QA: NA

MOL.20090210.0020

DOE/AL/62350-17F

ADSORPTION ISOTHERM SPECIAL STUDY

Final

May 1993

Work Performed Under Contract No. DE-AC04-91AL62350

Prepared for
U.S. Department of Energy
UMTRA Project Office
Albuquerque, New Mexico

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SUMMARY

For the last decade, the U.S. Department of Energy (DOE) has been engaged in tailings remediation at abandoned uranium mill sites. In the coming decade the focus will shift to groundwater restoration at these sites. For passive remediation strategies, such as natural flushing or applications of alternate concentration limits, prediction of contaminant plume travel distance and downgradient concentrations is of prime importance. Metal transport in groundwater is highly dependent on sorptive and desorptive characteristics of the aquifer matrix. This study was designed to 1) identify methods to determine adsorption that are applicable to Uranium Mill Tailings Remedial Action (UMTRA) Project sites, and 2) determine how changes in aquifer conditions affect metal adsorption, resulting retardation factors, and estimates of contaminant migration rates. U.S. Environmental Protection Agency (EPA)-recommended batch-type procedures and American Society for Testing and Materials (ASTM) procedures were used to estimate sediment sorption of uranium, arsenic, and molybdenum under varying groundwater geochemical conditions.

Aquifer matrix materials collected from three distinct locations at the DOE UMTRA Project site in Rifle, Colorado, were used as the adsorbents under different pH conditions. These conditions simulated geochemical environments under the tailings, near the tailings, and downgradient from the tailings. Grain size, total surface area, bulk and clay mineralogy, and petrographic features of the sediments were characterized.

EPA-recommended constant-ratio and variable-ratio methods yielded linear isotherms for uranium and molybdenum. Nonlinear isotherms resulted from arsenic adsorption. Variable ratio methods produced plots with greater scatter, which was most likely due to effects of cation competition for surface sorption sites. Uranium and molybdenum exhibited strong adsorption on sediments that were acidified to levels commonly found in tailings leachate. Changes in pH had much less effect on arsenic adsorption. Molybdenum showed very little to no adsorption under background pH conditions (pH=7 to 7.3), uranium was weakly sorbed, and arsenic was moderately sorbed. Retardation factors were calculated from the linear and nonlinear isotherm coefficients. Using site-specific hydrogeologic information, velocities were estimated for metal transport in the different pH environments. Results of this study show that the adsorption characteristics of the aquifer materials must be determined to estimate metal transport velocities in aquifers and to ultimately develop site-specific groundwater restoration strategies for the UMTRA Project.

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1.0 AQUIFER ADSORPTION DETERMINATION: AN INTEGRAL PART OF SITE CHARACTERIZATION

1.1 INTRODUCTION

The proposal for the *Adsorption Isotherm Special Study* was approved by the DOE in January 1992 and work began in February 1992.

At Uranium Mill Tailings Remedial Action (UMTRA) sites, a determination of the volume and extent of contaminated groundwater, the particular hazardous constituents in the groundwater, and their individual rates of movement in the aquifer, are critical for restoration action plan development and groundwater compliance strategy formulation. The groundwater restoration phase of the UMTRA Project began in April 1991 and site-specific groundwater characterization activities will begin in fiscal year 1993.

This study was conceived as a part of the technical foundation to this groundwater characterization effort. Results of this study include guidelines for aquifer matrix adsorption determination and an appraisal of hydrogeologic factors (e.g., geochemical and lithologic conditions) that affect velocities of hazardous constituents in groundwater. This information will be used in the future for groundwater characterization planning, selection of groundwater restoration alternatives, and groundwater compliance strategy development.

During the past 30 years, the adsorption of groundwater contaminants by geologic media has been extensively studied from a purely scientific perspective. However, few studies have attempted to transfer this information or these approaches to an engineering design application. The *Adsorption Isotherm Special Study* effected this transfer for the UMTRA Project through the evaluation and application of guidelines established by the U.S. Environmental Protection Agency (EPA) (EPA, 1991) for adsorption determination. The results were applied to the Rifle UMTRA site to help predict the rate of contaminant migration.

1.2 SCOPE OF STUDY

This study was designed to investigate the ability of isotherms generated by two methods to characterize sorption properties of hazardous constituents in acidified and alkaline environments:

- EPA-recommended batch test techniques.
- Distribution coefficients (K_d) generated by American Society for Testing and Materials (ASTM)-approved batch test techniques.

Two UMTRA sites were selected to provide aquifer materials, which were subjected to adsorption isotherm experiments. These sites, Shiprock and Rifle (new) [the "old" Rifle site is about 4 miles (mi) (6.4 kilometers [km]) upstream], were selected based on the site risk rank, developed by Technical Assistance Contractor (TAC) toxicologists, types of contaminants, and hydrogeologic features. Both sites satisfied the criteria because of good monitor well control (well-defined plumes), the presence of a variety of contaminants, difference in geologic terrains, and their presence in Category 1 or 2 on the risk rank list developed by the project toxicologists.

Initial adsorption experiments indicated that leachable uranium was present in the untreated Shiprock alluvium sediments, and it would have been extremely difficult to account for this excess uranium in our procedures. Therefore, only aquifer matrix material from the Rifle site was used in the batch tests used to construct isotherms. The Shiprock sediments will not be discussed further, although information is provided in the appendixes.

To develop a methodology for adsorption isotherm determination, the factors that affect adsorptive capacity of sediment must be evaluated. To do this, the grain size, total surface area, bulk and clay mineralogy, petrographic features, and chemistry of the Rifle sediments were characterized.

A subset of the hazardous constituents (i.e., arsenic, uranium, and molybdenum) that are of special concern to the UMTRA Project were selected for investigation because of their mobility in either acidic or alkaline groundwater. Furthermore, uranium and molybdenum form large groundwater plumes at some UMTRA sites, and arsenic is of toxicological concern at some UMTRA sites.

Adsorption parameters determined by the isotherm plots of each hazardous constituent are used in the calculation of retardation factors. Retardation factors are then used to estimate contaminant velocity relative to the bulk advective groundwater velocity for the aquifer.

1.3 THE TAILINGS-GROUNDWATER-AQUIFER MATRIX SYSTEM

1.3.1 Introduction

Uranium mill tailings at many UMTRA processing sites were commonly slurried onto unlined exposures of nearby geologic units or into shallow unlined retention ponds. More rarely, the tailings were slurried into pits excavated during mining operations. At many UMTRA sites, contaminant-rich acidic or alkaline tailings pore water has entered the subsurface and is interacting with the natural groundwater and sediment. The influx of these contaminated solutions into an aquifer system disturbs the natural chemical equilibrium that exists between the uncontaminated groundwater and the aquifer sediment. The composition of

contaminated groundwater at a given site is primarily the result of the tailings pore water chemistry, the natural groundwater chemistry, and the physical and chemical properties (e.g., sorption capacity and acid neutralization capacity) of the aquifer matrix material.

1.3.2 Tailings pore fluids

The chemistry of the pore fluids in uranium mill tailings depends largely on the processing methods that were used to extract uranium from ore. Uranium was commonly extracted using either alkaline or acid leach solutions. Acid leach operations typically used sulfuric acid (H_2SO_4) and an oxidant to strip uranium from the ore primarily as stable (sulfate, SO_4) complexes (e.g., uranyl sulfate UO_2SO_4 and uranyl bisulfate $UO_2(SO_4)_2^{2-}$). The tailings that remain after acid processing are saturated with a low-pH solution that is typically rich in metals and metalloids (e.g., iron, aluminum, manganese, cadmium, arsenic, selenium, molybdenum, chromium, and vanadium). Alkaline leach operations, however, typically use alkali and/or ammonium carbonate salts to selectively leach uranium as a carbonate species (e.g., $UO_2(CO_{3-4})$ from ore material (Merritt, 1971).

Due to the tendency of many metals to form relatively insoluble hydroxide and carbonate compounds under alkaline conditions, many of the metals that are abundant in acid tailings effluent (e.g., iron, aluminum, cadmium, chromium, and copper) are present at much lower concentrations in tailings pore water generated by alkaline leaching. Some contaminants at UMTRA sites (e.g., uranium, arsenic, selenium, and molybdenum) are relatively soluble in either alkaline (pH > 7.0) or very acidic (pH=0.5-2.0) conditions generated during alkaline or acid leaching. If precipitation of carbonates, sulfates, or hydroxides was the only mechanism for removing these elements from solution, high concentrations of these contaminants could be transported large distances from the tailings site by alkaline groundwater. The migration velocities of these contaminants are, however, attenuated relative to the advective groundwater velocity by sorption onto aquifer matrix materials.

1.3.3 Groundwater and aquifer matrix effects on sorption

At UMTRA Project sites, the aquifers that contain contaminated groundwater are typically unconsolidated floodplain alluvium deposits or sedimentary bedrock formations (sandstones, siltstones, shales, and limestones). These alluvial sediments contain material that have the ability to sorb metals (e.g., clays, organic material, and iron oxyhydroxides). The adsorption of hazardous constituents by the aquifer matrix is a process that affects the extent, concentrations, and rate of movement of metals in groundwater. The adsorption potential of an aquifer matrix for the transition metals appears to be determined, primarily, by the quantity of amorphous oxide coatings (iron, manganese, aluminum, and silica) present on grains and the amount of

particulate organic carbon present (Jenne and Zachara, 1987). Clay and zeolite minerals also contribute to adsorption of metals by aquifer matrix material. Colloidal particles that may be present on aquifer matrix materials may also be significant in the adsorption of heavy metal contaminants from the groundwater.

The geochemical condition of the groundwater composition (Eh, pH, concentrations of major cations and anions) also influences adsorption. Dissolved constituents may compete with heavy metals for the same adsorption sites. The extent of competition is dependent on concentrations of competing ions and the relative adsorption affinities for the surface sites (Jenne and Zachara, 1987). Dissolved ligands may complex with heavy metals under certain conditions making them more or less likely to be adsorbed on the aquifer matrix. The pH and redox state of groundwater will also affect the sorption of some contaminant species. Because a large pH difference is typical between the tailings and the aquifer systems and because both systems are usually oxidizing, pH is the more important of these two parameters.

The surface charge of a sorbing phase in the aquifer matrix is one factor that can significantly affect its ability to sorb an ion. In general, the surface charge of a sorbing phase will be more positive at low pHs and more negative at high pHs. The surface charge will be neutral at a pH value where the negative surface charge distribution equals the positive surface charge distribution (zero point of charge). Positively charged surfaces will, in general, tend to attract negatively charged ions (anions). Negatively charged surfaces will tend to attract positive ions (cations).

An aqueous phase moving through an aquifer can significantly modify the surface charge of the sediments. Uncontaminated groundwater at most UMTRA sites has a pH that is typical of alkaline groundwater in equilibrium with calcium carbonate ($CaCO_3$) (e.g., 7.0 to 8.0). It is not surprising, therefore, that the aquifer matrix at many of these sites contains abundant calcite. These calcite-bearing background sediments should have a more negative charge than sediments that have been affected by acidic (pH 2.0 to 3.0) tailings pore water. The alkaline matrix material should have, therefore, a greater tendency to sorb cationic contaminants such as cadmium, lead, antimony, and silver. However, if the sediment has equilibrated with acidic groundwater (as in a subtailings pile environment) sediment mineral surfaces will be more positively charged. This will cause increased adsorption of elements such as molybdenum, arsenic, and uranium, which exist predominately as anionic species (negatively charged complexes).

2.0 RIFLE HYDROGEOLOGIC AND GEOCHEMICAL INFORMATION

2.1 HYDROGEOLOGY

The following site information is taken from the Rifle remedial action plan (RAP) (DOE, 1992). The Rifle (new) UMTRA site is situated on floodplain alluvium deposits within the Colorado River valley near the town of Rifle, Colorado. Uranium and vanadium milling activities have taken place on the new Rifle site since the late 1950s (Figure 2.1).

The seepage flux of tailings leachate into groundwater has been estimated at 3.8 gallons (gal) [14.4 liters (L)] per minute. Groundwater occurs in the alluvium at depths ranging from 5 to 10 feet (ft) [1.5 to 3.0 meters (m)] below land surface. The saturated thickness is 20 to 25 ft (6.1 to 7.6 m) based on the average thickness of the alluvium. During high river stage, the water table rises to within 2 to 3 ft (0.6 to 0.9 m) below the tailings pile. Groundwater flow in the alluvial aquifer underlying the Rifle site is to the west, which is roughly parallel to the Colorado River. Aquifer tests performed in 10 alluvial monitor wells demonstrate an average hydraulic conductivity of 70 ft/day (20 m/day). Groundwater velocity is estimated to be 280 ft/yr (85.3 m/year), using an effective porosity of 0.27, and an average hydraulic gradient of 0.003 (DOE, 1992).

2.2 PLUME DISTRIBUTION AND CHEMISTRY

The contaminant plume from the tailings at the Rifle site extends more than 8000 ft (2400 m) downgradient and covers more than 400 acres (ac) [160 hectares (ha)] in the alluvium. The plume is characterized by concentrations of arsenic, cadmium, chromium, molybdenum, nitrate, selenium, silver, uranium, and net gross alpha activity, that exceed proposed EPA maximum concentration limits (MCL). Although cadmium, chromium, nitrate, and selenium are contaminants of concern at the Rifle site, this study has focused on the sorptive behavior of arsenic, uranium, and molybdenum. This subset of the hazardous constituents are of concern to the UMTRA Groundwater Project in general because of their mobility in either acidic or alkaline groundwater. Uranium and molybdenum form large groundwater plumes at some UMTRA sites and arsenic is of toxicological concern at some UMTRA sites. Maximum concentrations of these three constituents exceed statistical maximum background concentrations and EPA MCLs in groundwater downgradient of the tailings. Maps showing the uranium and molybdenum concentration isopleths in groundwater are shown in Figures 2.2 and 2.3. Arsenic has not migrated downgradient far enough for isopleth maps to be created; however, it is present at sufficient concentrations in the tailings area to be of toxicological concern.

