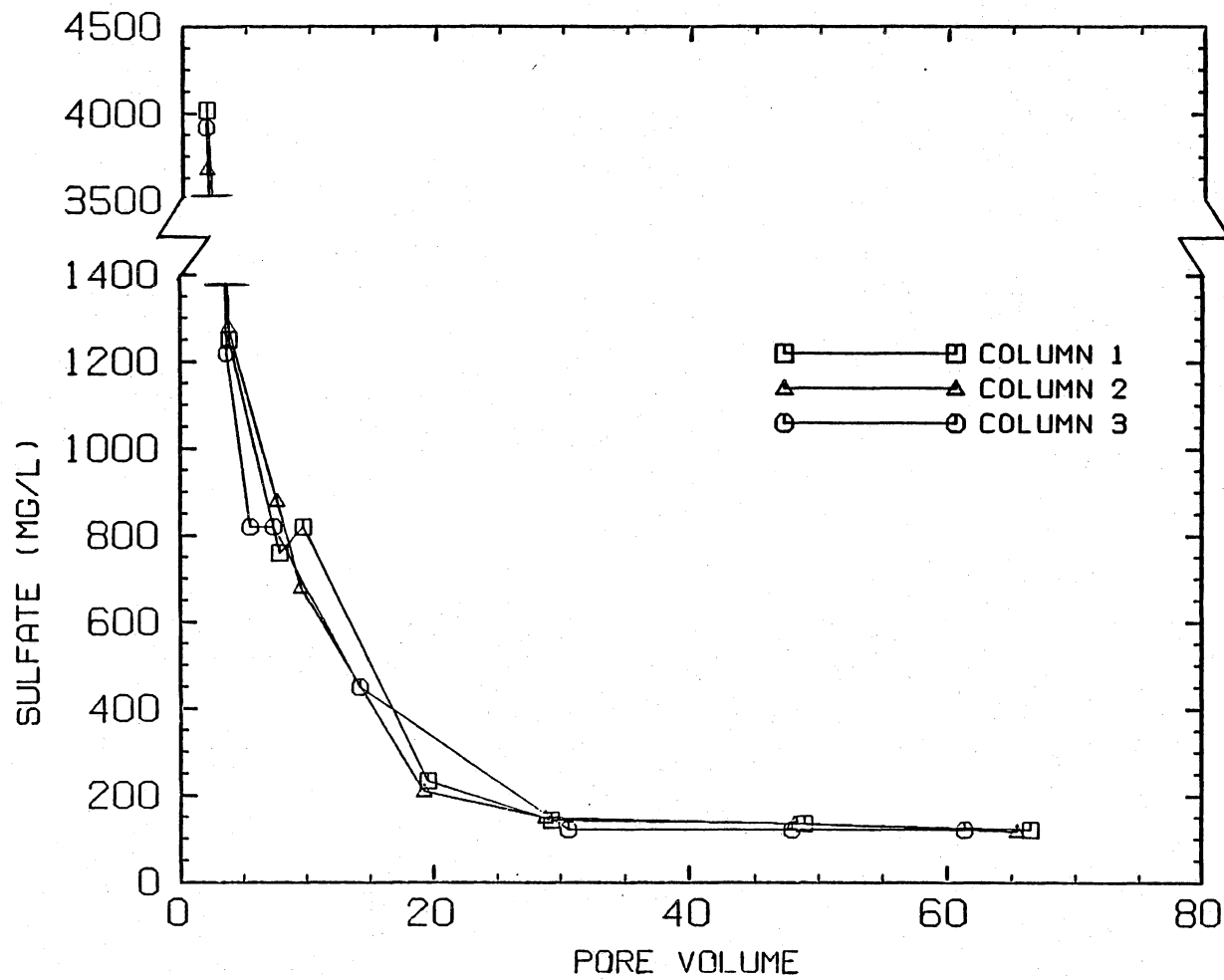


Figure C26. Variation in sulfate during column elution of Antrim spent shale.

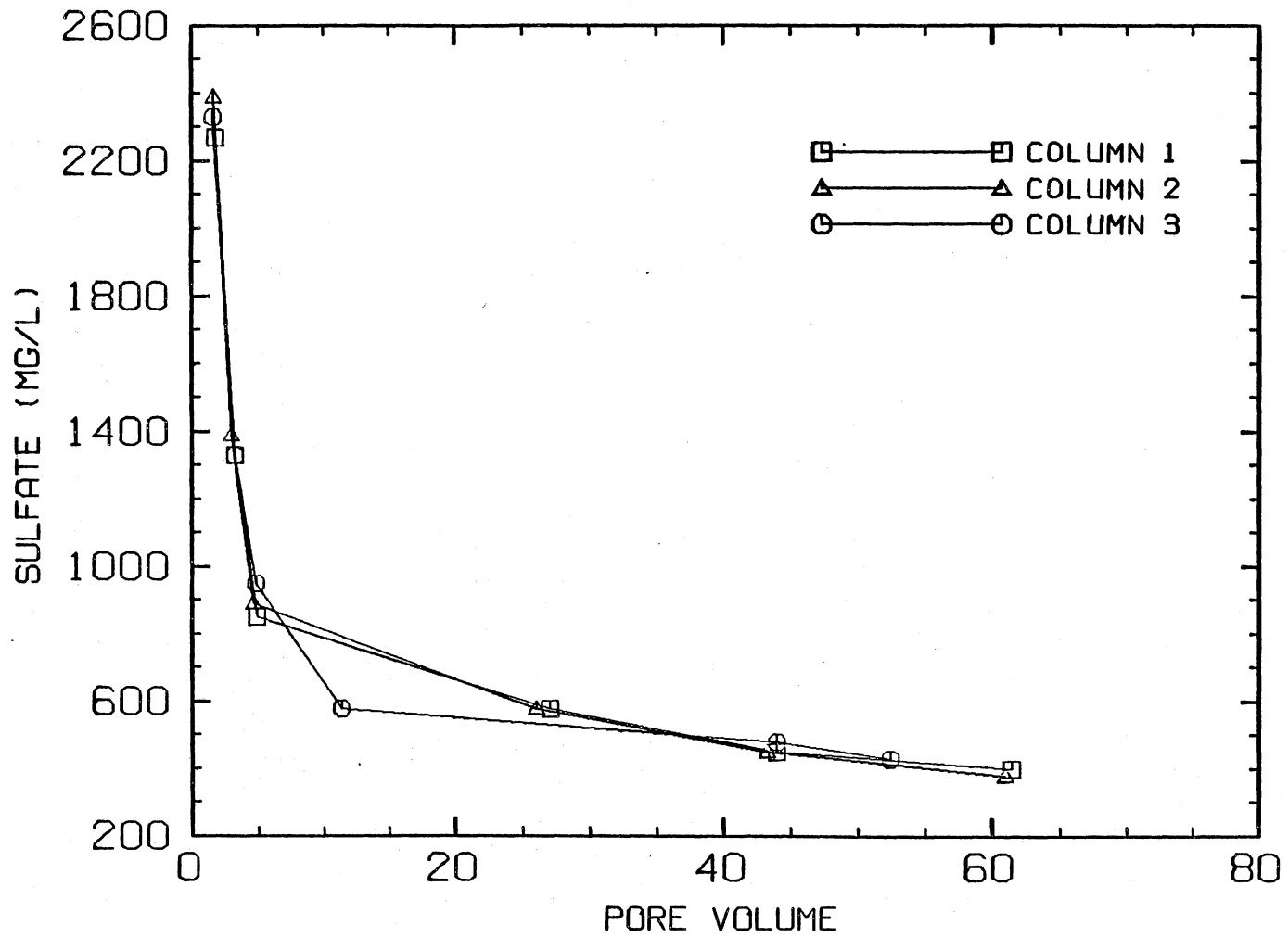


Figure C27. Variation in sulfate during column elution of Run 16 spent shale.

Appendix D

SINGLE-ION DESORPTION TRIALS

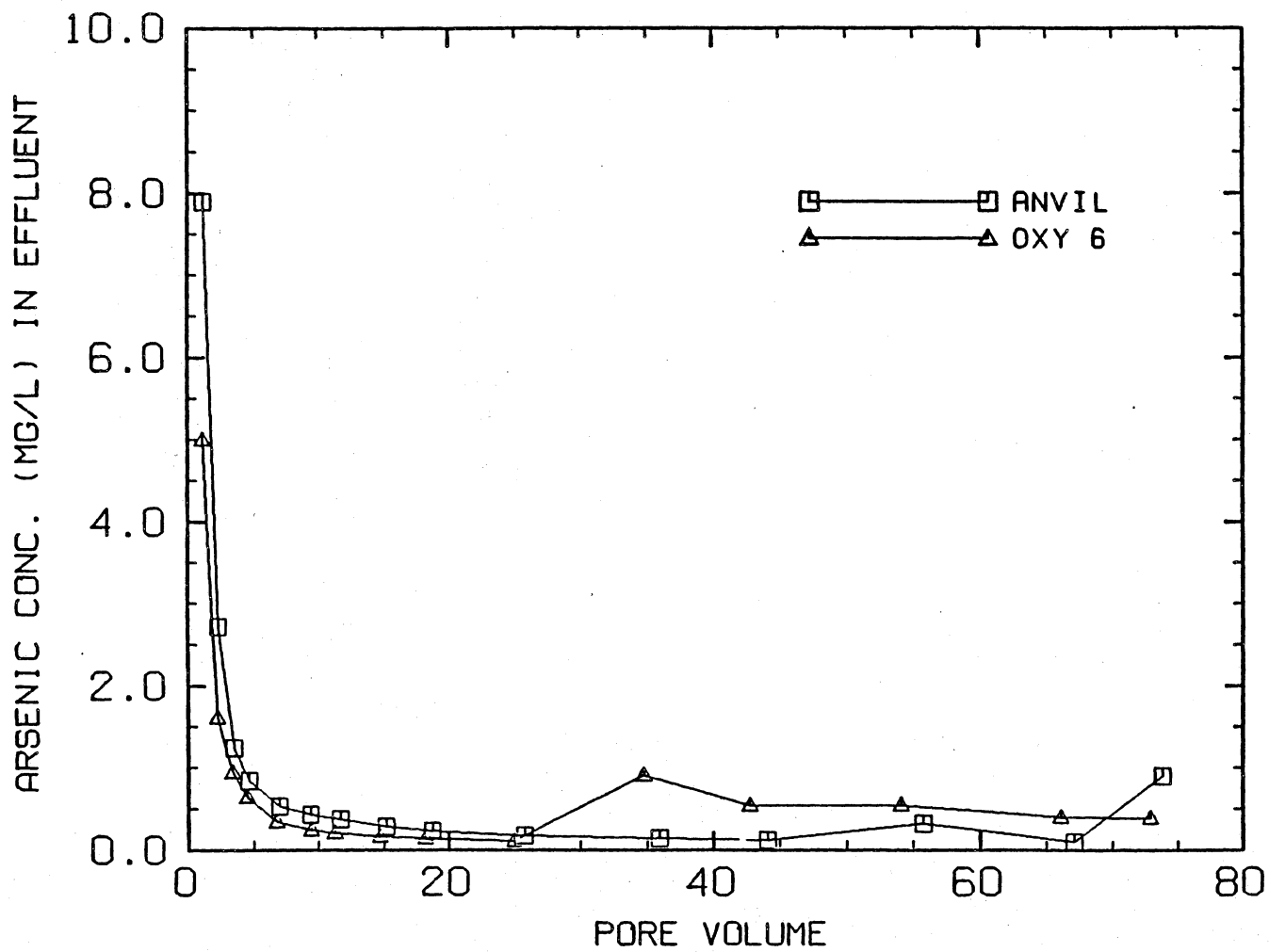


Figure D1. Desorption of arsenic from shale columns previously used in arsenic adsorption trials.