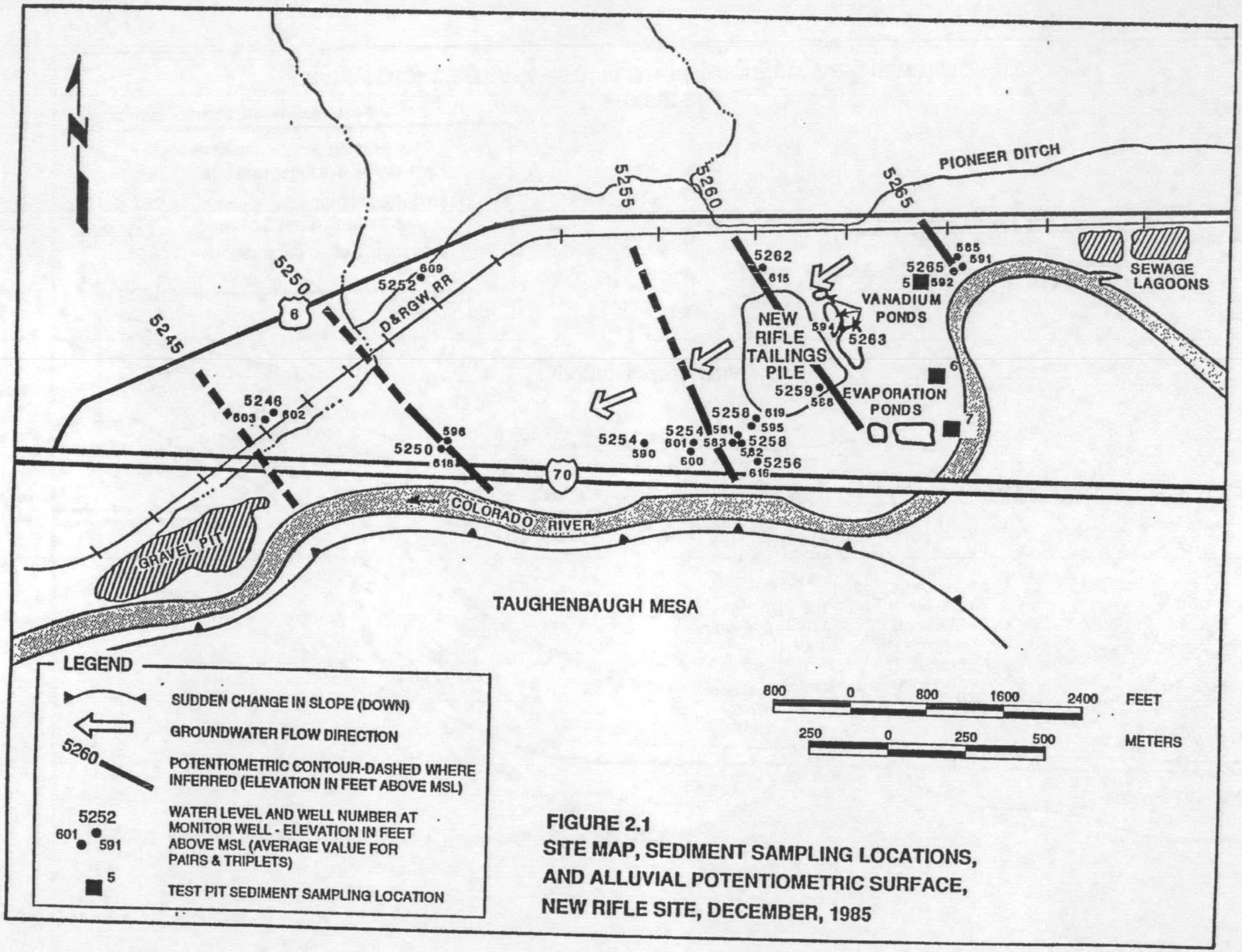
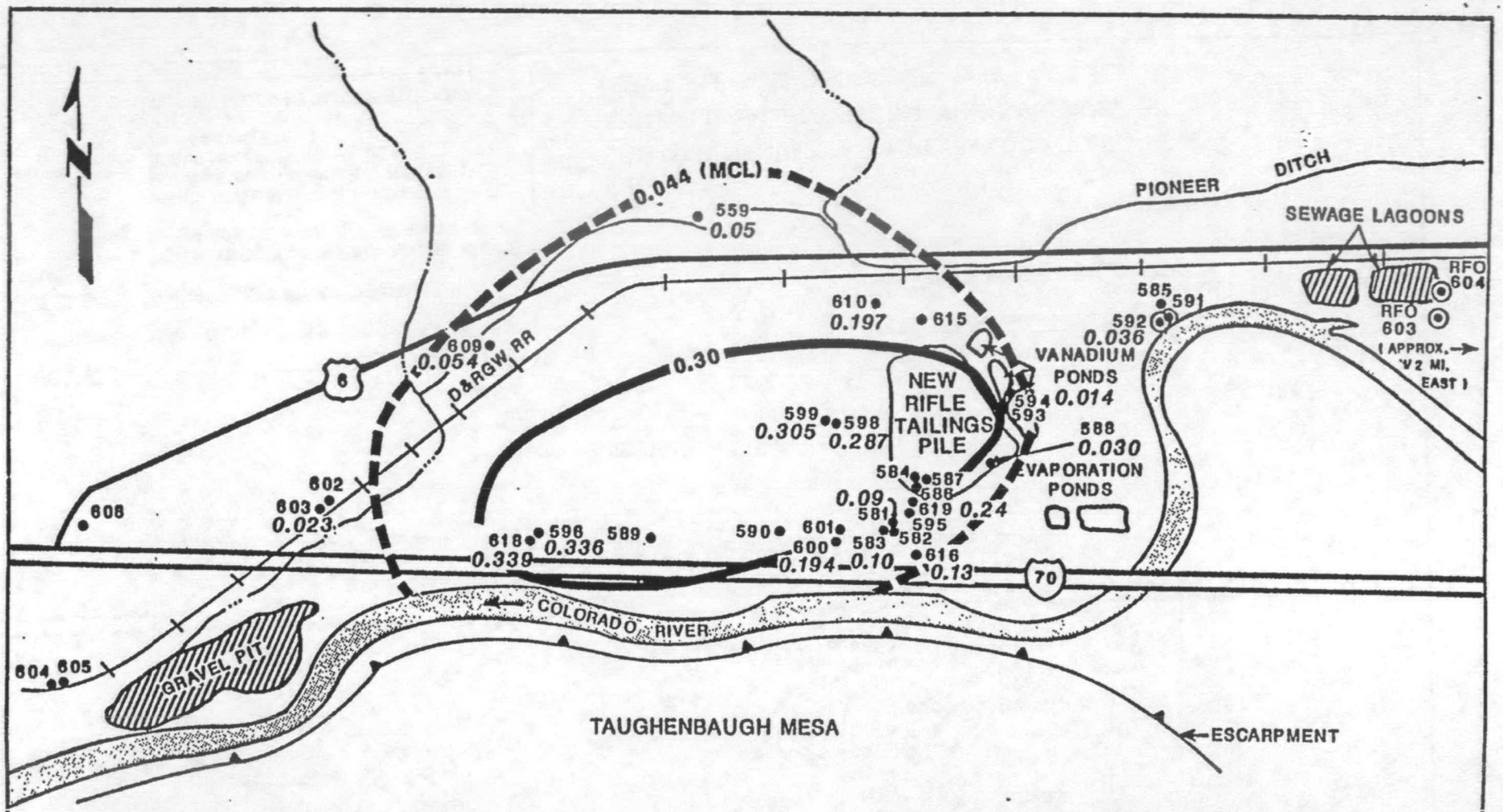
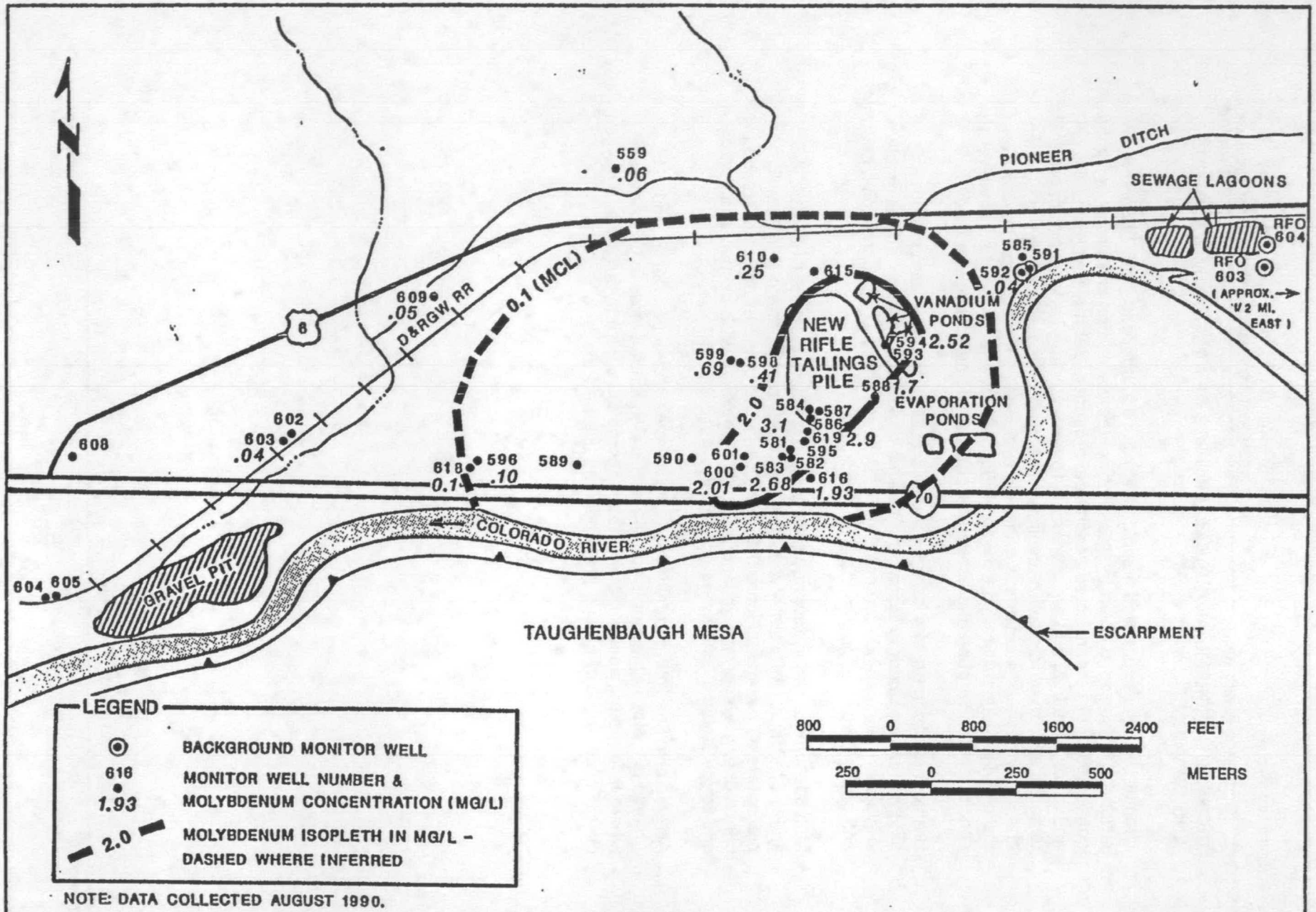


FIGURE 2.1
SITE MAP, SEDIMENT SAMPLING LOCATIONS, AND ALLUVIAL POTENTIOMETRIC SURFACE, NEW RIFLE SITE, DECEMBER, 1985



NOTE: DATA COLLECTED AUGUST 1990.

FIGURE 2.2
URANIUM CONCENTRATIONS IN ALLUVIAL GROUNDWATER, NEW RIFLE SITE



NOTE: DATA COLLECTED AUGUST 1990.

FIGURE 2.3
MOLYBDENUM CONCENTRATIONS IN ALLUVIAL GROUNDWATER, NEW RIFLE SITE

2.3 GENERAL GEOCHEMICAL CHARACTERISTICS OF ARSENIC, MOLYBDENUM, AND URANIUM

Uranium, molybdenum, and arsenic are toxic to animal and plant life and may enter the human food chain by intake of contaminated drinking water or by the consumption of contaminated agricultural products. All three elements are pH and redox sensitive, and are commonly found associated with uranium ore deposits and, therefore, with uranium mill tailings. Understanding the solution chemistry of these elements is critical in evaluating their sorption behavior on the alluvial sediments taken from the Rifle UMTRA site. A brief summary of the speciation and sorption characteristics of these elements is given below.

Uranium exists in the +4 or +6 valence states in natural aqueous environments. Under oxidizing and alkaline conditions, uranium forms stable anionic complexes with carbonate (CO_3^{2-}). Under more acidic conditions, neutral and cationic species predominate (Figure 2.4).

Molybdenum occurs in four naturally occurring valence states (+3, +4, +5, and +6). Under sufficiently reducing conditions molybdenum (Mo^{4+}) will precipitate as a sulfide (Figure 2.5). Under a wide range of aqueous Eh and pH conditions, however, molybdenum (Mo^{6+}) complexes with oxygen and hydrogen and forms stable anionic or neutral species (Figure 2.5).

Arsenic also has four naturally occurring valence states (-3, 0, +3, and +5). Arsenic is typically present in the +3 and +5 valence states in groundwater where it forms stable anionic and neutral complexes with hydrogen and oxygen over a wide range of Eh and pH conditions (Figure 2.6).

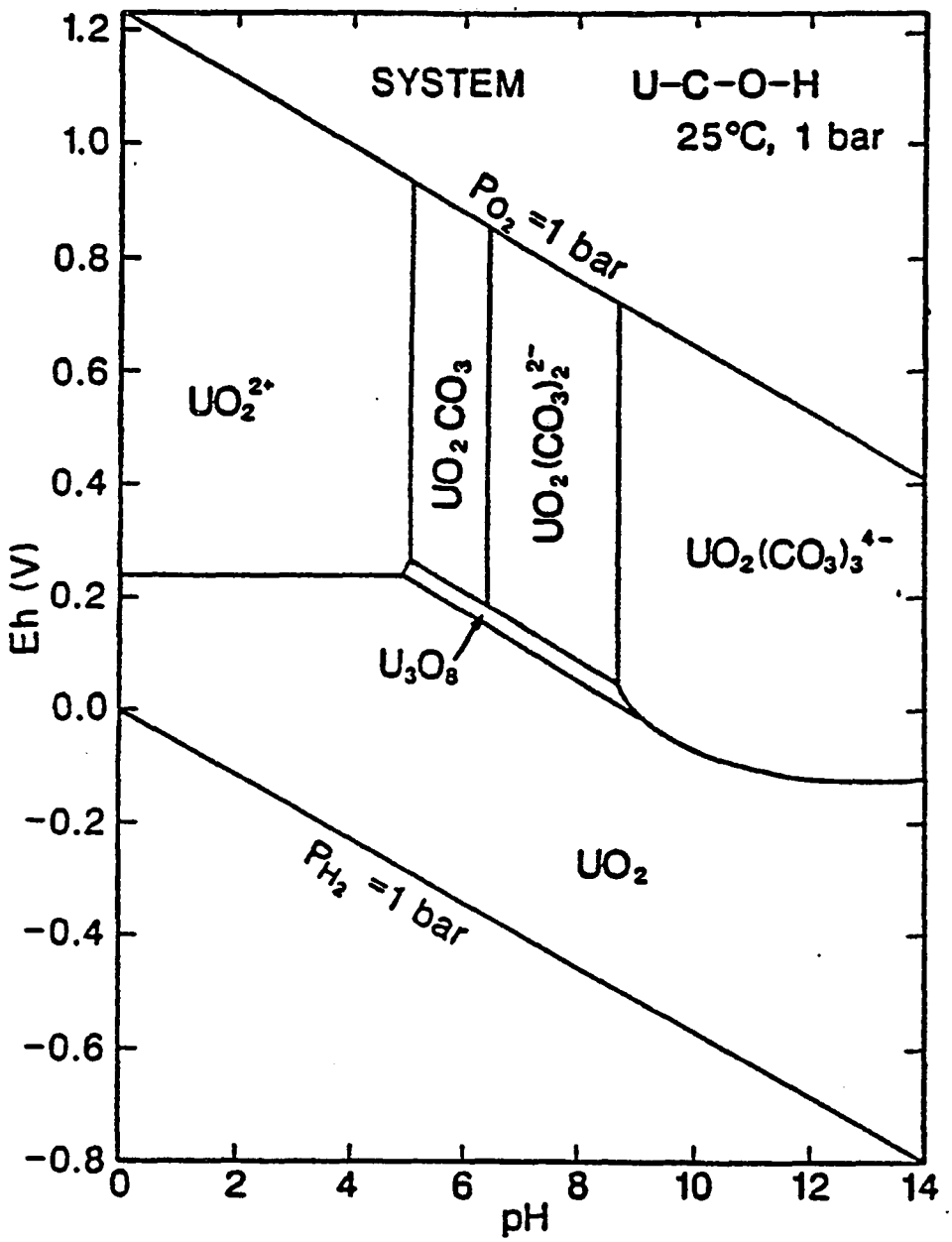


FIGURE 2.4
Eh-pH DIAGRAM FOR PART OF THE SYSTEM U-C-O-H

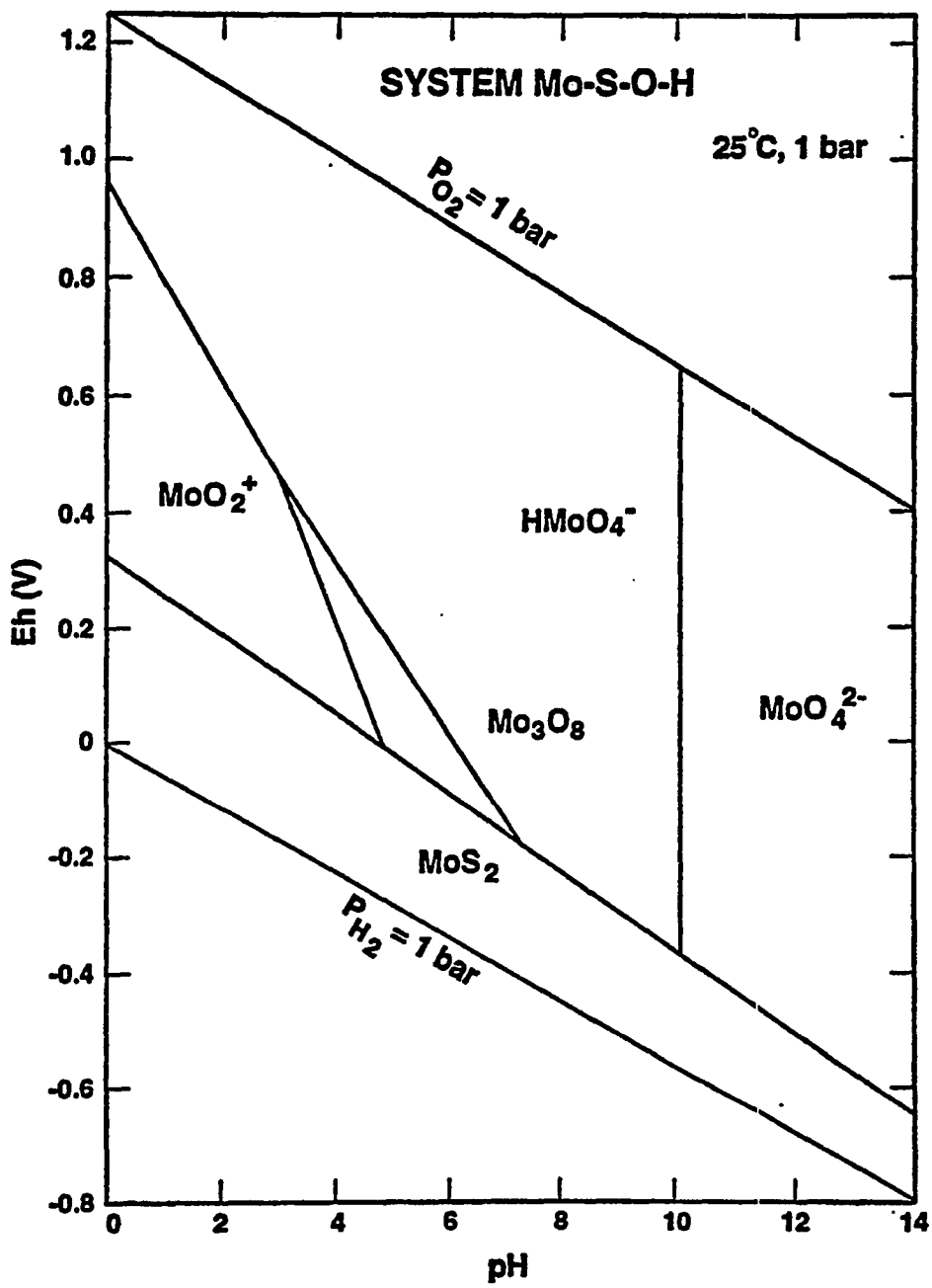


FIGURE 2.5
Eh-pH DIAGRAM FOR PART OF THE SYSTEM Mo-S-O-H

PATH: NON-SITE/ABS CHART

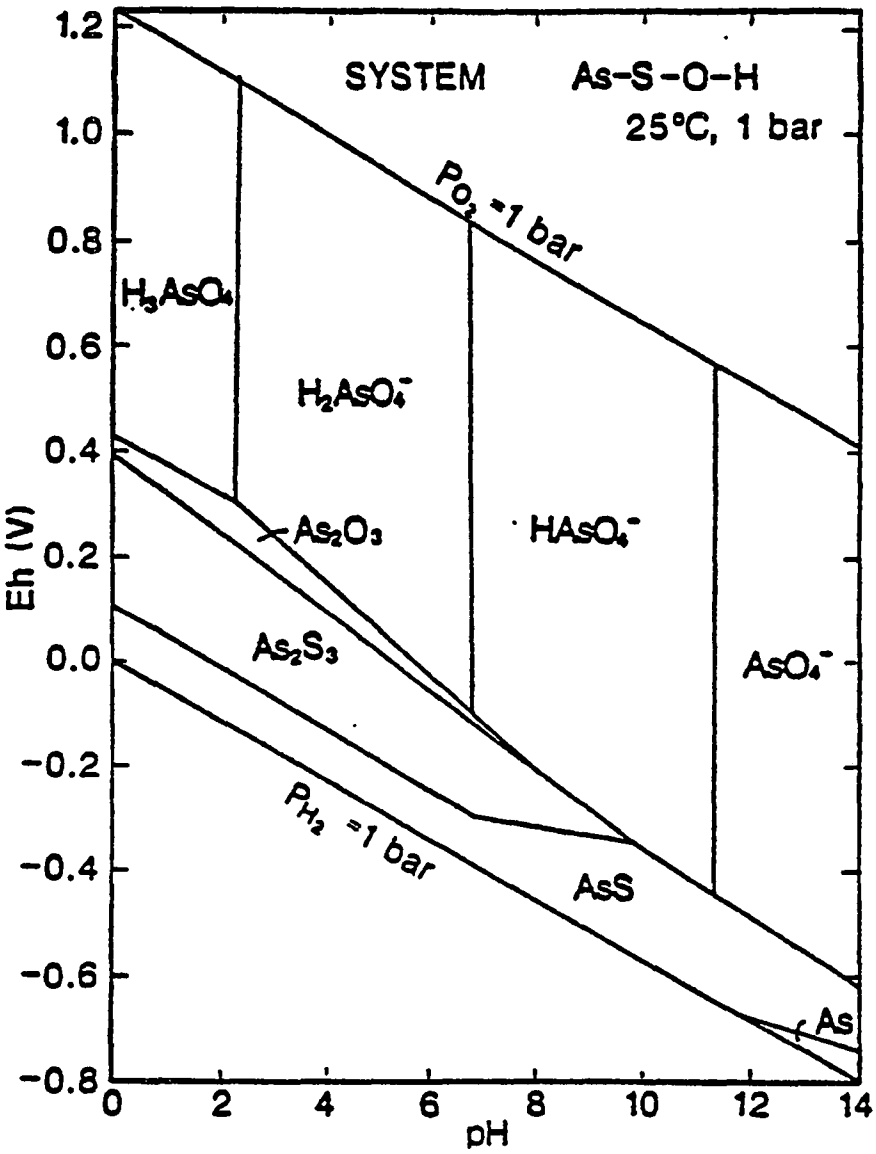


FIGURE 2.6
Eh-pH DIAGRAM FOR PART OF THE SYSTEM As-S-O-H

3.0 ADSORPTION ISOTHERM DETERMINATION: GENERAL PROCEDURES

3.1 INTRODUCTION

This section provides a brief description of the field work and laboratory work that was conducted for this special study. Included are summaries of aquifer matrix material (sediment) collection procedures, sediment characterization procedures, solution preparation techniques, and batch testing procedures. Appendixes A though F provide detailed information on the aquifer matrix characterization, laboratory procedures, and procedures and calculations used in the construction and analyses of adsorption isotherms.

3.2 AQUIFER MATRIX MATERIAL PREPARATION AND ANALYSIS

3.2.1 Sediment collection

At the Rifle site, seven test pits were excavated at locations upgradient of the known groundwater contamination. This was done to obtain sediment unaffected by tailings leachate but similar in mineral composition to sediment through which the contaminants are moving. During the excavation activities, a Morrison-Knudsen (MK) health physicist constantly surveyed the air and excavated material for radiation. A backhoe was used to excavate to a depth of 5 to 6 ft (1.5 to 1.8 m) and sediment samples were collected from three of the test pits (TP-5, TP-6, and TP-7) (Figure 2.1). The test pits chosen for sampling were in areas of undisturbed surface soils, where soils showed no response during the radiation survey by MK, and the excavation reached alluvial sediments. One or more of these criteria were not fulfilled for test pits TP-1, TP-2, TP-3, or TP-4. The test pits sampled did not reach the water table. Judging by the elevation of the river, the samples were collected from 2 to 4 ft (0.6 to 1.2 m) above the water table.

Below the top soil [approximately 1.5 ft (0.5 m) deep] no stratification was observed in the sediment profile. The sediments consisted of poorly sorted sandy to silty gravels and cobbles, which are brown to light brown. Approximately 400 pounds (lbs) (180 kg) of material was collected from each test pit.

3.2.2 Grain size distribution

All of the samples were delivered to Sergent, Hauskins, and Beckwith (SH&B) for grain size analysis and separation. The grain size analysis was determined by sieving and using a hydrometer. The grain size distribution of the Rifle sediments was similar for each test pit. Gravel content ranged from 56 to 68 percent. The sand fraction ranged from 26 to 33 percent. The silt content ranged from 4 to 8 percent, and the clay fraction ranged from 2 to 4 percent. More detailed grain size distribution information may be found in Appendix A.

SH&B also separated 400 lbs (180 kg) of each sample into distinct size fractions. The smallest fraction (-40 sieve size) consists of fine sand, silt, and clay. The next smallest fraction (+40/-10 sieve size) consists of medium, coarse, and very coarse sand sizes. These two size fractions were characterized with respect to geochemical and mineralogical composition and used in the batch adsorption tests.

The reasons for examination of the two finer fractions include 1) EPA batch testing methods stipulate a grain size of 10 mesh or finer, and 2) coarser fractions are much less likely to show significant sorption.

3.2.3 Lithologic analysis of the aquifer matrix material

Prior to UMTRA hydrology laboratory studies, the -40 mesh sieve fractions from Rifle test pits 5, 6, and 7 were characterized mineralogically using petrographic, x-ray diffraction (XRD), scanning electron microscope (SEM), and chemical methods. Optical petrography and SEM analysis were used to identify mineralogy, textures, and relationships between minerals. XRD was used to identify the clay present. Chemical methods were used to characterize carbonate content, soluble iron, and organic carbon content. The surface area per unit mass of the -40 sediment was also determined. These data were intended to characterize the -40 materials in terms of likely sorption properties. Although not used in sorption studies (except for trial runs), the +40/-10 mesh sieve fractions from the Rifle test pits were also mineralogically characterized.

Petrography

Thin section grain mounts of the -40 mesh and the +40/-10 mesh fractions from Rifle test pits 5, 6, and 7 were analyzed by quantitative petrographic methods at the University of New Mexico (UNM) Geology Department. Detailed petrographic information including 1) the percentage breakdown of minerals and rock fragments composition, 2) lithologic breakdown (percent) of all rock fragments, and 3) percentage breakdown of coated or uncoated grains may be found in Appendix B.