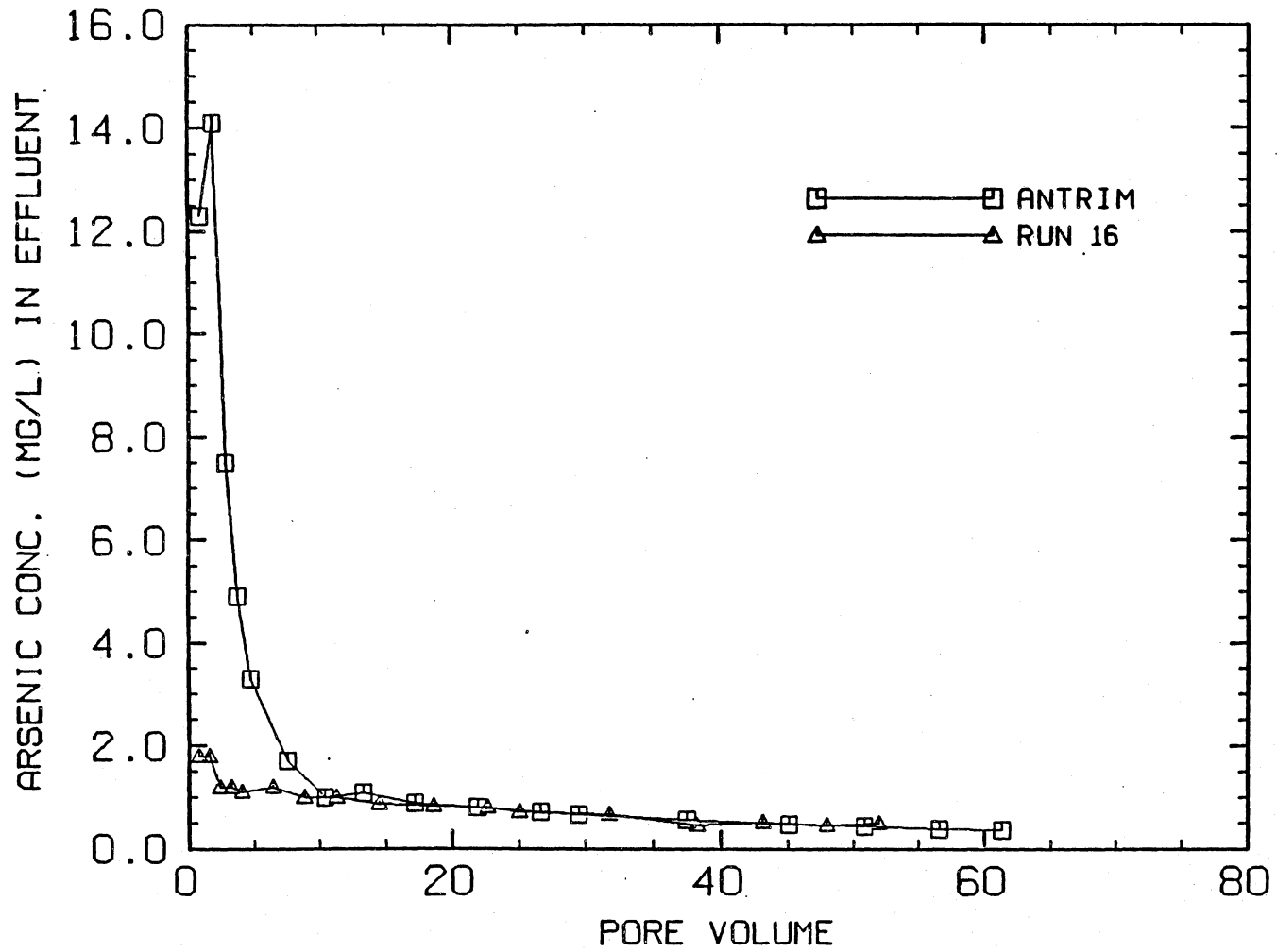


Figure D2. Desorption of arsenic from shale columns previously used in arsenic adsorption trials.

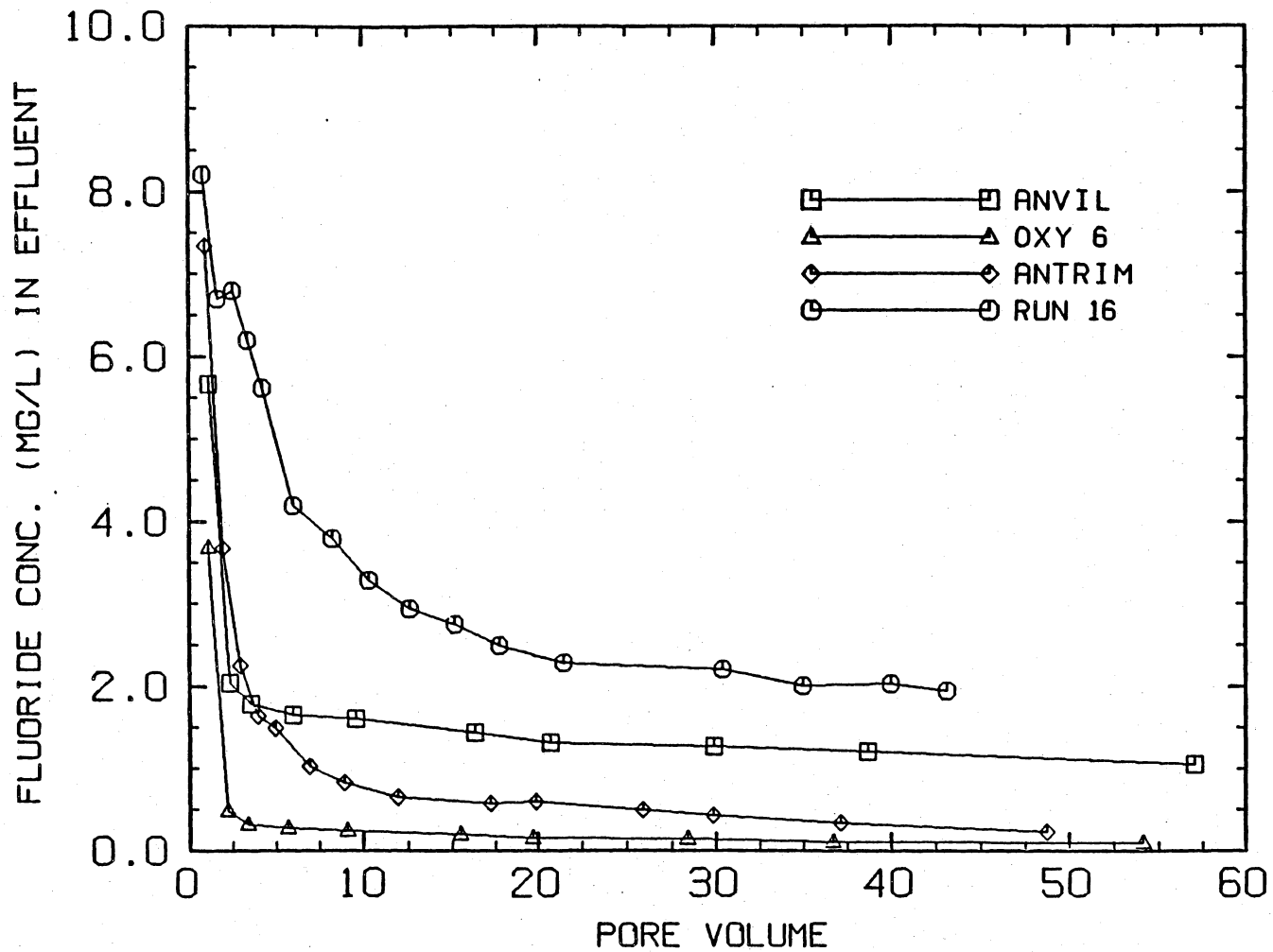


Figure D3. Desorption of fluoride from shale columns previously used in calcium adsorption trials.

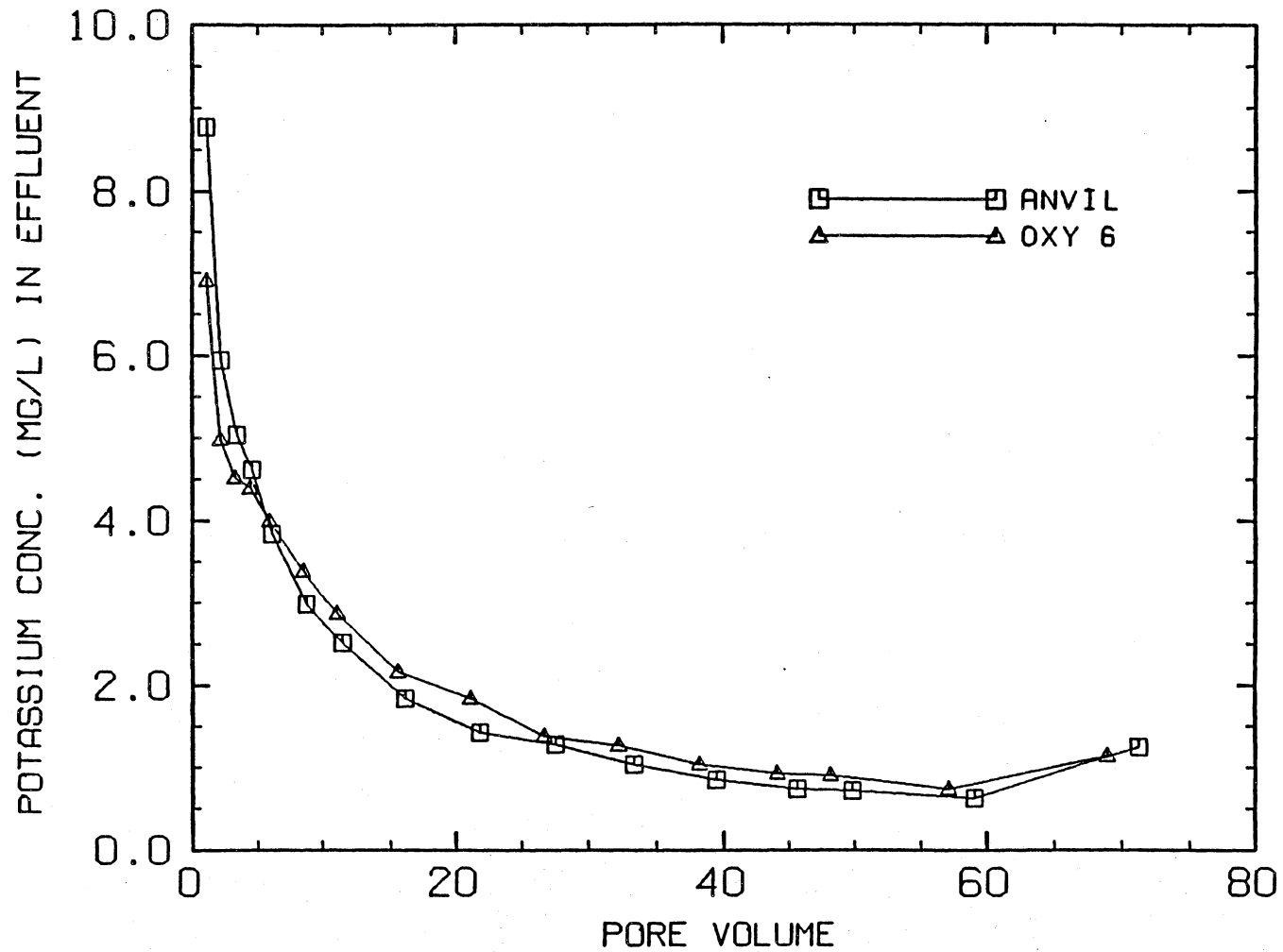


Figure D4. Desorption of potassium from shale columns previously used in potassium adsorption trials.