The -40 (medium sand and finer) and +40/-10 (finer and coarse sand) fractions from each test pit are largely the same in terms of percent and composition of mineral and rock fragments. The -40 mesh fraction can be described as a silty, arkosic, lithic very fine to medium grained sand. The +40/-10 mesh fraction is an arkosic, lithic, medium to very coarse grained sand. These sieve fractions were derived from non-indurated alluvial gravels, and are dominated by quartz and sedimentary rock fragments. The sedimentary rock fragments include clay/calcite-dolomite/iron oxide cemented siltstones, sandstones, limestones, and occasional argillaceous cherts. Other fragments include plagioclase and alkali feldspars, volcanic rocks, metamorphic rocks, granitic rocks, and more rarely, organic material, biotite, muscovite flakes, and resistant heavy minerals.

The quartz grains are largely monocrystalline or coarsely polycrystalline. Most of the feldspars are partially or completely replaced by smectite or illite clays. Coatings of clay, silt, and iron oxides found on coarser grains appear to be the same as the matrix materials found in the sedimentary rock fragments. This suggests that coated grains were formed recently within the sediment (perhaps by in situ weathering), or were the result of screening processes disrupting sedimentary rock fragments. In both size fractions approximately 15 to 30 percent of the grains are coated.

Scanning electron microscope observations

The SEM at UNM was used to make observations of the alluvial sediment grains from Rifle. Most of the grains observed were quartz with some potassium feldspar grains. Many grains were covered with surface coatings of clays. The clay overgrowths can occur as complete coverings or as small patches on the grains (Figure 3.1).

X-ray diffraction

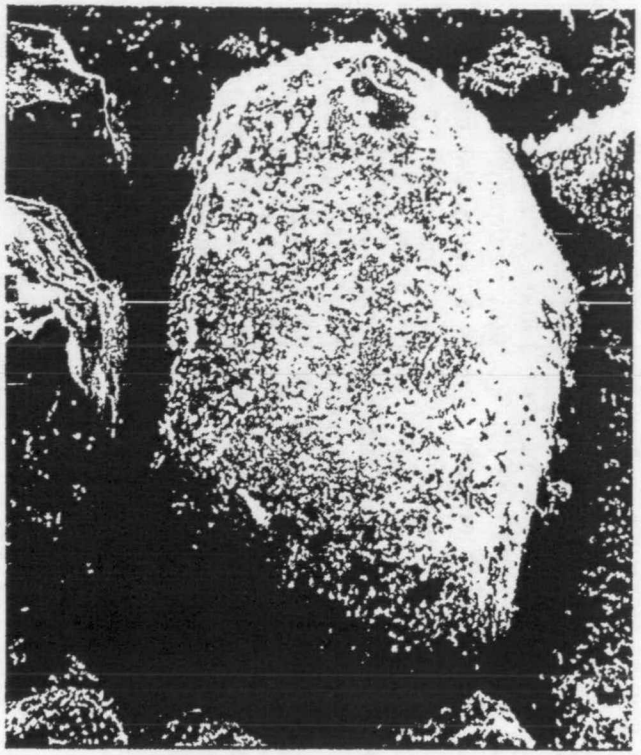
Whole rock XRD was performed by the University of Colorado on the -40 and -10/+40 mesh fractions from Rifle test pits 5, 6, and 7. XRD analyses of aquifer sediment sample bulk mineralogy indicate the presence of quartz, plagioclase feldspar, and minor amounts of carbonate in both Rifle and Shiprock samples. The Rifle samples also have trace amounts of phosphatic minerals. The clay mineralogy analyses indicate the presence of illite, kaolinite, and smectite in Rifle sediment samples.

For the -40 and +40/-10 mesh fractions from each test pit at Rifle, diffractograms were largely the same, suggesting the +40/-10 fractions consist, in part, of cemented aggregates of -40 mesh material. However, an x-ray peak at about 9.8 nanometers indicating a clay (possibly illite-muscovite), which is found on all of the diffractograms, is considerably stronger on diffractograms for the -40 mesh fraction, indicative of the enrichment of clays in this finer size fraction. More detailed information on the XRD data can be found in the diffraction subcontractor report (Appendix C).

Chemical analyses

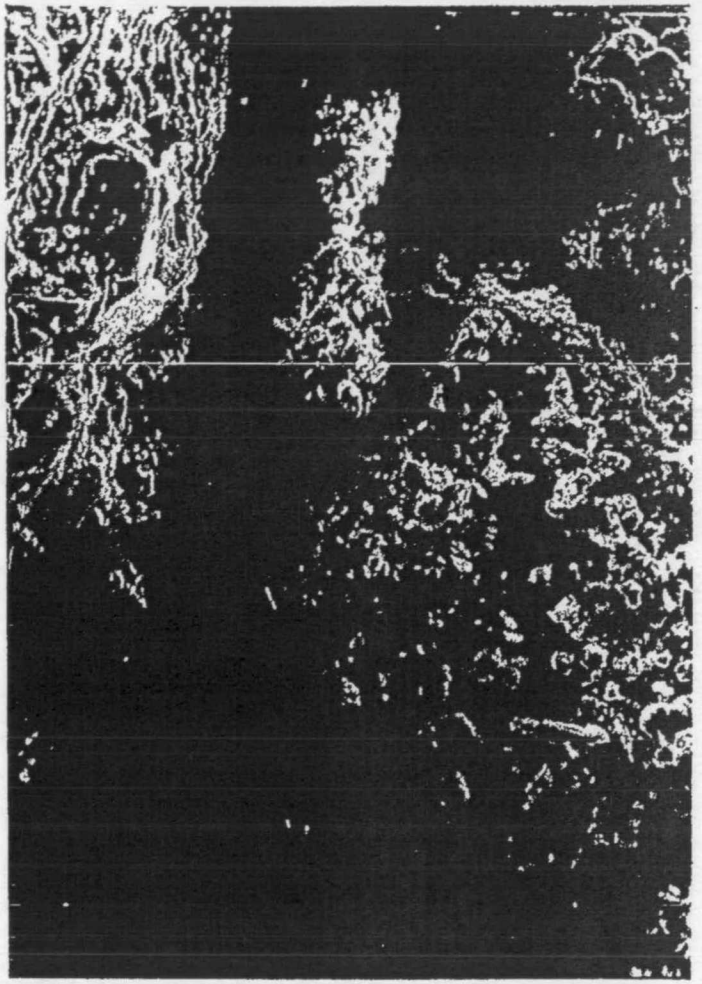
Untreated and acid-washed sediments (-40 mesh) from the Rifle test pits were chemically investigated at the TAC Hydrology Laboratory, and by Pittsburgh Mineral and Environmental Technology, Inc. Significant results are summarized below.

Estimated calcite content ranged from 12 to 15 percent for aquifer sediment and 8 percent for the sediment treated at pH 3. HCl-soluble iron ranged from 2.7 to 2.8 percent for both untreated and acidified sediment, indicating pH



SCALE: 50 MICROMETERS

a) QUARTZ GRAIN NEARLY COMPLETELY COVERED WITH CLAY COATING



SCALE: 50 MICROMETERS

b) SMALL PATCHES OF PARTICULATE CLAY ON SURFACE OF QUARTZ GRAIN

FIGURE 3.1
SCANNING ELECTRON PHOTOGRAPHS OF RIFLE AQUIFER MATRIX MATERIAL

reduction had minimal effect on iron coatings of the grains. Organic carbon content ranged from 0.33 percent to 0.62 percent for both untreated and acidified sediment, which also indicates acid washing had minimal effect on noncerbonate carbon content.

Surface area

Surface area determinations were completed by Dr. Douglas Smith at the UNM Center for Microengineered Ceramics using a gas adsorption technique and Brunauer, Emmett, and Teller analysis (Davis and Kent, 1990). Surface areas of the Rifle fine-grained fraction (-40) sediment samples ranged from approximately 3.3 to 3.7 m^2/g. The coarser fraction (+40/-10) samples showed greater variability in surface area ranging from 1.9 to 4.3 m^2/g. This is probably due to the fact that the coarser fraction contains agglomerations of clay-sized particles (high surface area) as well as individual mineral grains (lower surface area).

3.2.4 Preparation of sediment for adsorption isotherm experiments

Alkaline system

The aquifer matrix sediment required no preparation for adsorption experiments in an alkaline system representing background (upgradient) aquifer geochemistry.

Acidified system

One of the objectives of this study is to characterize adsorptive capacity of sediments under different geochemical regimes with an aquifer contaminated by uranium mill tailings leachate. As uranium mill tailings leachate from the tailings pile is acidic, pH was used as a gross indicator of geochemical conditions (Figure 3.2). Aquifer matrix sediment was treated with acidified water under pH 6 and pH 3 conditions to represent two geochemical environments. The pH 6-treated sediment may be representative of an aquifer material downgradient of an acidic tailings pile. The pH 3-treated sediment is more representative of an environment immediately beneath a tailings pile under saturated or variably saturated conditions (Figure 3.2).

Modification of the -40 mesh fraction obtained from Rifle test pit 5 was made by sulfuric acid leaching of carbonates. This was done to evaluate sorption reactions at the lower pH measurements encountered in the contaminated groundwater plume. Without acid treatment of the sediment, it was found that the high carbonate content of the sediment readily buffered the batch tests, resulting in significant pH increases. Procedures used in acidifying the aquifer sediment are described in Appendix D.

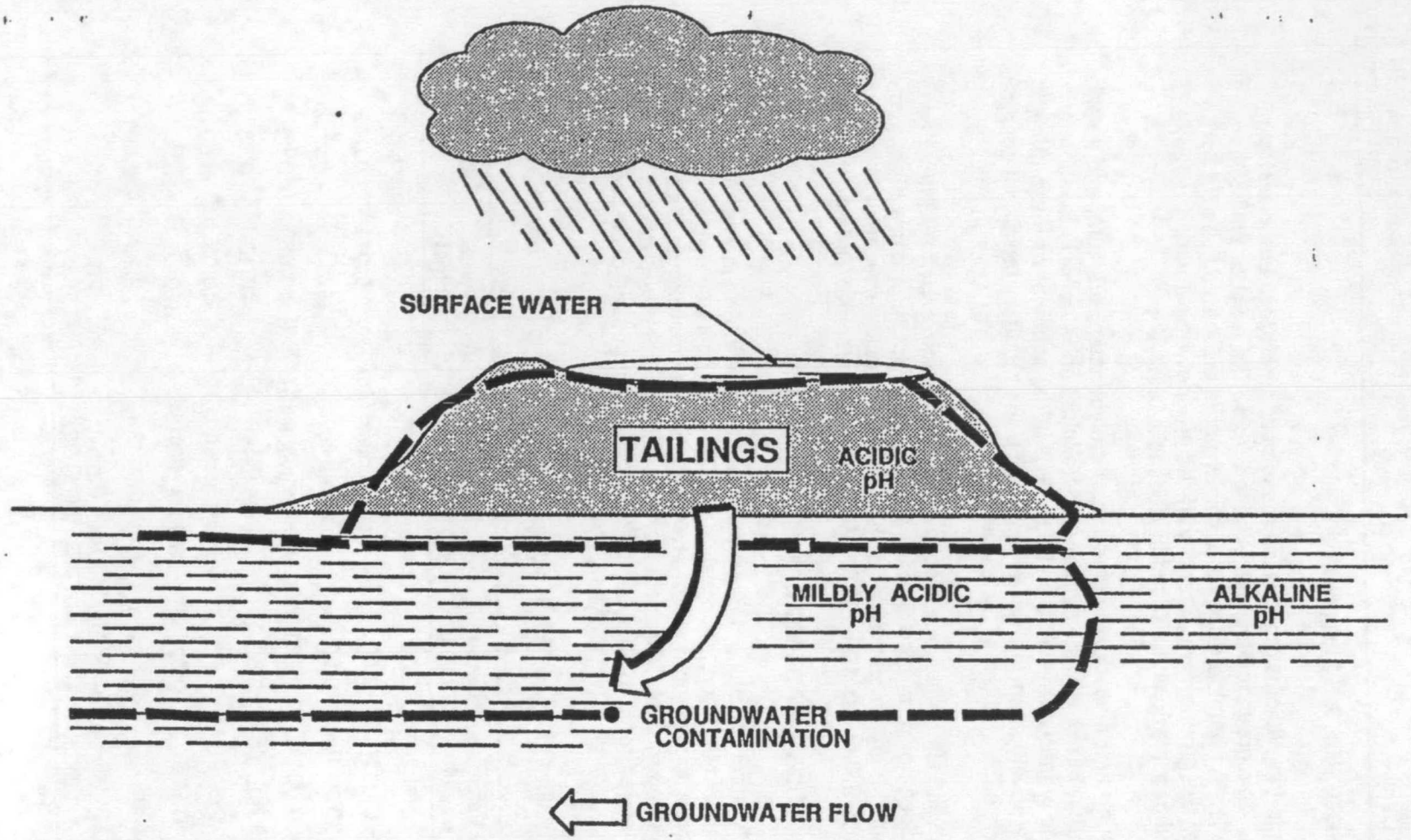


FIGURE 3.2
SCHEMATIC DIAGRAM OF pH-RELATED GEOCHEMICAL ENVIRONMENTS IN A TAILINGS LEACHATE-GROUNDWATER SYSTEM

3.3 STOCK SOLUTION PREPARATION

Background (upgradient) groundwater was used to prepare batch test stock solutions. This groundwater was obtained from Rifle monitor well 592 (Figure 2.1). A chemical analysis of this water is presented in Table 3.1. Storage of the groundwater, stability of the groundwater during storage, and associated observations are found in Appendix D.

Batch testing first investigated sorption of molybdenum, uranium, and arsenic (in that order) in the alkaline system, where initial and final pH measurements of batch tests were between 7.3 and 8.0. The initial behavior of these metals guided the development of further tests using the modified (acidified) solutions and materials.

To create valid isotherms, the groundwater from monitor well 592 must be stable (it does not form precipitates) when spiked with the metals of interest. Molybdenum, uranium, and arsenic showed no instability over the pH range of about 5.8 to 8.0 at the 10 mg/L level or less in unpreserved Rifle groundwater.

3.4 DETERMINATION OF ADSORPTION ISOTHERMS

The technique for obtaining data to construct an adsorption isotherm is relatively simple in theory. It consists of mixing an aqueous solution of known composition with a given mass of adsorbent (aquifer matrix material) for a specified period of time. Once the solution and adsorbent are mixed, the solution is separated and analyzed to determine changes in solute concentration.

Table 3.1 Water quality analyses from background monitor well 592 (stock solution)

Parameter	Value (mg/L)	Detection limit	Parameter	Value (mg/L)	Detection limit
Aluminum (Al)	0.122	0.05	Manganese (Mn)	0.696	0.002
Arsenic (As)	<0.001	0.001	Molybdenum (Mo)	0.011	0.005
Calcium (Ca)	130	0.02	Sodium (Na)	255	0.2
Cadmium (Cd)	<0.001	0.001	Ammonium (NH_4)	<0.06	0.06
Chlorine (Cl)	32.0	0.5	Nitrate (NO_3)	<0.13	0.13
Fluorine (F)	0.8	0.1	Phosphate (PO_4)	<0.03	0.03
Iron (Fe)	0.675	0.02	Sulfate (SO_4)	810	10
Potassium (K)	<2.0	2.0	Strontium (Sr)	2.23	0.001
Magnesium (Mg)	121	0.03	Total Organic Carbon (TOC)	7.1	1.0

The difference between initial and final concentrations is the amount that was adsorbed into the aquifer matrix material.

Two common methodologies determine sediment adsorption. One method is recommended by the EPA in the technical resource document *Batch-Type Procedures for Estimating Soil Adsorption of Chemicals* (EPA, 1991). The other method is recommended by the ASTM (ASTM, 1987). Both methods have been used in UMTRA Project studies in the past.

The chief difference between the two methods is in the number of points each requires to plot the function relating equilibrium concentration in water to mass adsorbed. The EPA method requires a series of points that are obtained by either varying the soil-to-solution ratio or varying the initial concentration of the contaminants in solution. The resultant data array may be linear or nonlinear. The ASTM method requires only one soil-to-solution ratio and only one initial concentration. Because this method results in only one point on the equilibrium concentration versus adsorption graph, the relationship can only be linear (the line is assumed to pass through the origin).

Batch testing using the EPA or ASTM method was conducted using the following general combinations of materials:

- Untreated aquifer sediment reacted with metal-spiked Rifle background water. This is the alkaline system, where final pH values were between 7.3 and 8.0. Equilibrium between the Rifle sediments and the raw background waters existed for most of the ratios used.

- Aquifer sediment reacted with metal-spiked, acidified Rifle background water. Equilibrium between the solid and solution did not exist initially as verified by large pH drifts observed during batch testing.

- Acid-treated solids reacted with acidified Rifle background waters; the solution pH was modified so that an approximate chemical equilibrium existed for the duration of the test.

3.4.1 EPA-recommended procedures

The EPA method of batch testing (EPA, 1991; Appendix D) used to investigate sorption of metals in solution into aquifer sediments requires the generation of an isotherm, consisting of several individual batch tests. The batch test results provide data points for the isotherm. The following two types of isotherms can be devised:

- Variable soil:solution ratio isotherms—The concentration of the contaminant is initially the same for the different ratios. Sorption is then a function of the soil:solution volume ratio. If the soil reacts with the solution during the

course of the experiment (implying disequilibrium), the chemistry of the soil and solution will vary for each ratio, complicating the sorption analysis.

- Constant soil:solution ratios—The concentration of the contaminant in groundwater is varied, usually geometrically downward, to a level usually near the detection limit of the metal. Because of the constant volume ratios, soil and solution chemistry are constrained to be the same for different batches, even if a reaction occurs.

Equilibration time determination

EPA-recommended procedures suggest 24 hours for initial sorption determinations. Procedures for the determination of equilibration time were also suggested by the EPA (1991). To evaluate equilibration time, individual uranium and molybdenum batch tests (points on an EPA isotherm) were on a rotary agitator for 36, 48, and 72 hours and compared to results obtained for a 24-hour rotation. The data are presented in Appendix D.

Results for the uranium equilibration time experiment indicate that 8 to 16 percent more adsorption occurred after 24 hours. However, there was no trend of increased adsorption with time as the 48-hour batch displayed more adsorption than either the 36-hour or 72-hour batches. The equilibration time experiment for uranium demonstrates that the 24-hour on a rotary agitator time is a conservative case.

Results for the molybdenum equilibration time experiment indicate that 1 percent more to 7 percent less adsorption occurred after 24 hours. This may indicate final molybdenum concentrations for each batch were within the range of analytical error. Alternatively, this may indicate that a solid phase that provides sorption sites for molybdenum dissolves with time which, in turn, decreases molybdenum sorption with time. However, given only a 7 percent difference between 24-hour and 72-hour equilibration times, 24-hour batches were used for time efficiency.

Detailed laboratory procedures and quality-control procedures followed in this special study are presented in Appendix D. The EPA technical resource document (EPA, 1991) describing this approach was followed as closely as possible.

3.4.2 ASTM procedures

The ASTM batch testing procedure (ASTM, 1987) uses a single soil:solution volume ratio to calculate a distribution coefficient (K_d). In the special study, the "modified ASTM method" of batch testing was used (JEG, n.d.), which is similar to the method used in previous UMTRA geochemical studies. The

modifications deal with soil and solution separation technique, and soil mass used. Details of the procedure are provided in Appendix D.

3.4.3 Relative costs of the procedures

In terms of relative cost estimates for the EPA and ASTM procedures, the major difference is the number of analyses required. It is assumed that costs of aquifer matrix characterization and solution preparation time would be approximately equivalent for the two procedures. Therefore, it can be estimated that the EPA method would cost approximately seven times more than the ASTM method because approximately seven additional batch tests are required for the EPA method. Absolute costs would be site specific, depending on constituents of interest, number of sediment samples collected, and number of variations of batch test conditions.

4.0 RESULTS OF ADSORPTION ISOTHERM EXPERIMENTS

This section describes the calculation of adsorption parameters from the isotherm graphs and presents observations of adsorption differences with respect to methodologies, pH conditions, and sediments.

4.1 ADSORPTION PARAMETER DETERMINATION

Once the isotherms have been plotted, a distribution coefficient (K_d) can be determined in the case of a linear relation, which is simply the slope of the line. The distribution coefficient is then used, along with aquifer bulk density and porosity, to estimate a retardation factor (R_d). The retardation factor is used, in turn, to obtain the velocity of the contaminant in groundwater by dividing it into the advective groundwater velocity determined from field-measured hydrogeologic parameters. The hydrogeologic parameters used in calculations for this study were obtained from the Rifle RAP (DOE, 1992).

In the case of a nonlinear adsorption isotherm, a linear regression technique must be used to obtain a generalized equation describing the observed curve. The equation describes the change in adsorption with respect to the contaminant concentration in solution. The change in adsorption with concentration also results in a change of retardation factor with concentration which, in turn, results in a change in contaminant migration velocity in the groundwater with respect to concentration.

Two commonly known isotherm regression equations are used to generalize adsorption data. These are referred to as the Freundlich and Langmuir equations. These two equations have many derivatives that researchers have used to match with observed adsorption data (for example, double reciprocal Langmuir equation).

An equation that has been widely used for solid-liquid systems is the following Freundlich equation:

$$x/m = K_f C^{1/n}$$

where x is the amount of the hazardous constituent metal adsorbed, m is the mass of adsorbent, C is the equilibrium concentration of the solute, and K_f and 1/n are constants. These constants are determined statistically when the expression is in the following logarithmic form:

$$\log(x/m) = \log K_f + 1/n \log C.$$

By taking the logarithms of both sides of the equation, the constants K_f and 1/n are solved as a linear regression. In this study, the linear regression procedures presented in the EPA technical resource document (EPA, 1991) were followed.

The Langmuir equation has also been widely used to describe adsorption data for solid-liquid systems. The most commonly used Langmuir expression is generalized as follows:

$$x/m = \frac{K_L M C}{1 + K_L C}$$

where K_L and M are the Langmuir constants, all other variables have been defined previously. Some investigators have argued that the Langmuir constant K_L is related to the bonding energy between the adsorbed ion and the adsorbent. The constant M is generally accepted as the maximum amount or concentration that an adsorbent can retain (EPA, 1991). These procedures with example calculations are found in Appendix E. All calculations for this study are found in Appendix F.

4.2 DESCRIPTION OF ISOTHERM EXPERIMENTAL CONDITIONS

Variable and/or constant soil:solution isotherms were constructed using the results of batch tests of Rifle background sediment and Rifle alkaline background water that had been spiked with uranium, arsenic, and molybdenum. ASTM batch tests were also conducted on these elements under these conditions.

To evaluate the sorption behavior of molybdenum, arsenic, and uranium in an aquifer that had been affected by an acidic plume from a tailings pile, the carbonate-rich sediment from Rifle test pit 5 was acidified with dilute sulfuric acid (Appendix D). Two batches of acidified sediment were prepared. One batch was strongly acidified to simulate the impact of tailings pore water on the alkaline sediment immediately beneath the Rifle tailings. A second batch was acidified to a much lesser extent to simulate the less pervasive effects of low pH groundwater on sediments downgradient of the tailings pile.

Separate aliquots of Rifle background water were acidified to a pH of 5.8 and 2.8 with sulfuric acid and spiked with uranium, arsenic, and molybdenum. The pH 5.8 background groundwater was then equilibrated with the mildly acidified sediment batch and the pH 2.8 background groundwater was equilibrated with the strongly acidified sediment batch. The final equilibrium pH of the individual batch tests depended upon the soil:solution volume ratio of the batch tests and whether the slightly or strongly acidified sediment was used.

4.3 SORPTION BEHAVIOR OF URANIUM

4.3.1 Introduction

A series of batch tests with variable soil:solution volume ratios (i.e., 1:1, 1:2, 1:3, 1:4, 1:6, 1:8, and 1:10) were conducted using Rifle background water

spiked with 10 mg/L uranium and background sediment from test pits 5, 6, and 7. Duplicate, triplicate, and quadruplicate variable-ratio batch tests were conducted on uranium in the alkaline system using sediment from test pits 6 and 7 (Table 4.1). A single series of variable ratio batch tests was performed on sediment from test pit 5 (Table 4.1). Uranium adsorption in the variable ratio batch tests from all three test pits was insufficient to generate a full six-point isotherm. The minimum soil:solution ratio that generated sufficient sorption of uranium in the alkaline system that could be reproducibly measured was 1:4 (Table 4.1). Nevertheless, those variable ratio batch tests (1:1, 1:2, 1:3, and 1:4) that demonstrated sufficient sorption to be precisely measured were used to construct four-point isotherms for test pits 5, 6 and 7 (Figure 4.1). The mean of these replicate analyses was used to construct the isotherm plots for test pits 6 and 7.

4.3.2 Discussion

Alkaline groundwater, variable ratio isotherms

As discussed above, insufficient adsorption allowed definition of a true uranium isotherm (minimum of 6 points required) for background sediment from any of the test pits. Nevertheless, if the origin of the graph is considered part of the data set, the sorption data from the three test pits define three distinct lines (Figure 4.1). The variable slopes of these lines (Figure 4.1) demonstrate systematic differences in the uranium sorption characteristics between the sediment from test pits 5, 6, and 7.

Alkaline groundwater, constant ratio isotherms

Constant soil:solution ratio (1:2) batch tests were performed on sediments from test pits 5 and 6 using Rifle background water that had been spiked with variable concentrations of uranium (Table 4.2). Only four samples from test pit 6 and three samples from test pit 5 demonstrated measurable sorption (Table 4.2). The test pit 6 data define an isotherm that is nearly coincident with the variable ratio isotherm from test pit 7 (Figures 4.1 and 4.2). The test pit 5 data define an isotherm that is nearly coincident with the variable ratio isotherm from test pit 5 (Figures 4.1 and 4.2).

ASTM batch tests were also performed on sediment from each of the three test pits using 10 mg/L uranium-spiked background water. The results of these tests are shown in Table 4.3 and plotted in Figure 4.1. A comparison of the slopes (K_ds) of the lines defined by the ASTM batch tests and the lines defined by the variable ratio batch tests indicates that less uranium adsorption occurred during the ASTM batch tests.