Appendix E

MULTI-ADSORBATE SORPTION/DESORPTION TRIALS

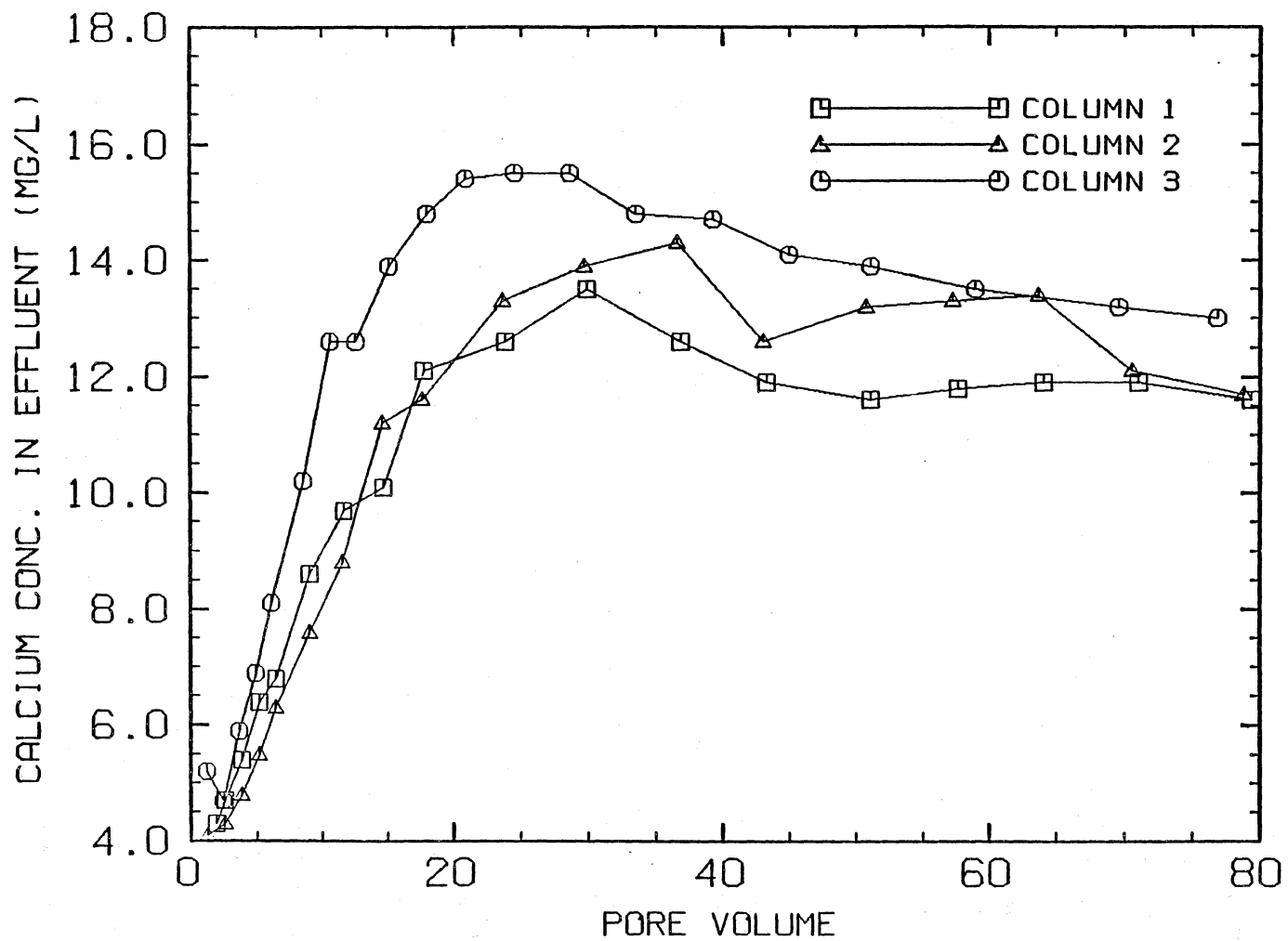


Figure E1. Breakthrough curves for calcium in multi-adsorbate column trials with Oxy spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

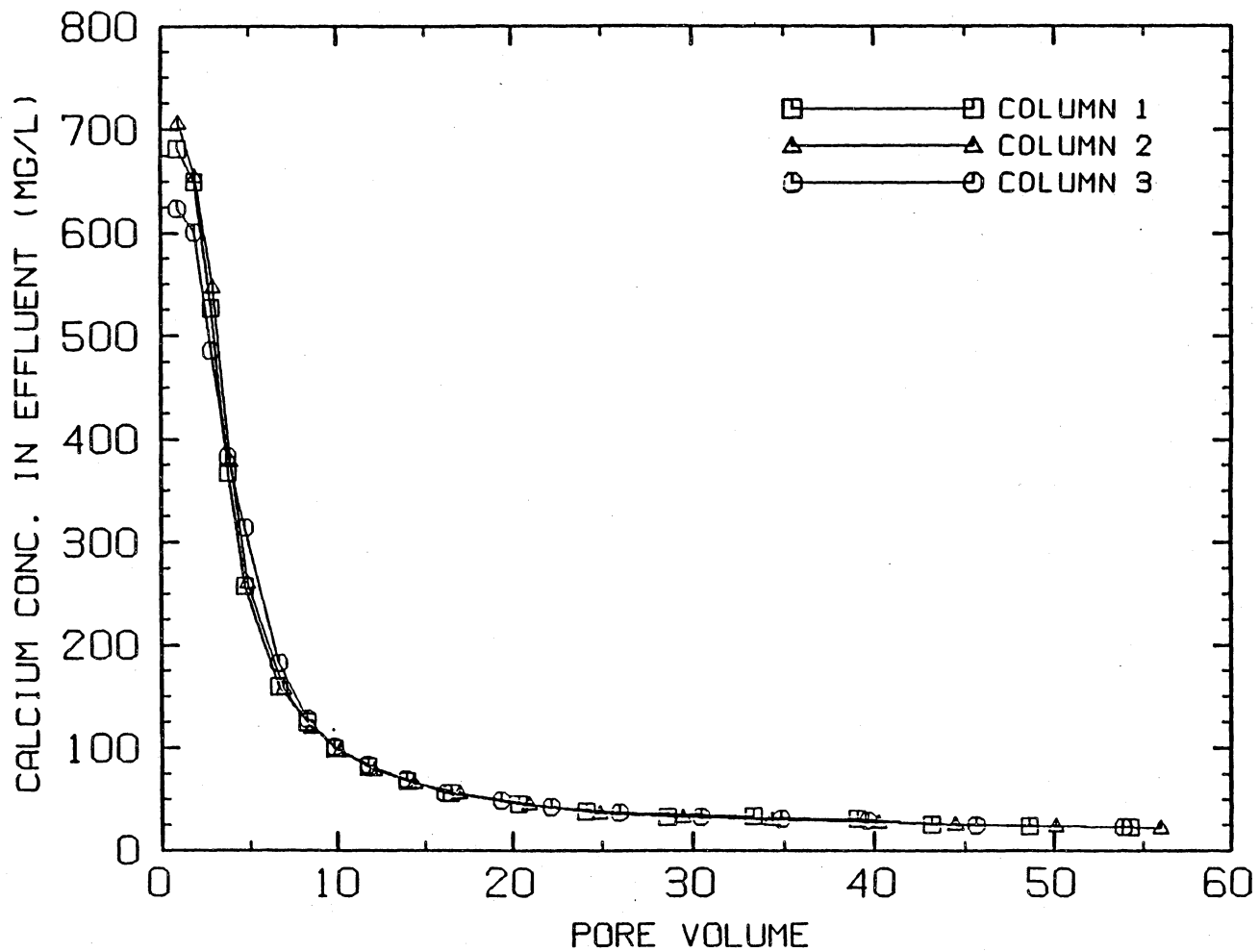


Figure E2. Breakthrough curves for calcium in multi-adsorbate column trials with Antrim spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

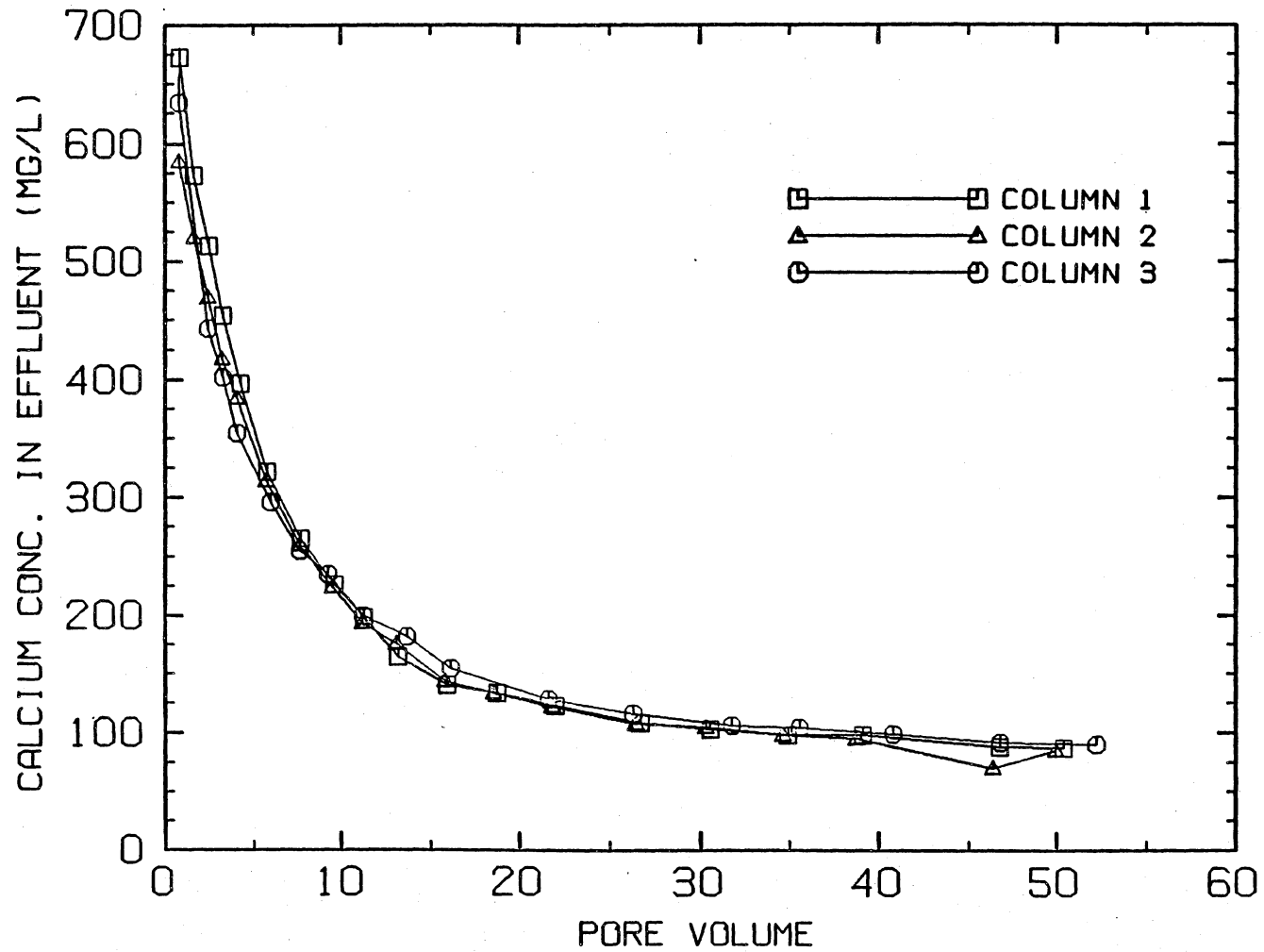


Figure E3. Breakthrough curves for calcium in multi-adsorbate column trials with Run 16 spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