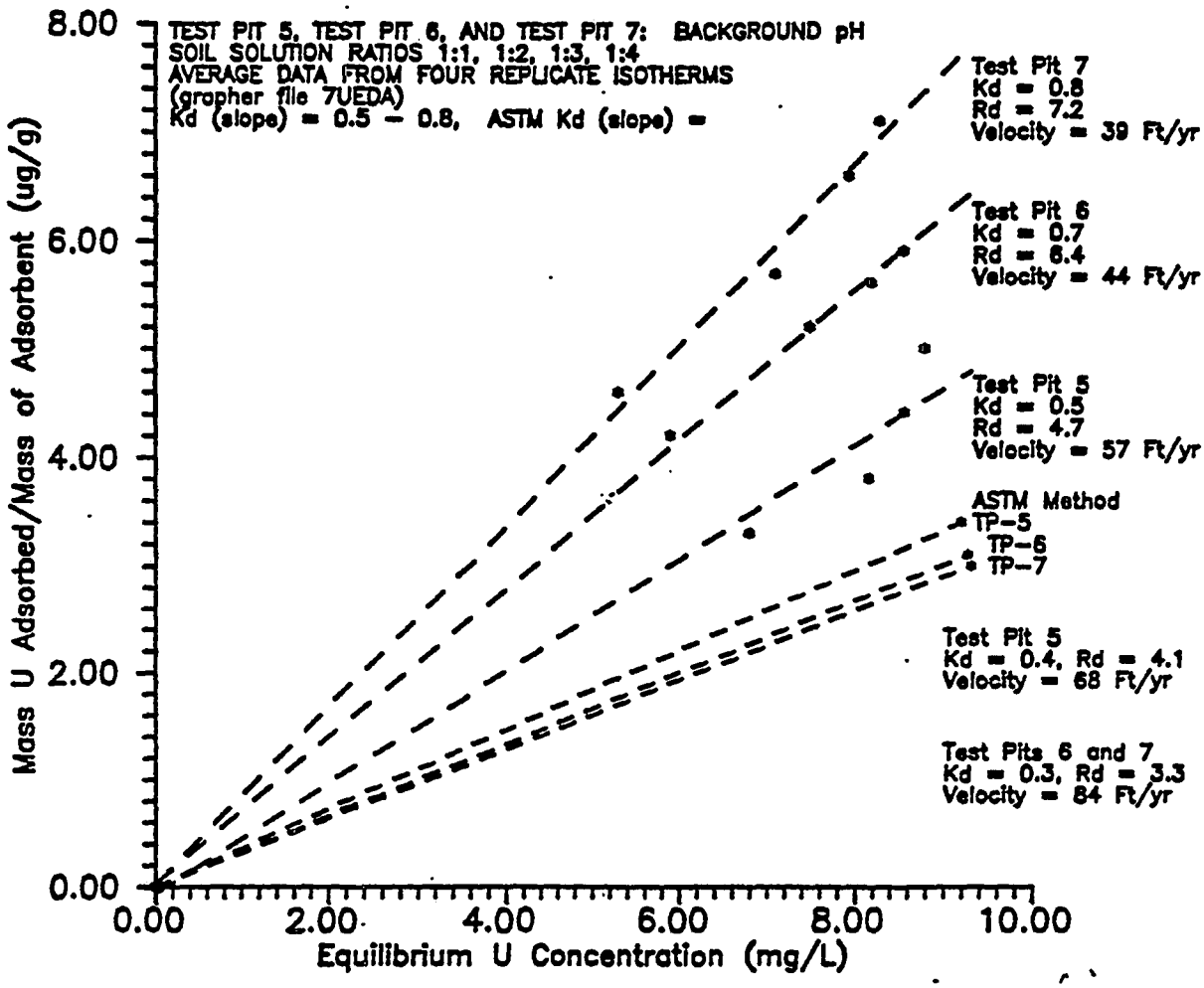


FIGURE 4.1
URANIUM VARIABLE RATIO ISOTHERMS, BACKGROUND pH

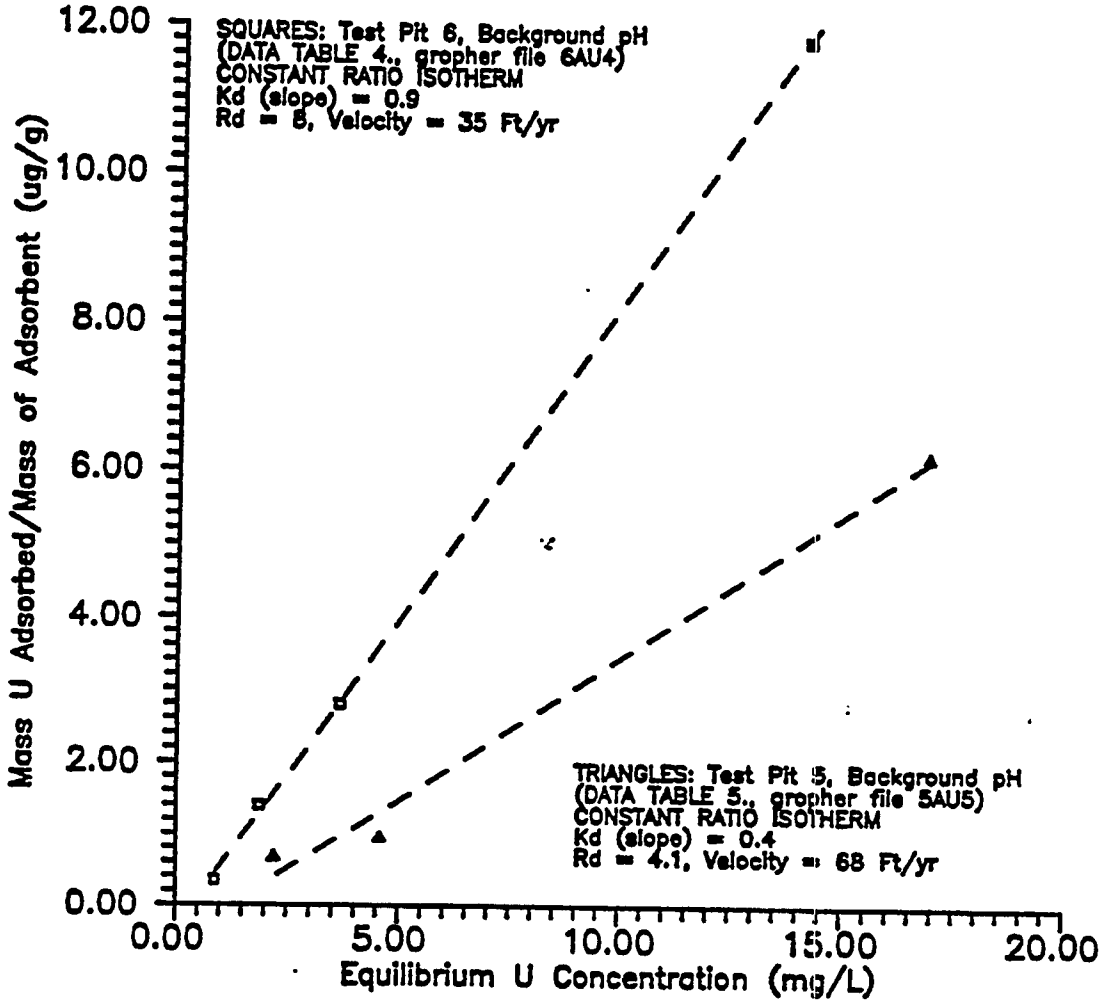


FIGURE 4.2
URANIUM CONSTANT RATIO ISOTHERMS, BACKGROUND pH

Table 4.1 Uranium variable ratio isotherm data, alkaline pH, test pits 5, 6, and 7

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (μg/g)
Adsorbent material: TP-5 (-40)					
1:1	10.0	6.79	170.00	170.00	3.3
1:2	10.0	8.17[a]	100.00	200.00	3.8
1:3	10.0	8.57	70.00	210.00	4.4
1:4	10.0	8.80[a]	62.50	250.00	5.0
1:6	10.0	9.28	40.00	240.00	4.6[b]
1:8	10.0	9.48	32.00	256.00	4.6[b]
1:10	10.0	9.49[a]	25.00	250.00	5.6[b]
Adsorbent material: TP-6 (-40)					
1:1	10.0	5.69	170.00	170.00	4.4
1:2	10.0	7.12[a]	100.00	200.00	5.9
1:3	10.0	7.90	70.00	210.00	6.5
1:4	10.0	8.15[a]	62.50	250.00	7.6
1:6	10.0	8.59	40.00	240.00	8.8
1:8	10.0	9.94	32.00	256.00	–[b]
1:10	10.0	9.41[a]	25.00	250.00	6.4[b]
Adsorbent material: TP-6 (-40) Duplicate					
1:1	10.0	5.60	170.00	170.00	4.5
1:2	10.0	7.20	100.00	200.00	5.7
1:3	10.0	7.69	70.00	210.00	7.1
1:4	10.0	8.67	62.50	250.00	5.5
1:6	10.0	8.18	40.00	240.00	11.2
1:8	10.0	8.69	32.00	256.00	10.9
1:10	10.0	8.32	25.00	250.00	17.3

Adsorbent weight and solution volume precision equals ± 0.04

Table 4.1 Uranium variable ratio isotherm data, alkaline pH, test pits 5, 6, and 7 (Continued)

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (μg/g)
Adsorbent material: TP-6 (-40) Triplicate					
1:1	10.0	6.1	170.00	170.00	4.0
1:2	10.0	7.8	100.00	200.00	4.5
1:3	10.0	8.4	70.00	210.00	5.0
1:4	10.0	8.9	62.50	250.00	4.6
1:6	10.0	9.5	40.00	240.00	3.3[b]
1:8	10.0	10.1	32.00	256.00	0[b]
1:10	10.0	10.2	25.00	250.00	0[b]
Adsorbent weight and solution volume precision equals ± 0.04					
Adsorbent material: TP-6 (-40) Quadruplicate					
1:1	10.0	6.1	170.00	170.00	4.0
1:2	10.0	7.8	100.00	200.00	4.5
1:3	10.0	8.8	70.00	210.00	3.8
1:4	10.0	9.6	62.50	250.00	1.8[b]
1:6	10.0	9.5	40.00	240.00	3.3[b]
1:8	10.0	9.7	32.00	256.00	2.8[b]
1:10	10.0	9.7	25.00	250.00	3.5[b]

Adsorbent weight and solution volume precision equals ± 0.04 g or mL
[a]Different analysis batch.
[b]Less than 10% adsorbence.
μg = micrograms.

Table 4.1 Uranium variable ratio isotherm data, alkaline pH, test pits 5, 6, and 7 (Continued)

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (μg/g)
Adsorbent material: TP-7 (-40)					
1:1	10.0	5.49	170.00	170.00	4.6
1:2	10.0	7.19[a]	100.00	200.00	5.7
1:3	10.0	7.96	70.00	210.00	6.3
1:4	10.0	7.95[a]	62.50	250.00	8.4
1:6	10.0	9.63	40.00	240.00	2.5[b]
1:8	10.0	9.70	32.00	256.00	2.8[b]
1:10	10.0	9.28[a]	25.00	250.00	7.7[b]
Adsorbent material: TP-7 (-40) Duplicate					
1:1	10.0	4.78	170.00	170.00	5.3
1:2	10.0	6.67	100.00	200.00	6.8
1:3	10.0	7.97	70.00	210.00	6.2
1:4	10.0	8.13	62.50	250.00	7.7
1:6	10.0	9.64	40.00	240.00	8.5
1:8	10.0	8.70	32.00	256.00	10.8
1:10	10.0	9.58	25.00.00	250.00	4.7[b]
Adsorbent material: TP-7 (-40) Triplicate					
1:1	10.0	5.5	170.00	170.00	4.6
1:2	10.0	7.2	100.00	200.00	5.7
1:3	10.0	7.9	70.00	210.00	6.5
1:4	10.0	8.8	62.50	250.00	5.0
1:6	10.0	10.5	40.00	240.00	0[b]
1:8	10.0	9.6	32.00	256.00	3.6[b]
1:10	10.0	9.4	25.00	250.00	6.5[b]

Adsorbent weight and solution volume precision equals ± 0.04 g or mL
[a]Different analysis batch.
[b]Less than 10% adsorbence.
μg = micrograms.

Table 4.1 Uranium variable ratio isotherm data, alkaline pH, test pits 5, 6, and 7 (Concluded)

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (μg/g)
Adsorbent material: TP-7 (-40) Quadruplicate					
1:1	10.0	5.5	170.00	170.00	4.6
1:2	10.0	7.3	100.00	200.00	5.5
1:4	10.0	8.2	62.50	250.00	7.4
1:6	10.0	9.1	40.00	240.00	5.7[b]
1:8	10.0	9.7	32.00	256.00	2.8[b]
1:10	10.0	9.7	25.00	250.00	3.5[b]

Adsorbent weight and solution volume precision equals ± 0.04 g or mL
[a]Different analysis batch.
[b]Less than 10% adsorbence.
μg = micrograms.

Table 4.2 Uranium constant ratio isotherm data, alkaline pH, test pits 5 and 6

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (μg/g)
Adsorbent material: TP-5 (-40)					
1:2	20.05	16.93	100.00	200.00	6.2
1:2	5.05	4.57	100.00	200.00	0.96
1:2	2.55	2.21	100.00	200.00	0.68
1:2	1.05	1.12	100.00	200.00	–
1:2	0.55	0.572	100.00	200.00	–
1:2	0.15	0.295	100.00	200.00	–
Adsorbent material: TP-6 (-40)					
1:2	20.05	14.17	100.00	200.00	11.8
1:2	5.05	3.65	100.00	200.00	2.8
1:2	2.55	1.87	100.00	200.00	1.4
1:2	1.05	0.882	100.00	200.00	3.4
1:2	0.55	0.580	100.00	200.00	–
1:2	0.15	0.228	100.00	200.00	–

Adsorbent weight and solution volume precision equals ± 0.04 g or mL

Table 4.3 Uranium adsorption data, ASTM method

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (μg/g)
Adsorbent material: various (A = -40, B = +40/-10)					
1:4	9.32	9.21	TP5A 62.50	250.00	3.4[a]
1:4	9.32	9.90	TP5B 62.50	250.00	6.0[a]
1:4	9.32	9.31	TP6A 62.50	250.00	3.0[a]
1:4	9.32	10.18	TP6B 62.50	250.00	—
1:4	9.32	9.28	TP7A 62.50	250.00	3.1[a]
1:4	9.32	9.88	TP7B 62.50	250.00	6.8[a]
Adsorbent material: TP5 (-40) Sediment treated at pH 6, acidified sediment, ASTM method					
1:4	10.00	2.90	25.00	250.00	28.6

Adsorbent weight and solution volume precision equals ± 0.04 g or mL
[a]Less than 10% adsorbence.

Acidified sediment and groundwater

A constant ratio (1:10) isotherm (Figure 4.3) was constructed for the strongly acidified system using initial solution uranium concentrations that ranged from 1.05 to 10.05 mg/L (Table 4.4). A variable ratio (1:1 to 1:10) isotherm (Table 4.4) was constructed for the mildly acidified system (Figure 4.3). These isotherms clearly demonstrate that uranium is progressively more strongly adsorbed on the progressively more acidified systems. One point of the variable ratio isotherm was generated by the same initial concentration of uranium in solution and the same 1:10 soil-to-solution ratio that was used to construct one point of the constant ratio isotherm.

4.4 SORPTION BEHAVIOR OF ARSENIC

4.4.1 Introduction

Variable soil:solution batch tests were performed on Rifle background water (spiked with 2.0 mg/L arsenic) and sediment from test pit 5 in three different pH environments. Freundlich or Langmuir best-fit regression equations were determined for the arsenic adsorption curves in each pH environment. ASTM batch tests were performed on sediment in the more acidified pH environment.