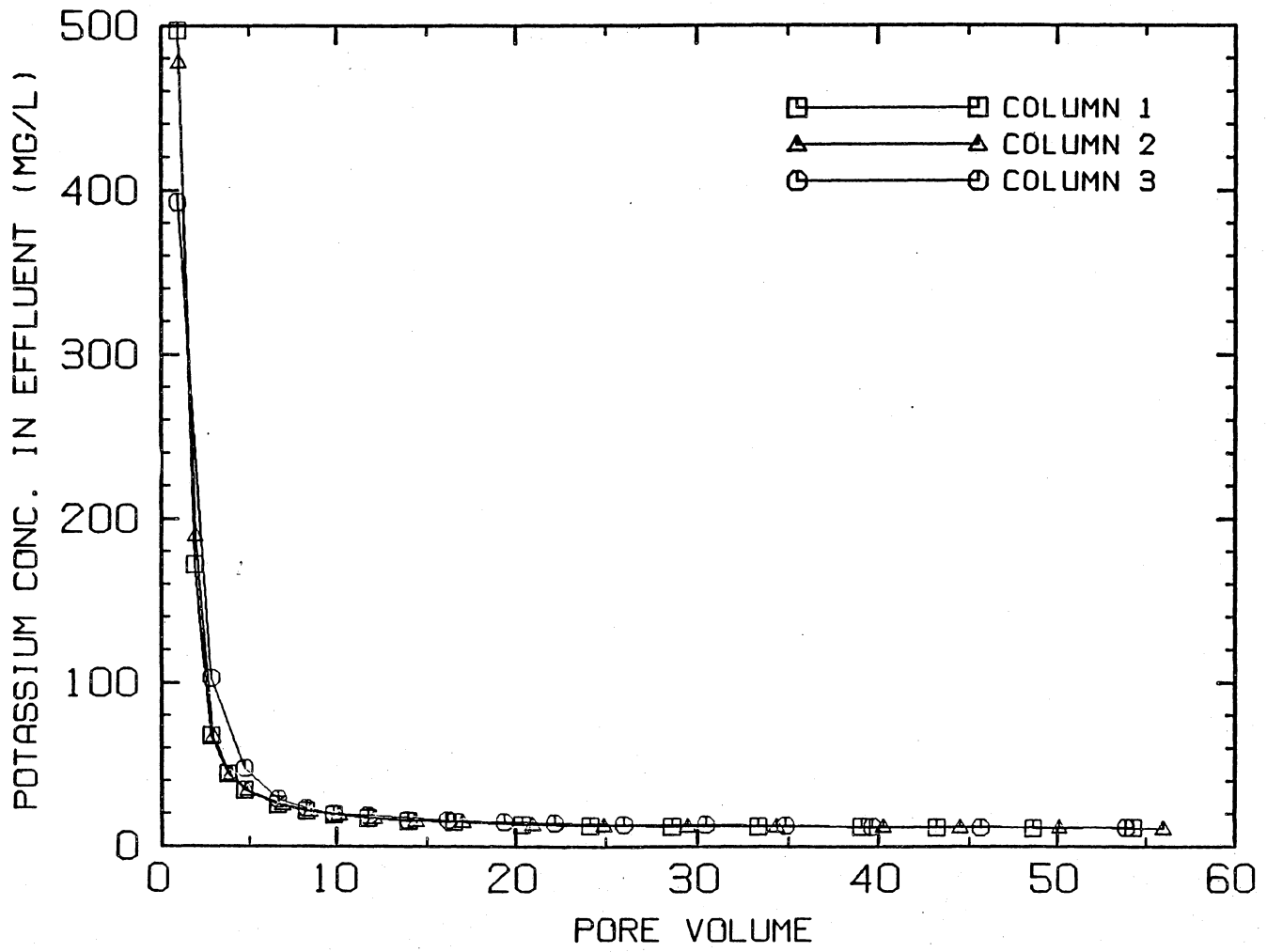


Figure E 4. Breakthrough curves for potassium in multi-adsorbate column trials with Antrim spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

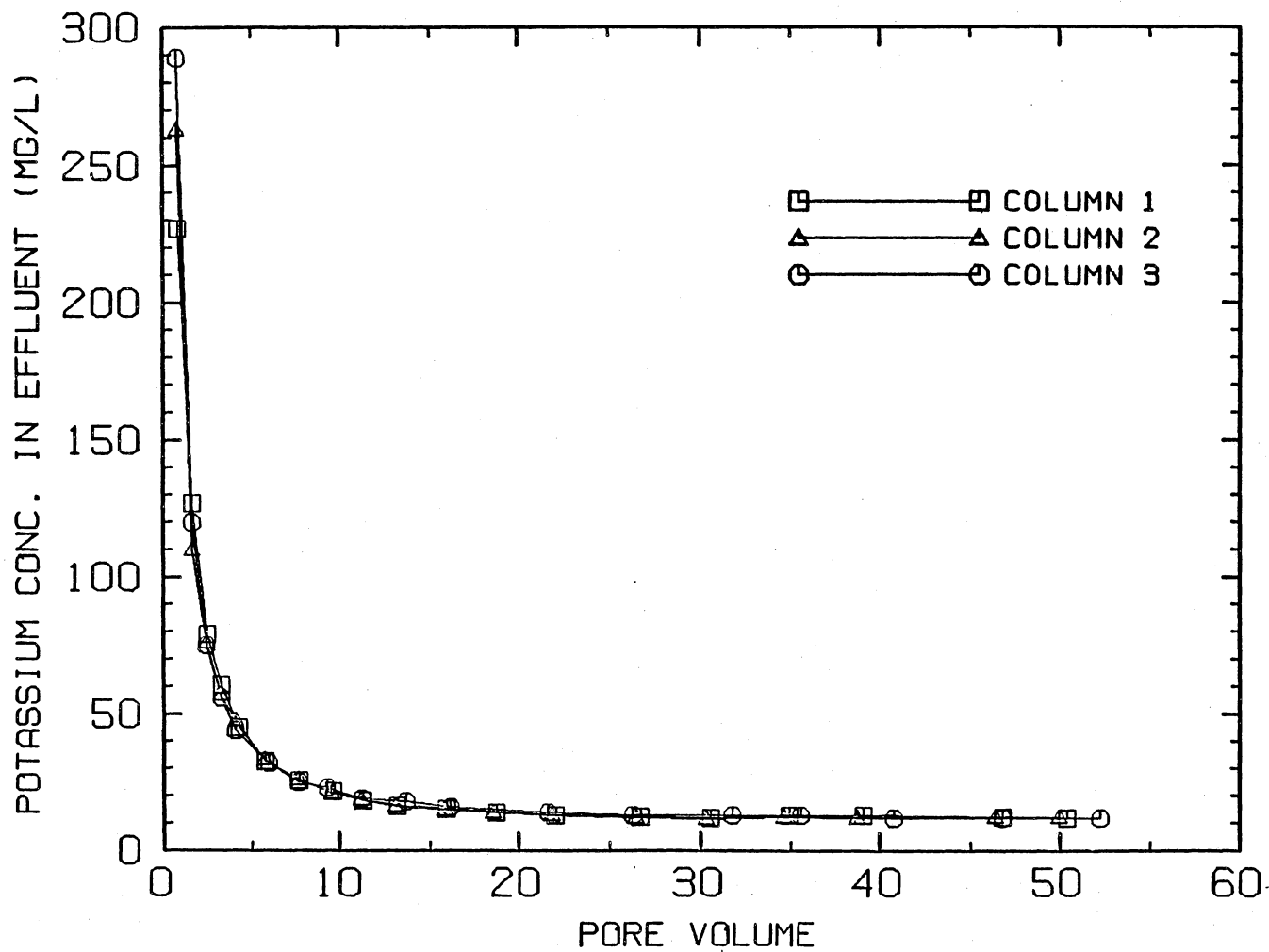


Figure E5. Breakthrough curves for potassium in multi-adsorbate column trials with Run 16 spent shale; adsorbate consisted of As, Ca, Cd, F and K in distilled water.

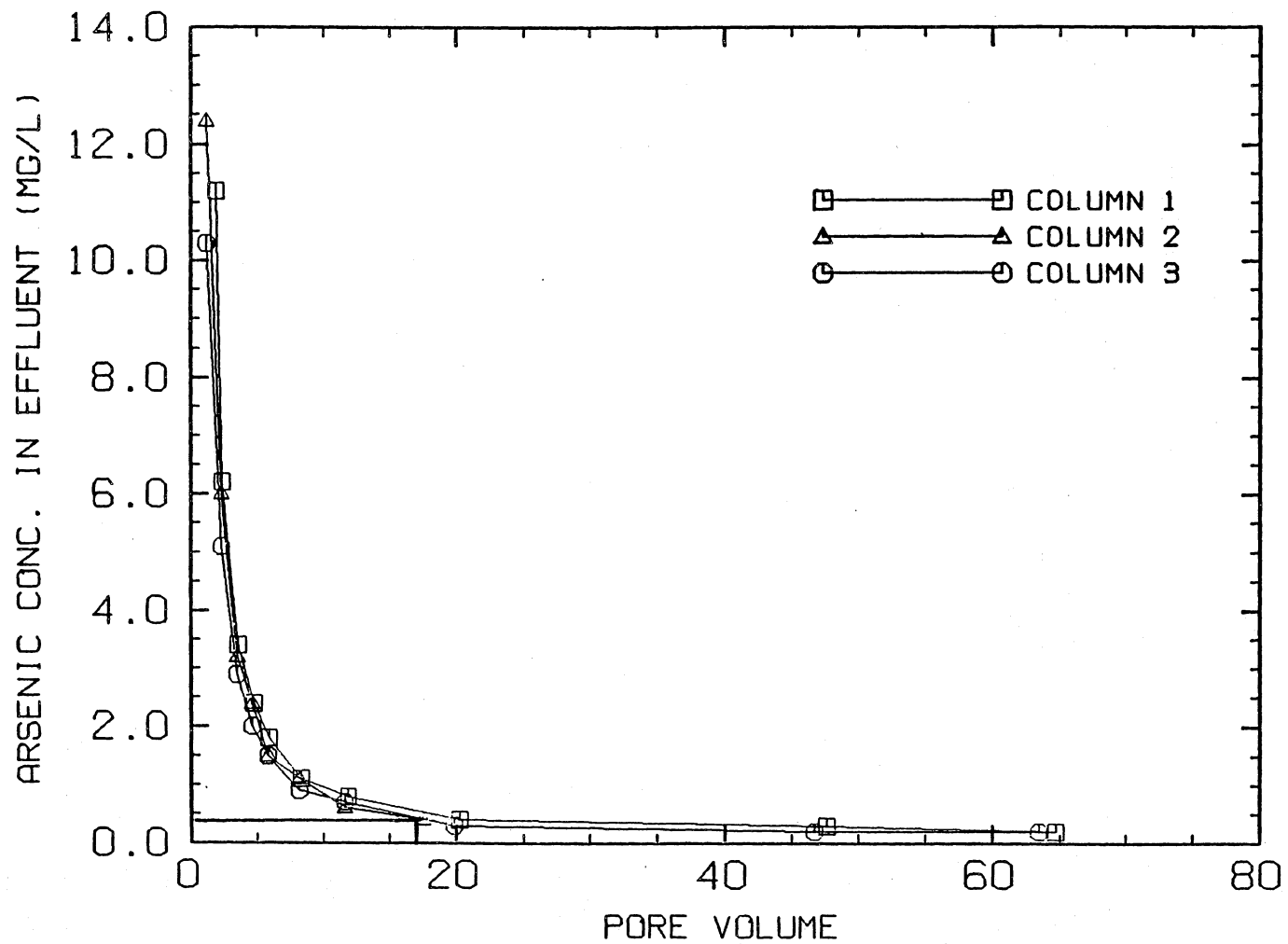


Figure E6. Desorption of arsenic from columns of Anvil raw shale which were previously used in multi-adsorbate experiments; results of three trials provided.