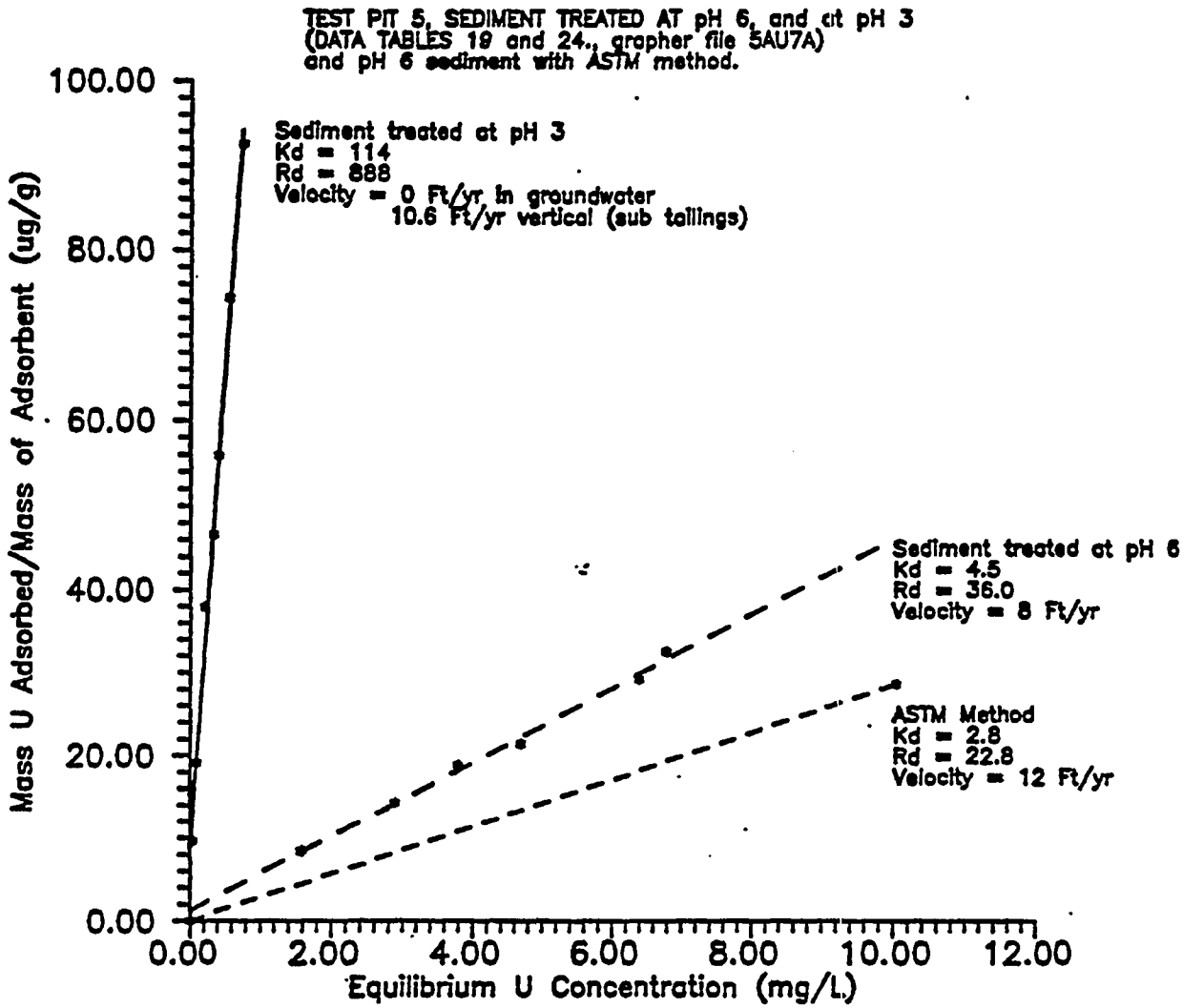


FIGURE 4.3
URANIUM ISOTHERMS, ACIDIFIED CONDITIONS

Table 4.4 Uranium adsorption data, acidified conditions, test pit 5

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (µg/g)
Adsorbent material: TP-5 (-40) Sediment treated at pH 3, acidified sediment (AW-II)					
1:10	10.05	0.75	25.00	250.00	92.5
1:10	8.05	0.56	25.00	250.00	74.4
1:10	6.05	0.41	25.00	250.00	55.9
1:10	5.05	0.34	25.00	250.00	46.6
1:10	4.05	0.21	25.00	250.00	37.9
1:10	2.05	0.09	25.00	250.00	19.1
1:10	1.05	0.04	25.00	250.00	9.6
1:10[a]	5.05	0.33	25.00	250.00	46.7
1:10[b]	5.05	0.23	25.00	250.00	47.7
Adsorbent material: TP-5 (-40) Sediment treated at pH 6, acidified sediment (AW-I)					
1:1	10.05	1.60	170.00	170.00	8.4
1:2	10.05	2.90	100.00	200.00	14.3
1:3	10.05	3.80	70.00	210.00	18.8
1:4	10.05	4.70	62.50	250.00	21.4
1:6	10.05	3.10	40.00	240.00	41.7
1:8	10.05	6.40	32.00	256.00	29.2
1:10	10.05	6.80	25.00	250.00	32.5

Adsorbent weight and solution volume precision equals ± 0.04 g or mL
[a]Duplicate batch.
[b]Triplicate batch.

4.4.2 Discussion

Variable soil:solution batch tests were performed on Rifle background water (spiked with 2.0 mg/L arsenic) and sediment from test pit 5. Significant arsenic sorption occurred even at a soil-to-water ratio of 1:40 (Table 4.5). The Freundlich regression equation provided the best fit to the six-point isotherm that was generated using these batch test data (Figure 4.4). Variable soil:solution batch tests were also performed on arsenic in the moderately acidified system (Table 4.6). The variable-ratio batch tests on the mildly acidified systems yielded an isotherm that best fit a Freundlich linear regression equation, which is very similar to the one generated for arsenic in the alkaline system (Figure 4.5).

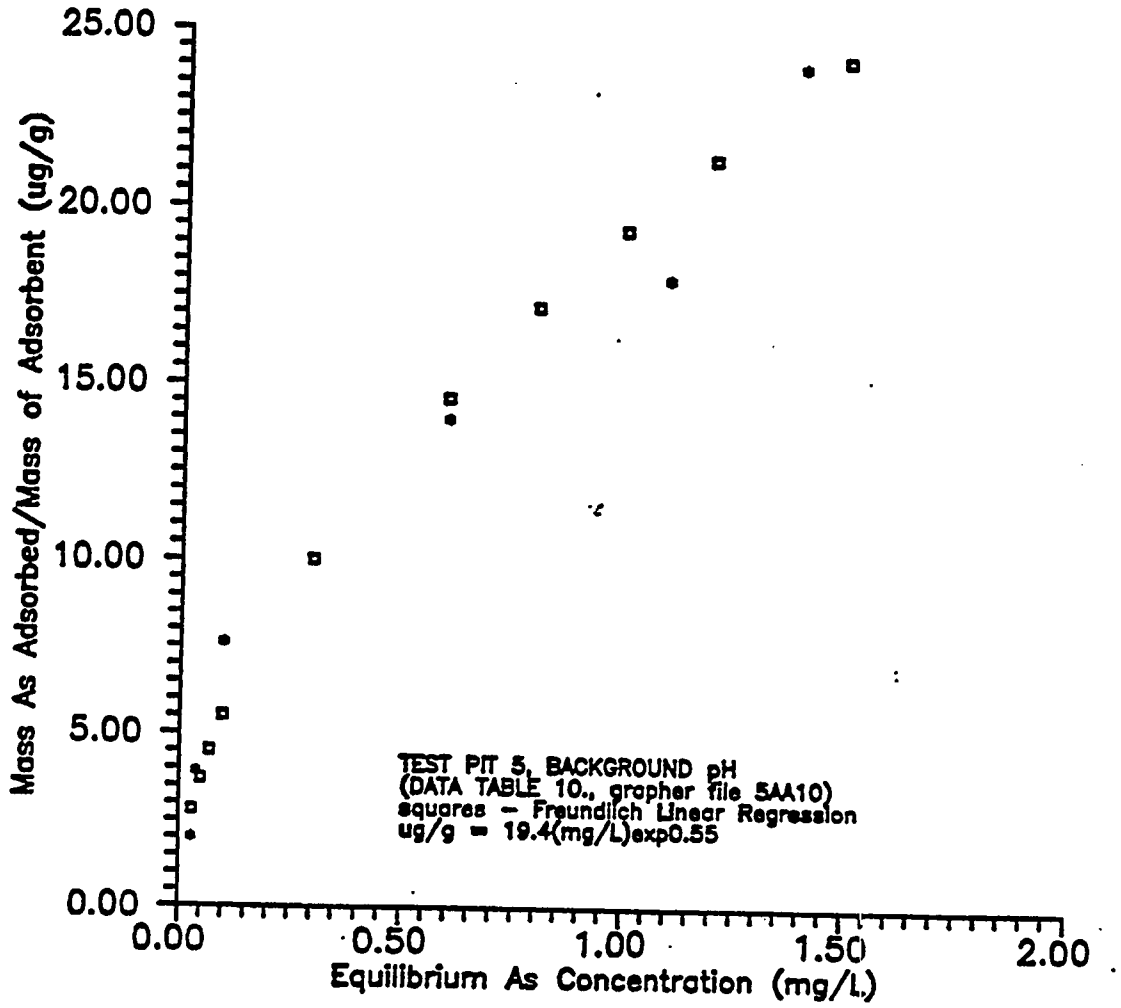


FIGURE 4.4
ARSENIC VARIABLE RATIO ISOTHERM AT BACKGROUND pH WITH FREUNDLICH REGRESSION CURVE

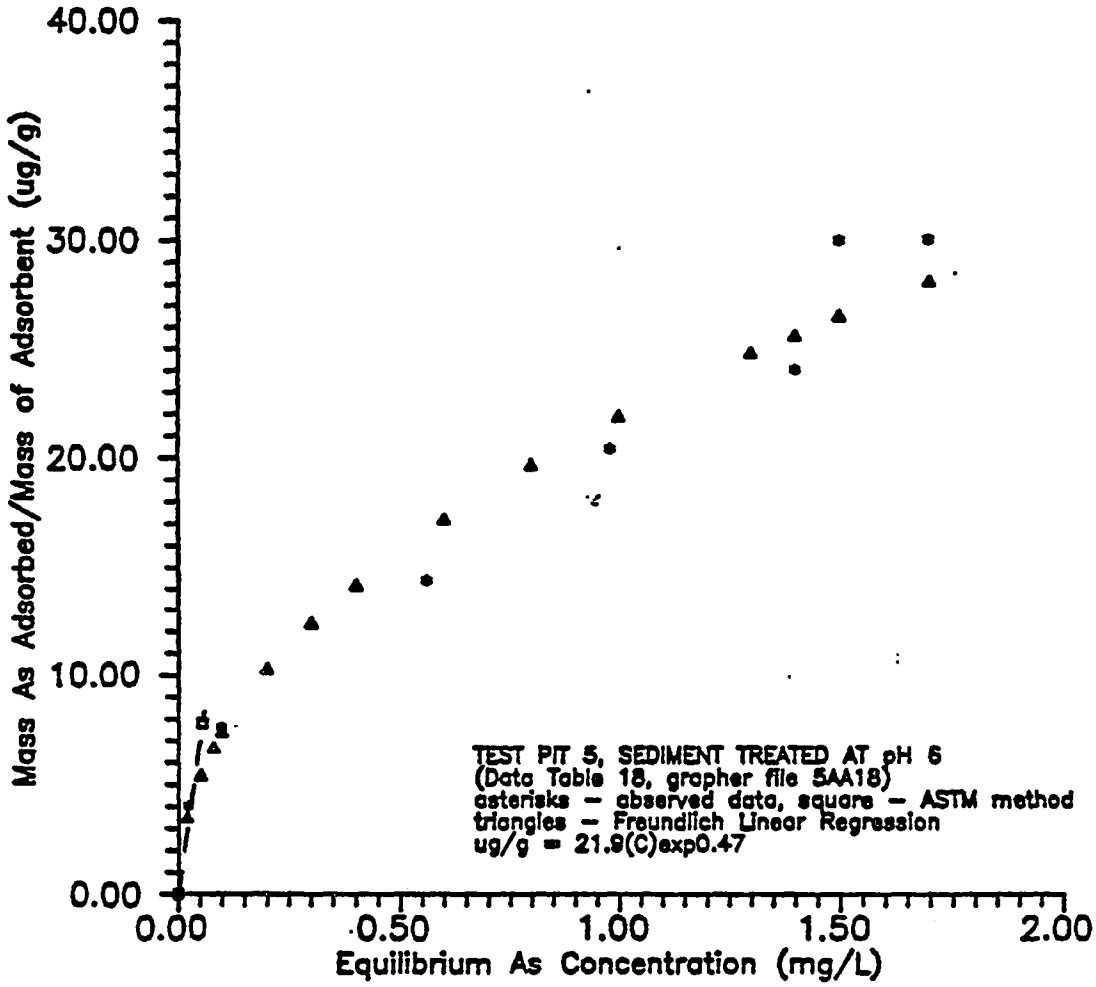


FIGURE 4.5
ARSENIC VARIABLE RATIO ISOTHERM, ACIDIFIED SEDIMENT, WITH FREUNDLICH REGRESSION CURVE

Table 4.5 Arsenic variable ratio isotherm data, alkaline pH, test pit 5

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (µg/g)
Adsorbent material: TP-5 (-40)					
1:1	2.00	0.03	170.00	170.00	2.0
1:2	2.00	0.041	100.00	200.00	3.9
1:4	2.00	0.1	62.50	250.00	7.6
1:10	2.00	0.6	25.00	250.00	14.0
1:20	2.00	1.1	12.50	250.00	18.0
1:40	2.00	1.4	6.25	250.00	24.0

Adsorbent weight and solution volume precision equals ± 0.04 g or mL

Table 4.6 Arsenic variable ratio isotherm data, acidic conditions, test pit 5

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (µg/g)
Adsorbent material: TP-5 (-40) Sediment treated at pH 6, acidified sediment (AW-I)					
1:2	2.00	0.039	100.00	170.00	3.9
1:4	2.00	0.117	62.50	200.00	7.5
1:10	2.00	0.520	25.00	210.00	12.4
1:20	2.00	0.950	12.50	250.00	21.0
1:40	2.00	1.420	6.25	240.00	23.2
1:60	2.00	1.640	4.17	256.00	21.6
1:100	2.00	1.740	2.50	250.00	30.0

Adsorbent weight and solution volume precision equals ± 0.04 g or mL

The extreme difference in uranium adsorption between the pH 5.85 and the pH 2.85 systems is not, therefore, an artifact of the type of batch tests (variable versus constant ratio) used to construct these isotherms.