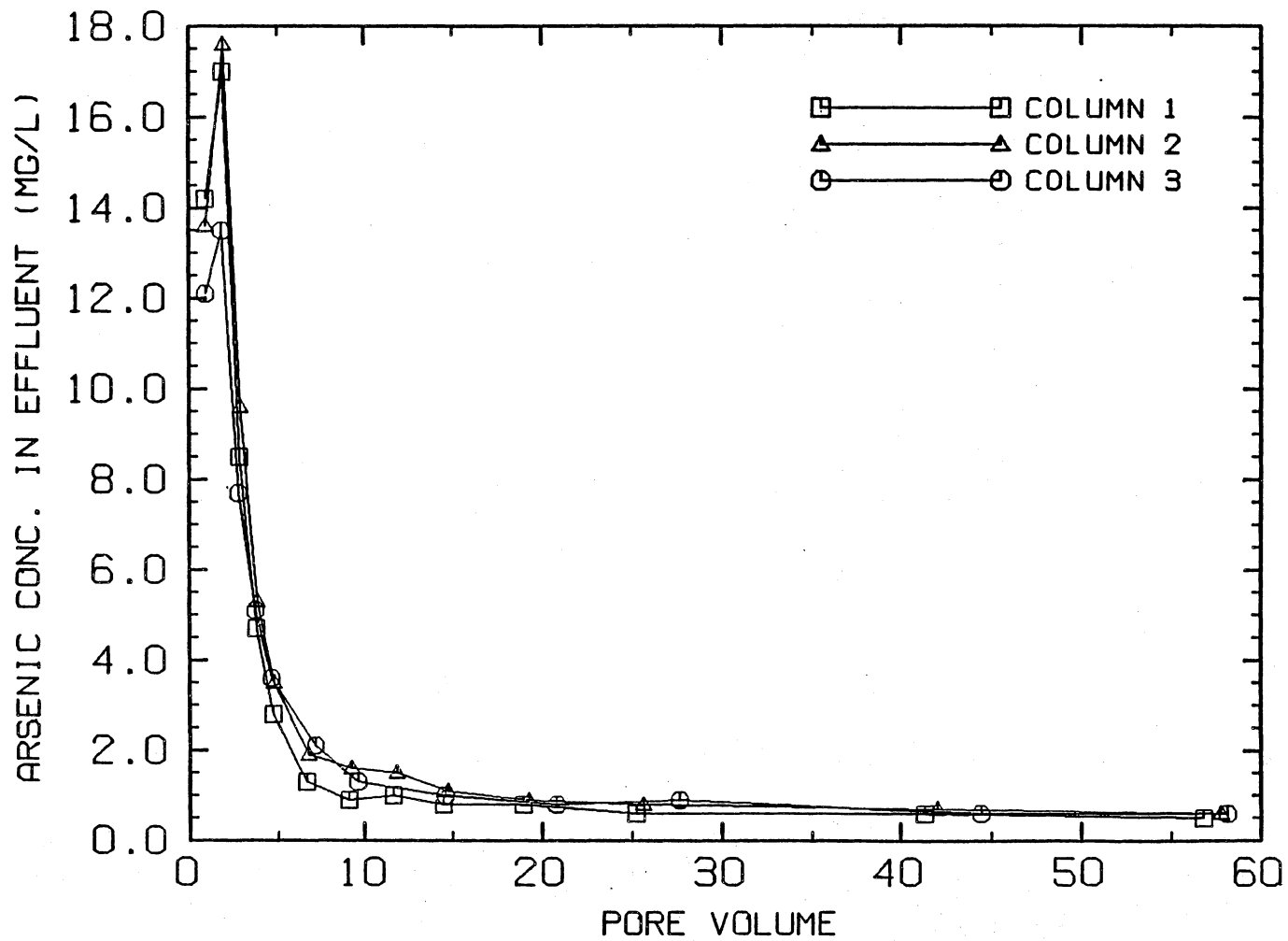


Figure E7. Desorption of arsenic from columns of Antrim spent shale which were previously used in multi-adsorbate experiments; results of three trials provided.

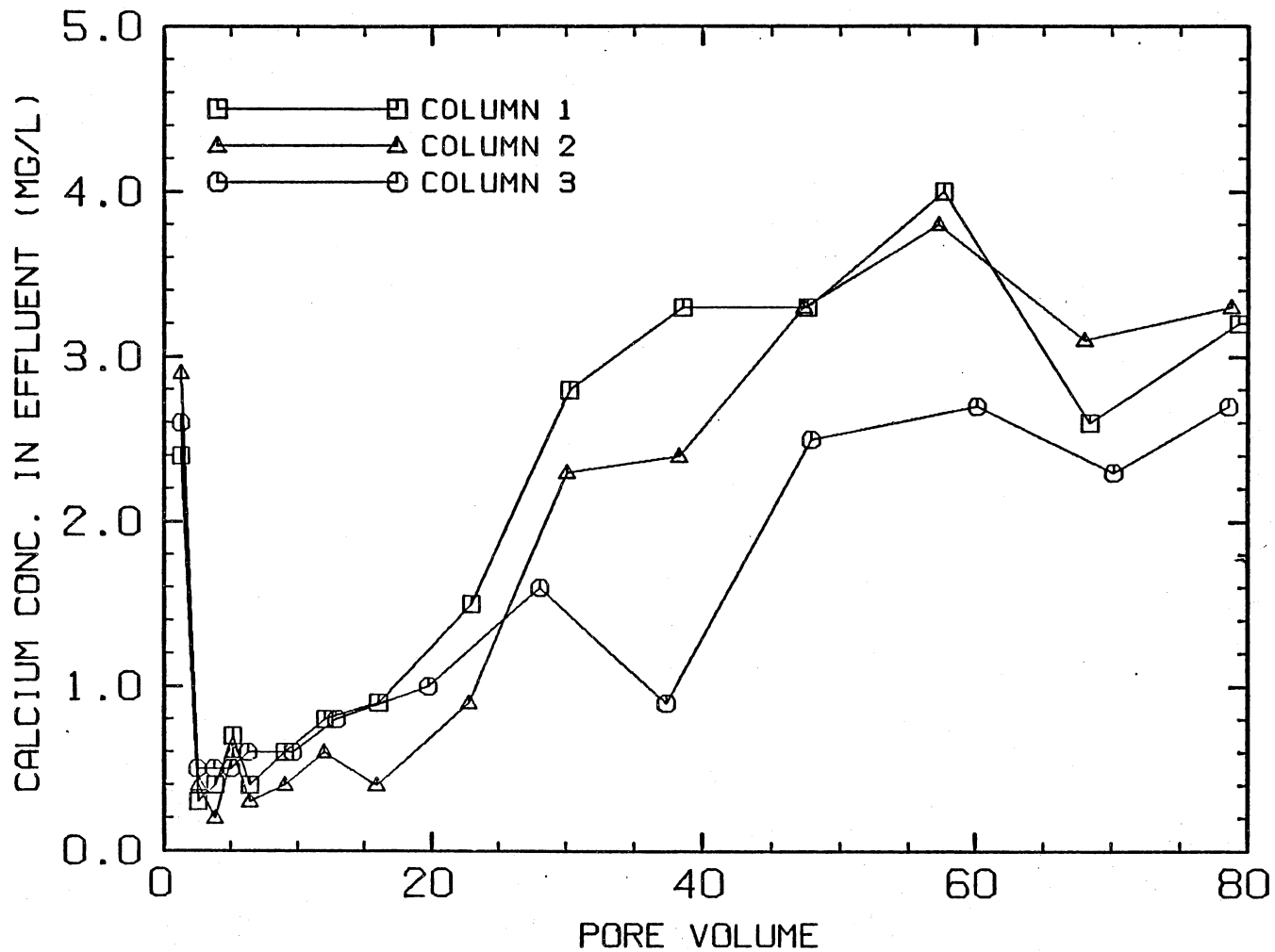


Figure E8. Desorption of calcium from columns of Oxy spent shale which were previously used in multi-adsorbate experiments; results of three trials provided.

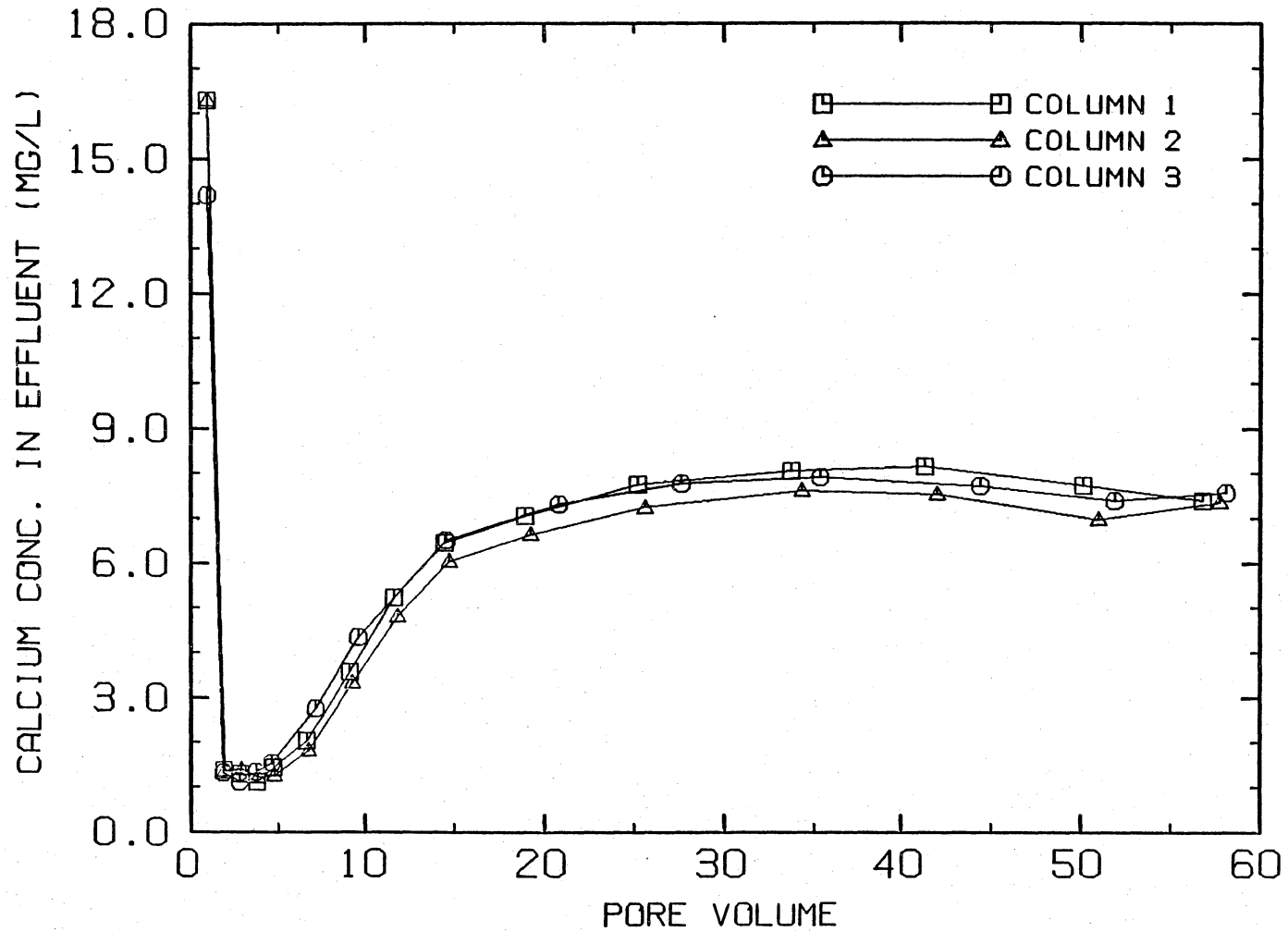


Figure E 9. Desorption of calcium from columns of Antrim spent shale which were previously used in multi-adsorbate experiments; results of three trials provided.

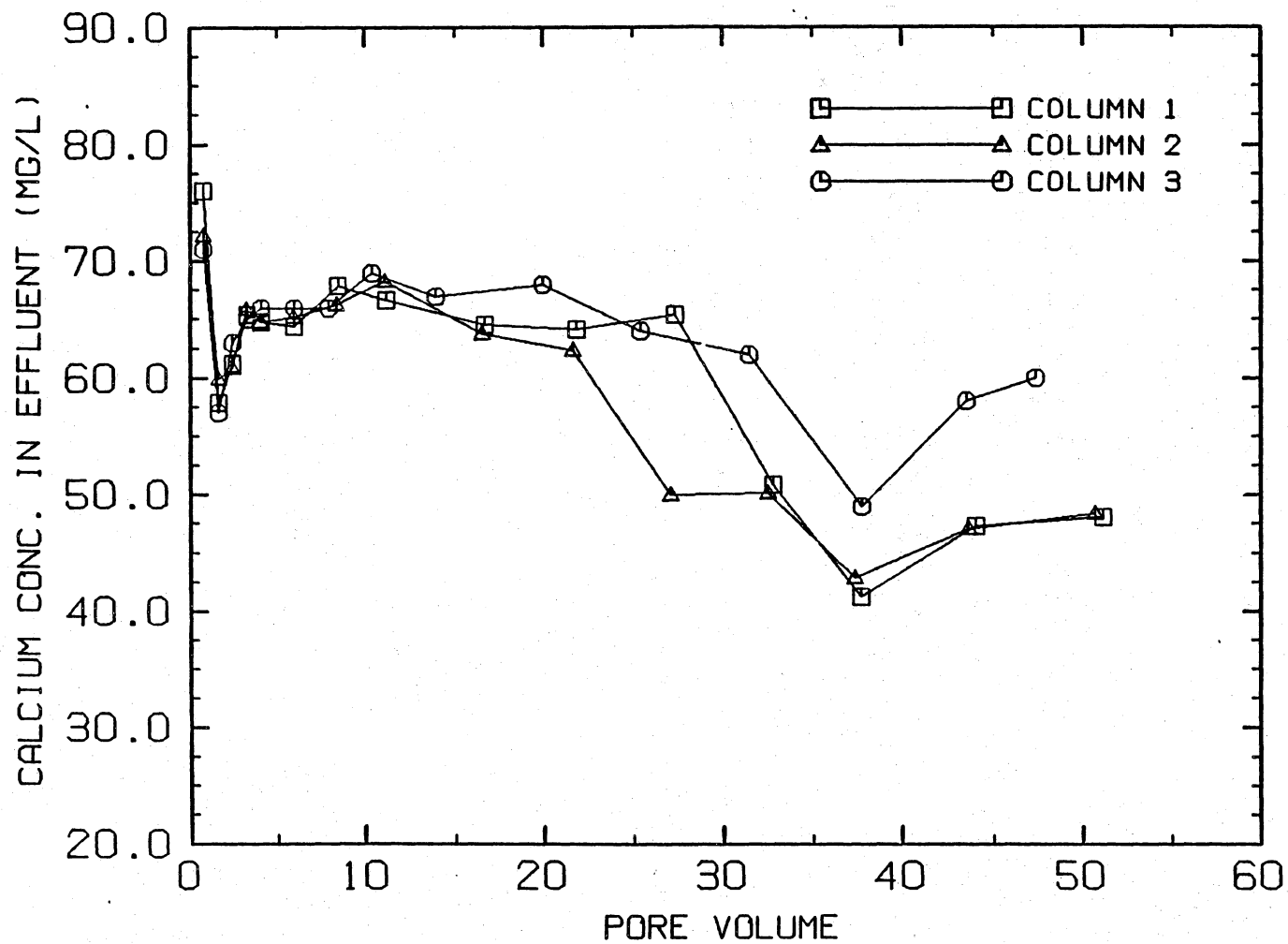


Figure E10. Desorption of calcium from columns of Run 16 spent shale which were previously used in multi-adsorbate experiments; results of three trials provided.

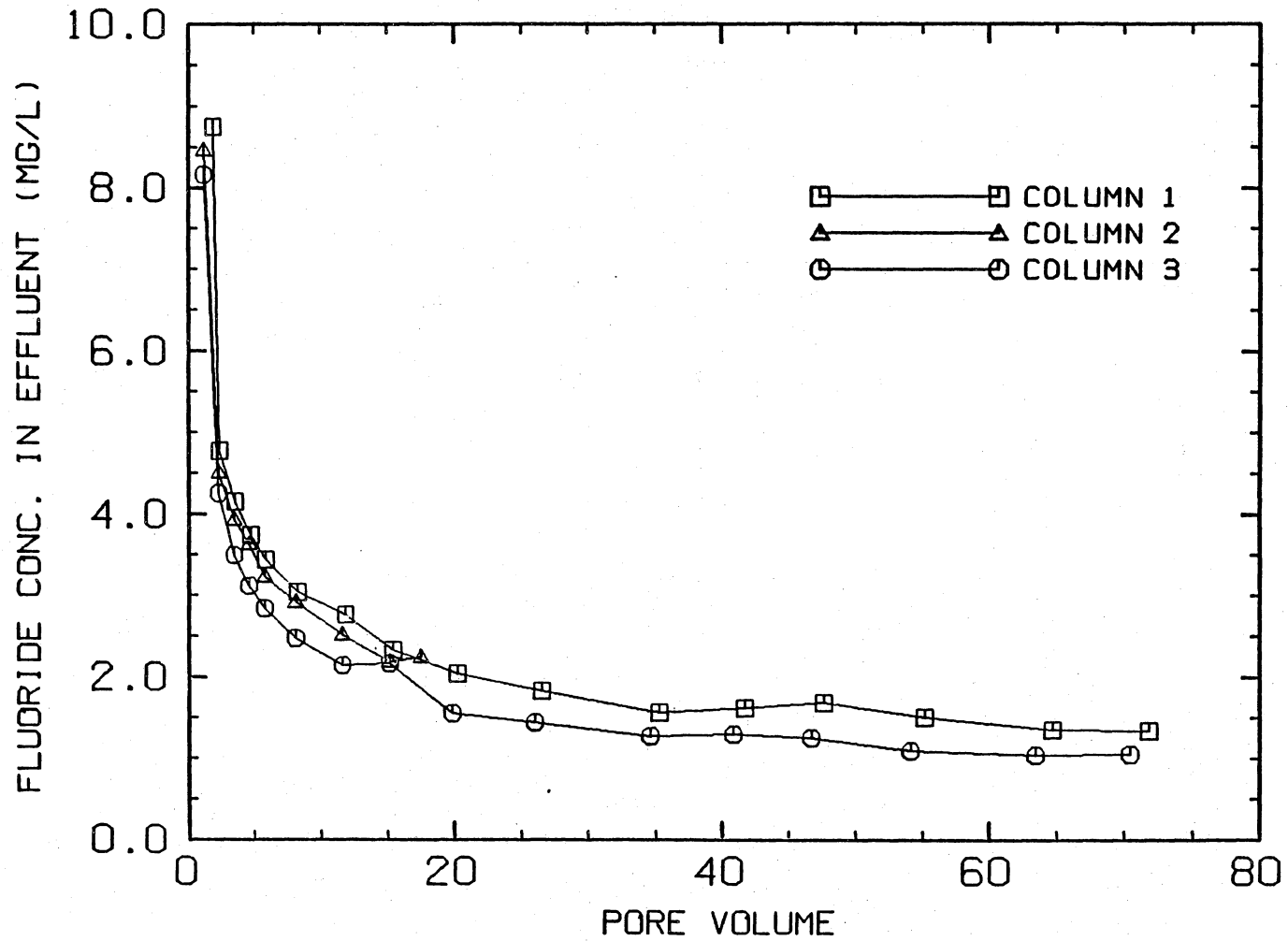


Figure E11. Desorption of fluoride from columns of Anvil raw shale which were previously used in multi-adsorbate experiments; results of three trials provided.

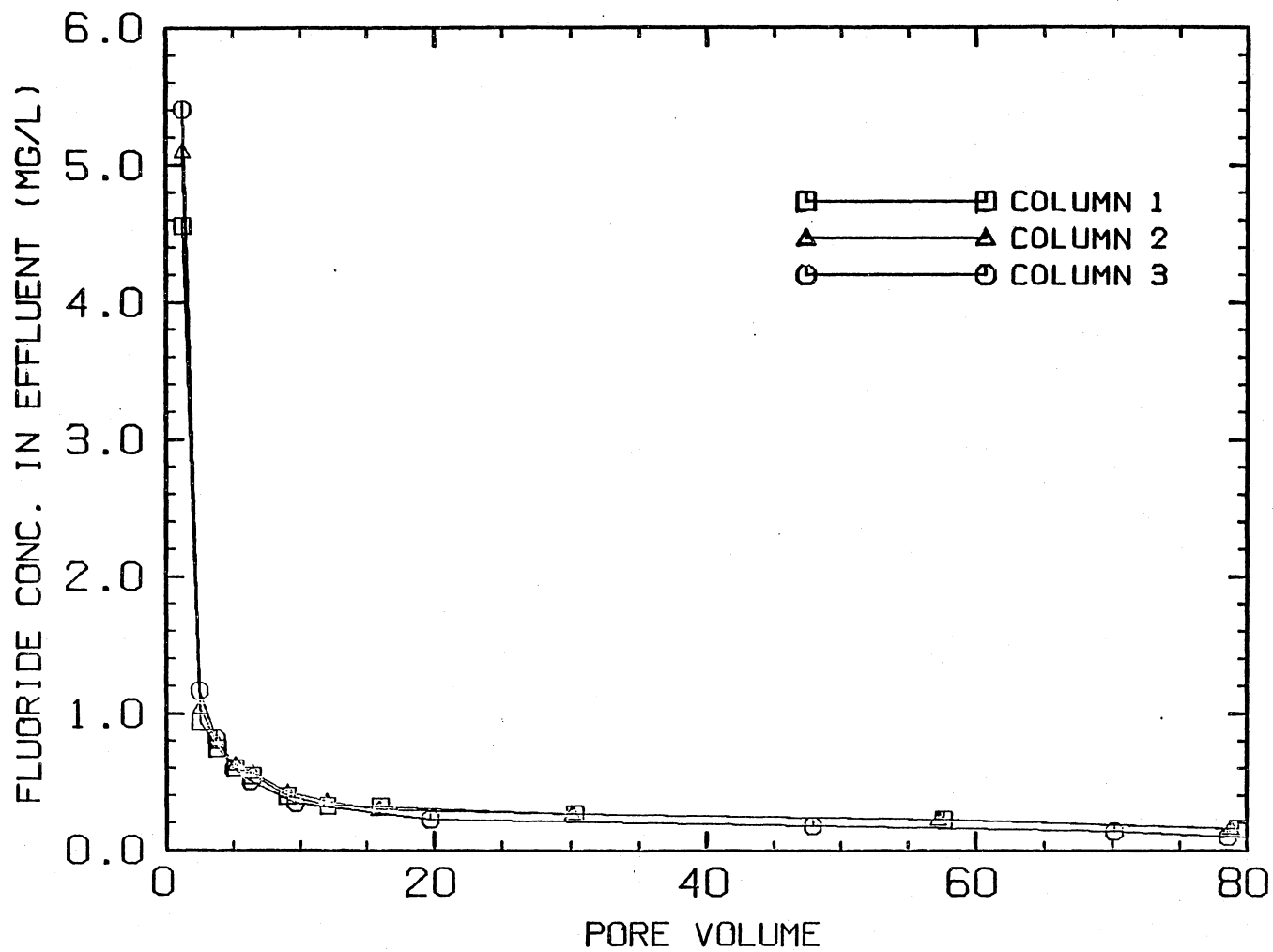


Figure E 12. Desorption of fluoride from columns of Oxy spent shale which were previously used in multi-adsorbate experiments; results of three trials provided.

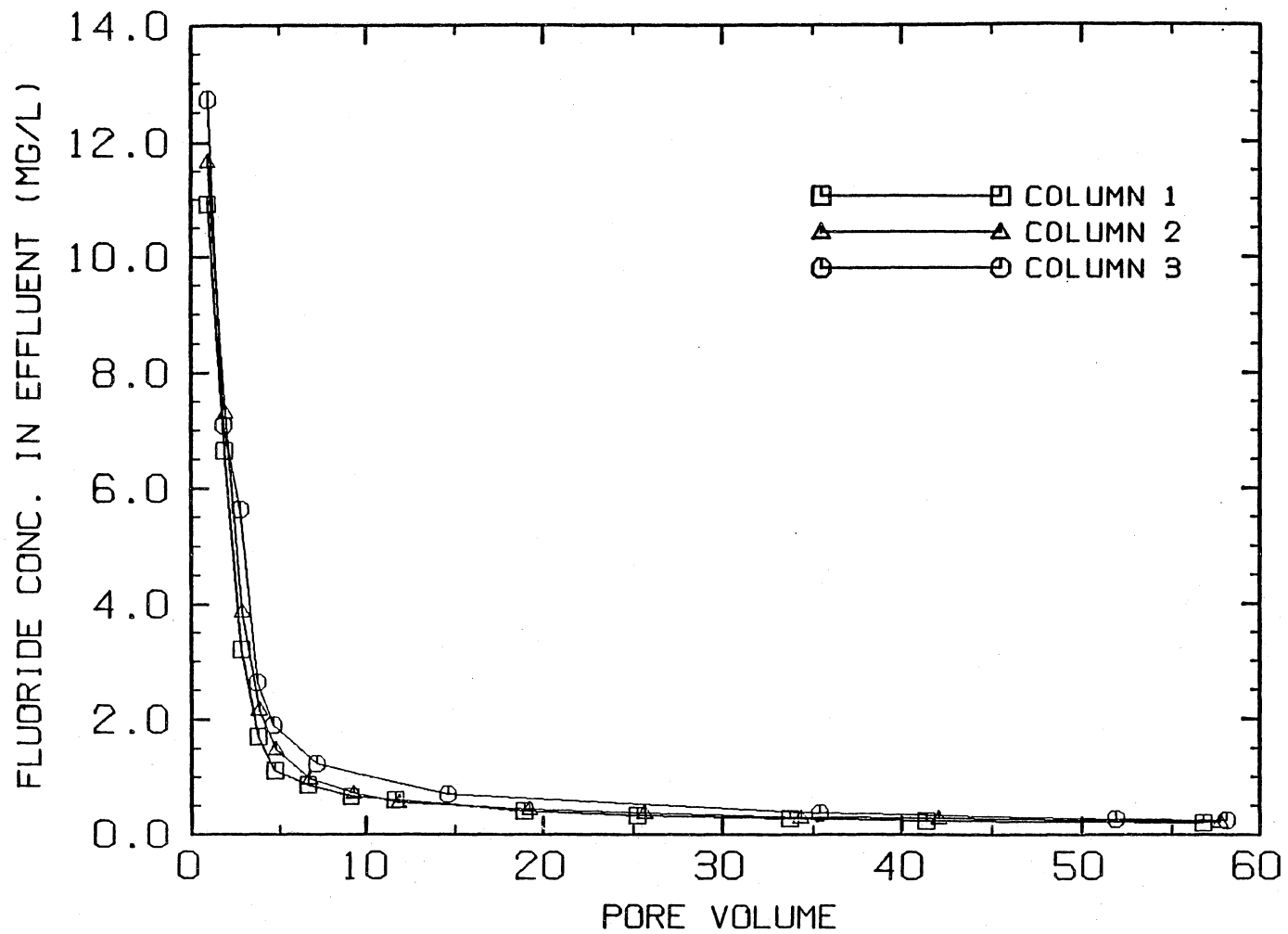


Figure E13. Desorption of fluoride from columns of Antrim spent shale which were previously used in multi-adsorbate experiments; results of three trials provided.

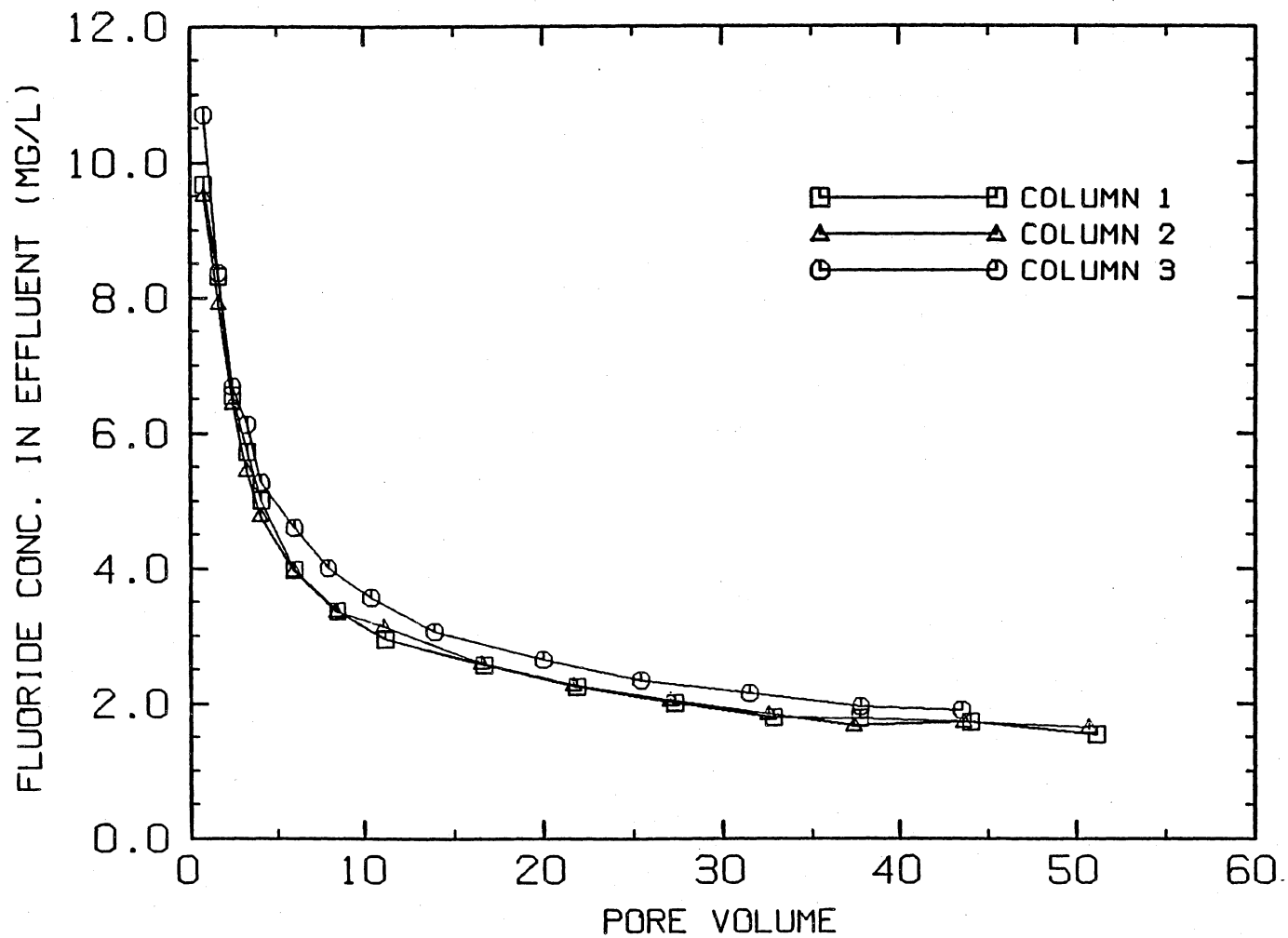


Figure E14. Desorption of fluoride from columns of Run 16 spent shale which were previously used in multi-adsorbate experiments; results of three trials provided.

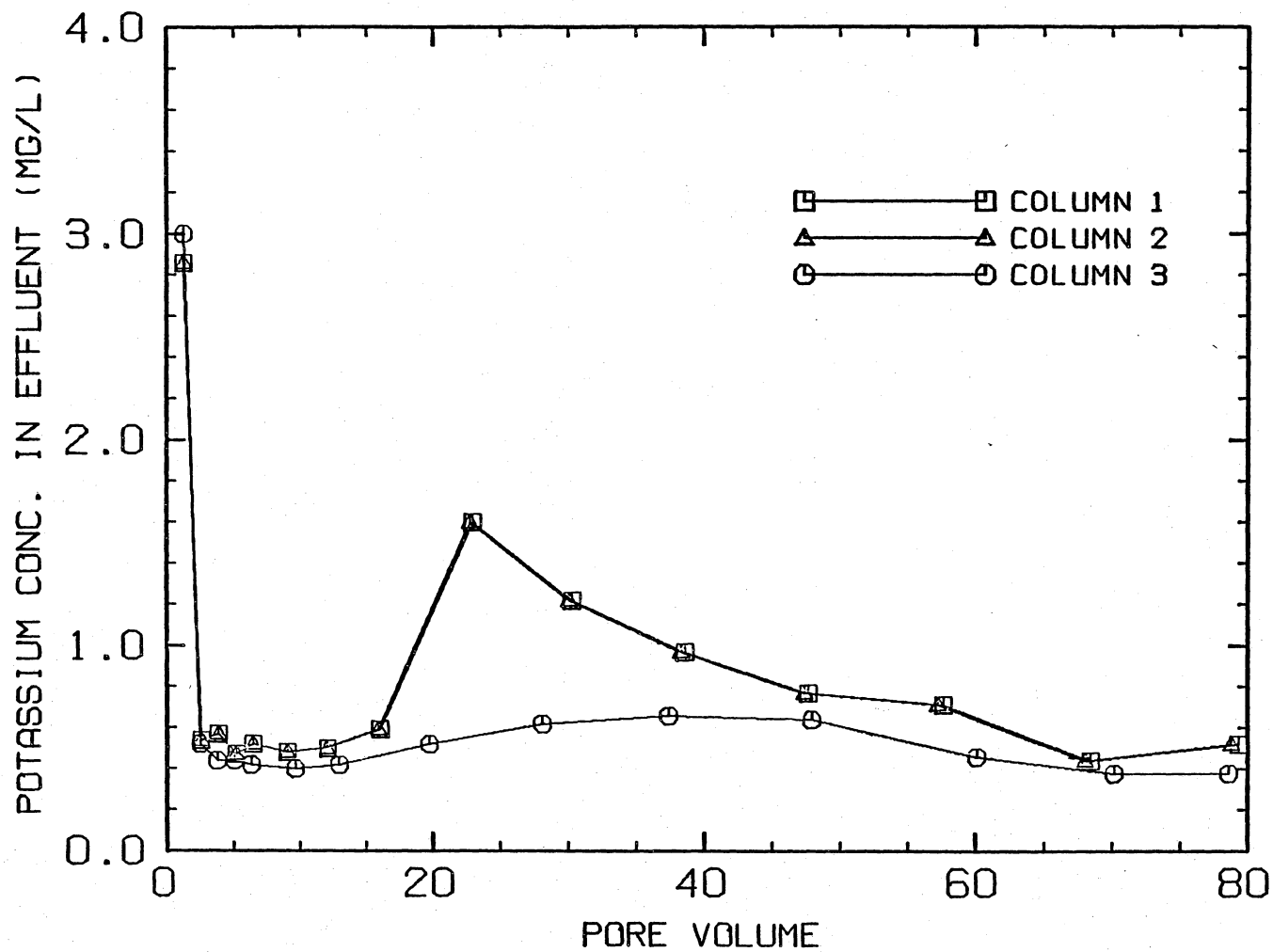


Figure E15. Desorption of potassium from columns of Oxy spent shale which were previously used in multi-adsorbate experiments; results of three trials provided.

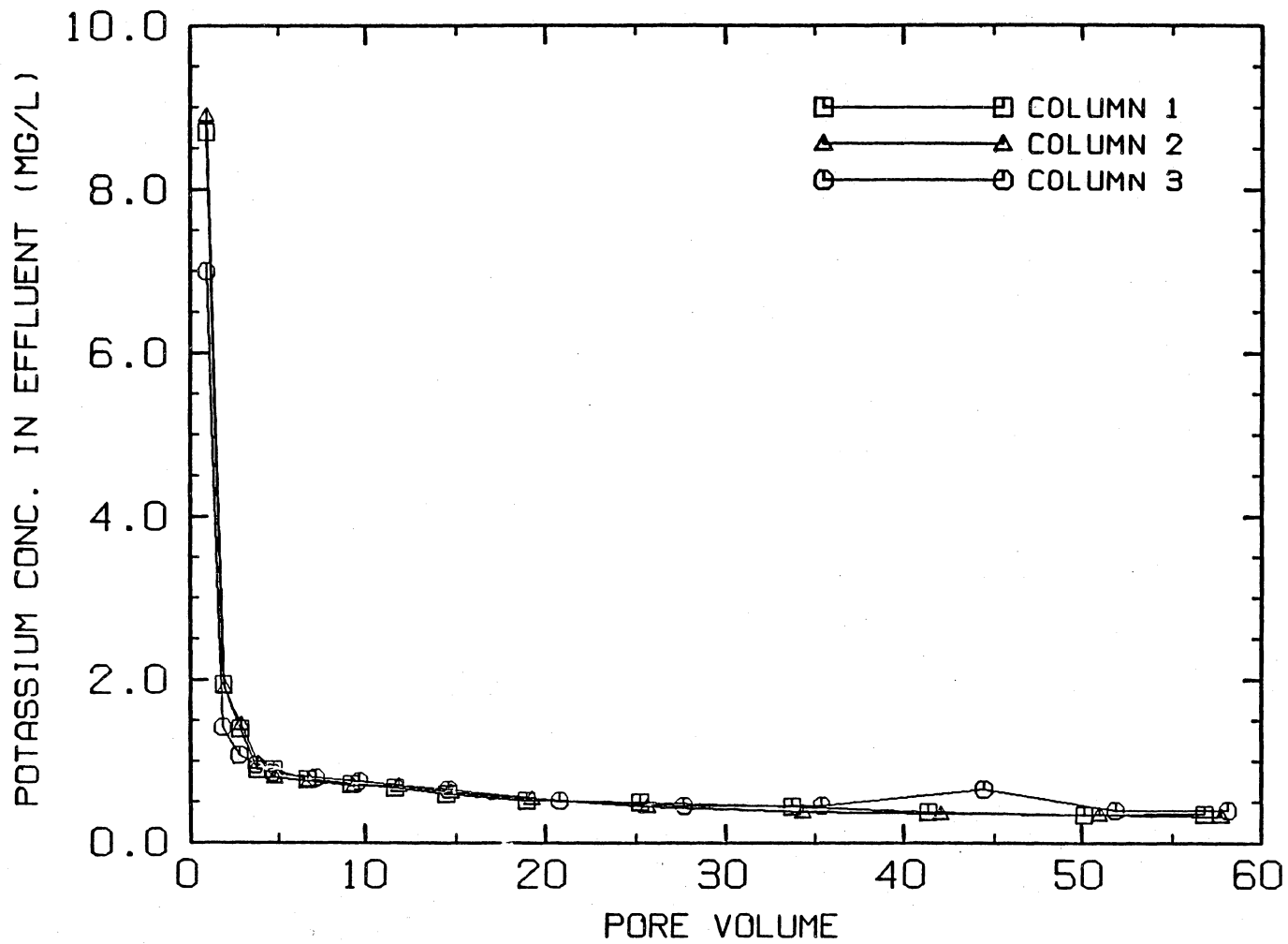


Figure E16. Desorption of potassium from columns of Antrim spent shale which were previously used in multi-adsorbate experiments; results of three trials provided.

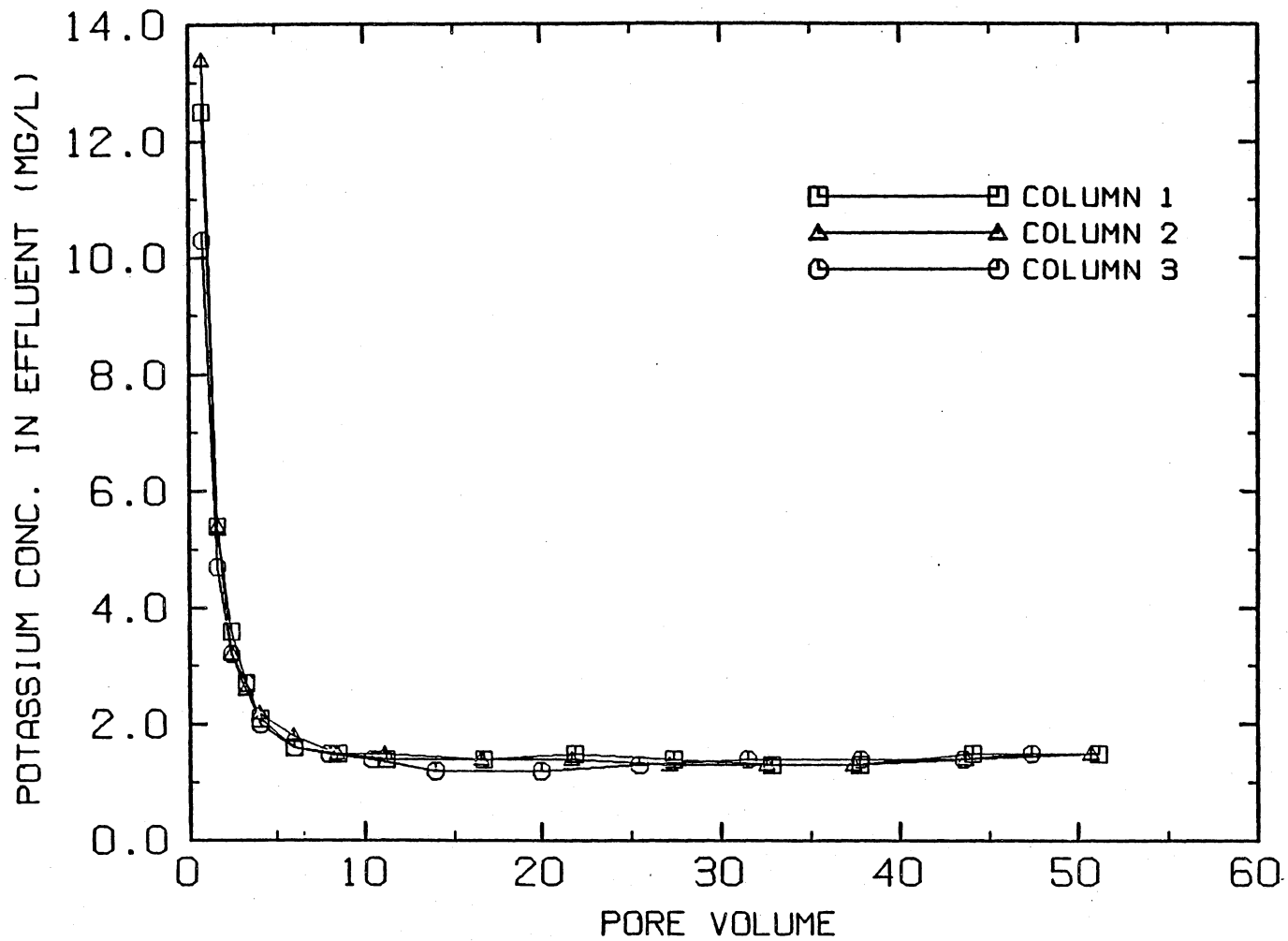


Figure E17. Desorption of potassium from columns of Run 16 spent shale which were previously used in multi-adsorbate experiments; results of three trials provided.

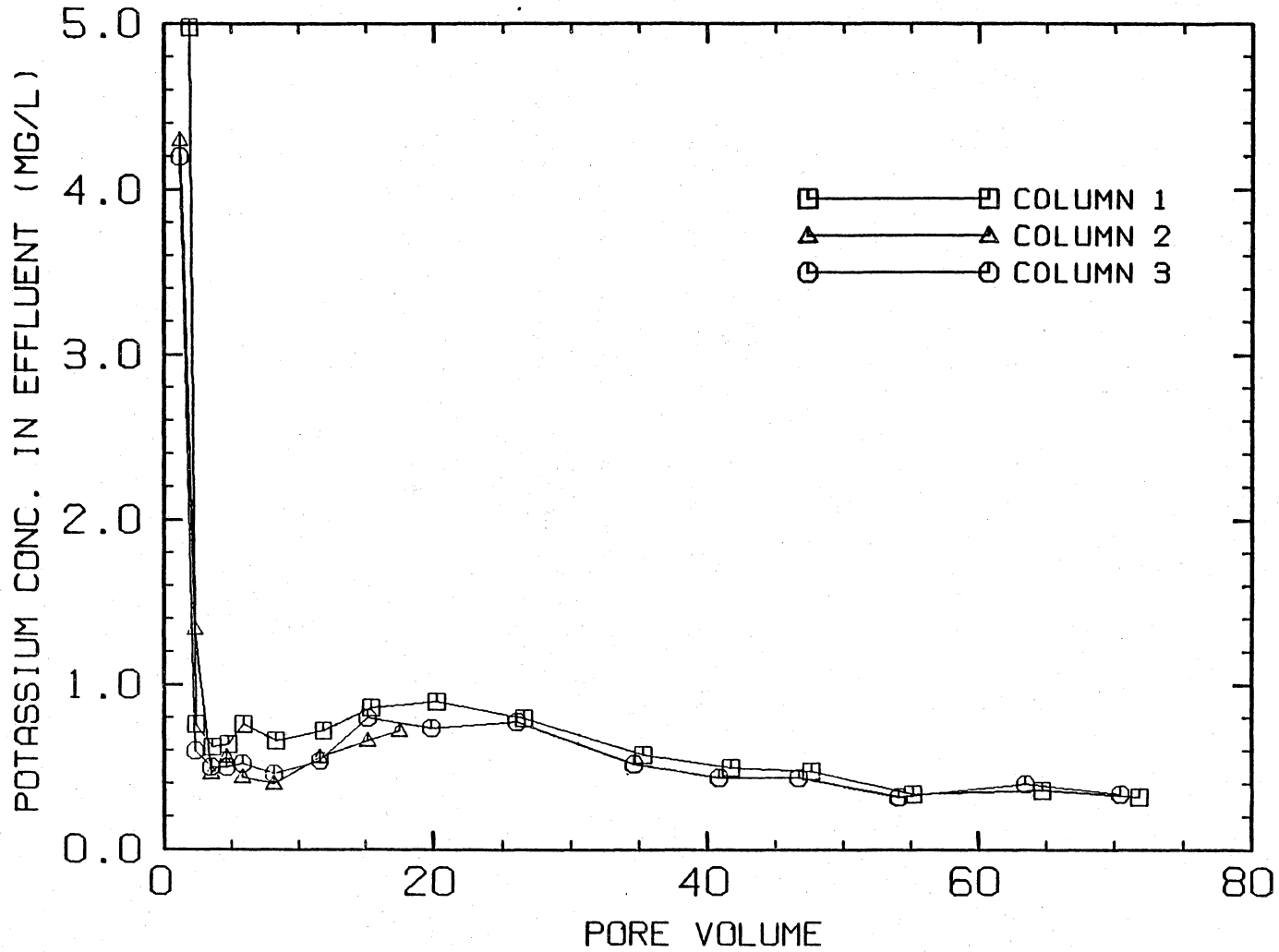


Figure E18. Desorption of potassium from columns of Anvil raw shale which were previously used in multi-adsorbate experiments; results of three trials provided.

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