Constant ratio batch tests were performed on arsenic in the more strongly acidified system (Table 4.7), producing a curve for which the Langmuir regression equation provided the best fit (Figure 4.6). In contrast to the progressively greater sorption observed for uranium and molybdenum in the acidified systems, these batch tests demonstrated less sorption of arsenic in the more acidified system than in the less acidified and alkaline systems (Figures 4.4 through 4.6).

Table 4.7 Arsenic constant ratio isotherm data, acidic conditions, test pit 5

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (μg/g)
Adsorbent material: TP-5 (-40)					
Sediment treated at pH 3, acidified sediment (AW-II)					
1:10	8.00	5.09	25.00	250.00	29.1
1:10	6.00	3.58	25.00	250.00	24.2
1:10	5.00	2.79	25.00	250.00	22.1
1:10	4.00	2.12	25.00	250.00	18.8
1:10	2.00	0.93	25.00	250.00	10.7
1:10	1.00	0.098	25.00	250.00	9.0
1:10	0.50	0.27	25.00	250.00	2.3

Initial concentration, adsorbent weight, and solution volume precision equals ± 0.04 g or mL

The observed tendency of arsenic to sorb less in the more acidified system was somewhat surprising given the contrasting behavior of molybdenum and uranium. One possible explanation for this behavior is a change in the predominant species of arsenic from $HAsO_4^{2-}$ to $H_2AsO_4^-$ as the pH drops below approximately 6.5 (Figure 2.6). If the dominant mechanism of arsenic sorption is electrostatic, the species with a single negative charge should be less strongly sorbed than the species with a double negative charge. This difference could more than offset the increased sorptive capacity of the more strongly acidified sediment. Another possible explanation is that the increased acidity of the batch test solutions has dissolved some of the phases in the sediment that strongly sorb arsenic (for example, iron oxyhydroxides) (EPRI, 1984).

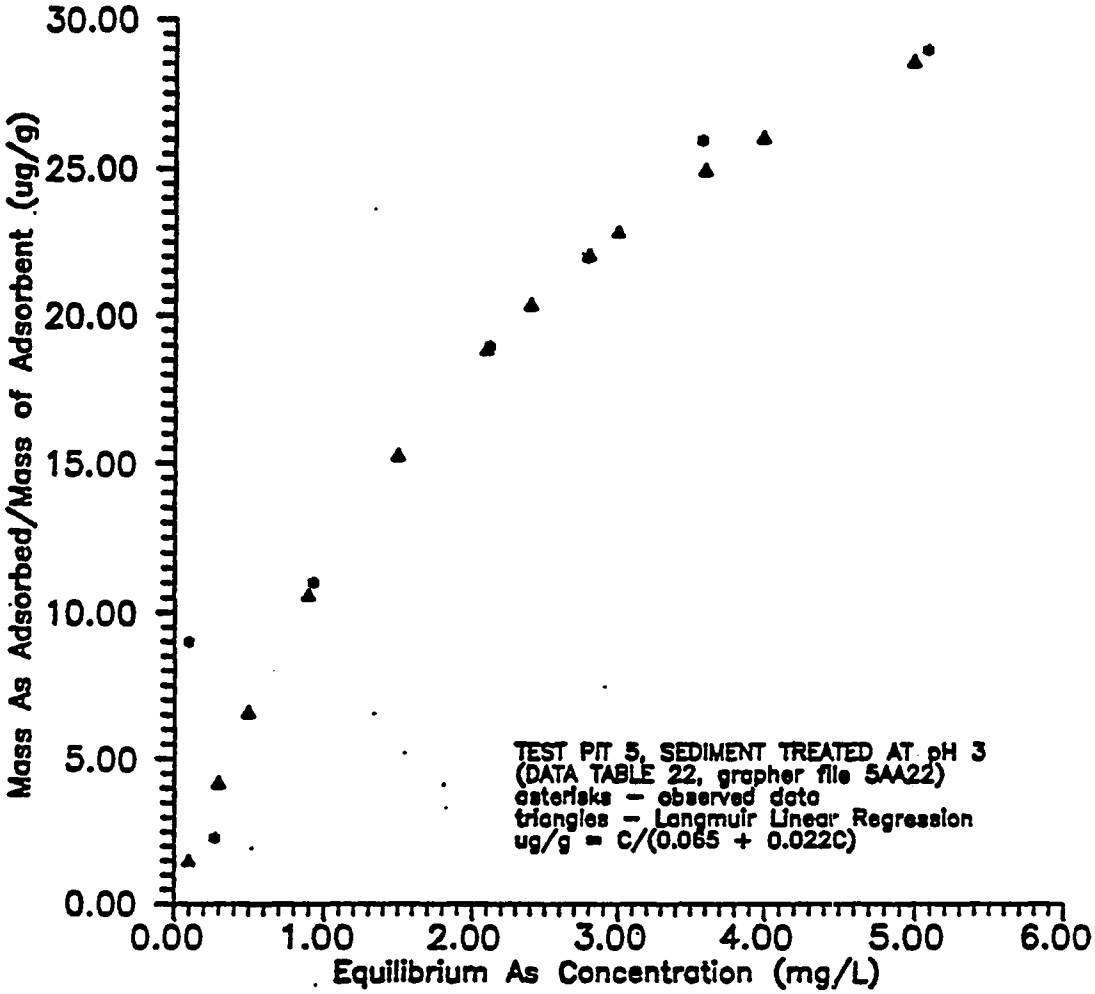


FIGURE 4.6
ARSENIC CONSTANT RATIO ISOTHERM, ACIDIFIED SEDIMENT, WITH LANGMUIR REGRESSION CURVE

An ASTM batch test was conducted on the mildly acidified sediment. The sorption of arsenic demonstrated by the ASTM batch test (1:4 ratio) (Table 4.8) was comparable to that observed for the 1:4 ratio batch tests of arsenic in the background and mildly acidified systems (Figure 4.5).

Table 4.8 Arsenic adsorption data, ASTM method

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (μg/g)
Adsorbent material: TP5 -40					
Sediment treated at pH 3, acidified sediment, ASTM method					
1:4	2.00	0.056	62.50	250.00	7.8
1:4	2.00		62.50	250.00	

Adsorbent weight and solution volume precision equals ± 0.04 g or mL

4.5 SORPTION BEHAVIOR OF MOLYBDENUM

4.5.1 Introduction

EPA method batch tests of molybdenum were conducted in the alkaline system, on the mildly acidified sediment, and on the more acidified sediment. Adsorption isotherms could be plotted only for the molybdenum on the more acidified sediment. The ASTM method was also used to determine molybdenum adsorption on the more strongly acidified sediment.

4.5.2 Discussion

As no adsorption of molybdenum was detected in the alkaline and mildly acidified systems, a comparison of the EPA-approved isotherms and the ASTM batch tests could not be made. Constant ratio (1:10) and variable ratio (1:1 to 1:15) isotherms were constructed, however, with the sorption data from the more strongly acidified system (Tables 4.9 and 4.10). The constant and variable ratio data arrays and an ASTM batch test for molybdenum in the more strongly acidified system are plotted in Figure 4.7. The constant ratio isotherm and the line defined by the ASTM batch test have similar slopes although the constant ratio isotherm indicates a higher sorption of molybdenum per gram of sediment (Figure 4.7). The variable ratio isotherm, however, has a slope that is much steeper than either the ASTM construct or the constant ratio isotherm. The 1:10 batch test for the variable ratio isotherm, however, plots on the best-fit line through the 1:10 constant ratio data (Figure 4.7).

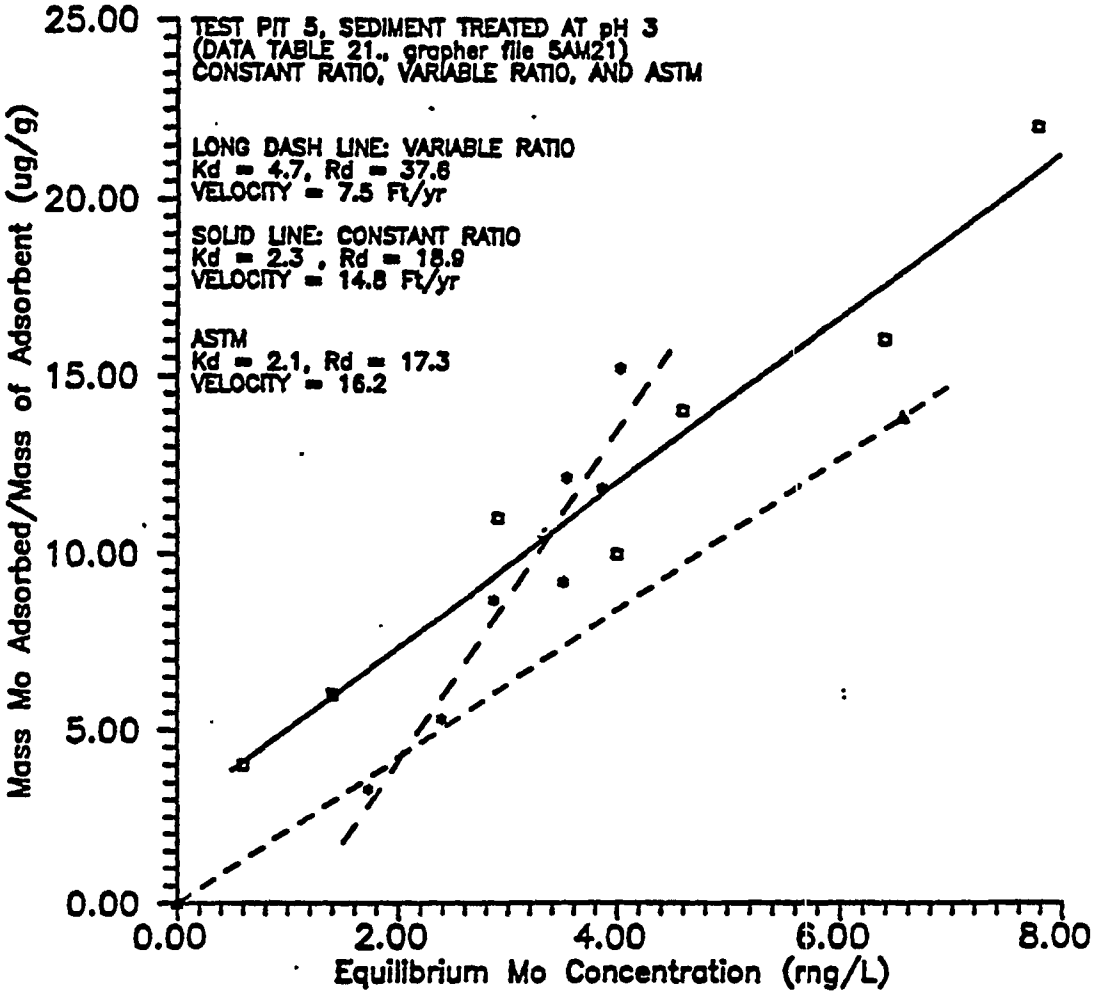


FIGURE 4.7
MOLYBDEMUM VARIABLE RATIO AND CONSTANT RATIO ISOTHERMS, ACIDIFIED SEDIMENT

Table 4.9 Molybdenum variable ratio and constant ratio isotherm data, acidified conditions, test pit 5

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (µg/g)
Adsorbent material: TP-5 (-40)					
Sediment treated at pH 3, acidified sediment (AW-II)					
1:1	5.0	1.73	170.00	170.00	3.3
1:2	5.0	2.39	100.00	200.00	5.3
1:4	5.0	2.87	62.50	250.00	8.7
1:6	5.0	3.51	40.00	240.00	9.2
1:8	5.0	3.54	32.00	256.00	12.1
1:10	5.0	3.87	25.00	250.00	11.8
1:15	5.0	4.04	16.00	240.00	15.2
Adsorbent material: TP-5 (-40)					
Sediment treated at pH 3, acidified sediment (AW-II)					
1:10	10.05	7.80	25.00	250.00	22.5
1:10	8.05	6.44	25.00	250.00	15.6
1:10	6.05	4.56	25.00	250.00	14.4
1:10	5.05	3.97	25.00	250.00	10.3
1:10	4.05	2.91	25.00	250.00	10.9
1:10	2.05	1.37	25.00	250.00	6.3
1:10	1.05	0.60	25.00	250.00	4.0

Adsorbent weight and solution volume precision equals ± 0.04 g or mL

Table 4.10 Molybdenum adsorption data, ASTM method

Soil:solution ratio	Initial concentration (mg/L)	Equilibrium concentration (mg/L)	Adsorbent weight (g)	Volume of solution (mL)	Amount adsorbed (µg/g)
Adsorbent material: TP5 (-40)					
Sediment treated at pH 3, acidified sediment, ASTM method					
1:4	10.00	6.56	25.00	250.00	13.8

Adsorbent weight and solution volume precision equals ± 0.04 g or mL

Tests for the equilibrium pH on the variable ratio batch test solutions indicate that the pH of these solutions decreases as the soil-to-solution ratio decreases. At lower soil:solution ratios, the pH of batch test solutions is lower than the pH of batch test solutions generated at higher soil-to-solution ratios. Test results in the alkaline and acidified systems clearly demonstrate that lower pH batch tests demonstrate increased molybdenum sorption on the Rifle sediments.

Variable ratio batch tests in the acidified system with soil:solution ratios lower than 1:10 have a lower pH than the 1:10 constant ratio batch test solutions. This suggests that the higher molybdenum sorption of the variable ratio batch tests (and therefore the steeper slope of this isotherm) may be an artifact of pH variations in the batch test solutions.

4.6 COMPARISON OF DIFFERENT METHODOLOGIES

Uranium, arsenic, and molybdenum K_ds determined from the EPA variable or constant ratio methods were compared with uranium K_ds determined from the ASTM method. In the background (alkaline) case for uranium, the ASTM method produced K_ds that were lower than the K_ds generated by the variable ratio isotherms (Figure 4.1). The EPA method constant ratio isotherms for uranium produced K_ds that were either higher than or very similar to the ASTM values (Figure 4.2). Furthermore, the ASTM-derived K_ds for uranium showed very little variability for sediments of different test pits. Values ranged from 0.3 to 0.4 resulting in migration velocities differing by 24 percent (Figure 4.1). The EPA variable ratio isotherms produced K_ds ranging from 0.8 to 0.5 resulting in migration velocities differing by 46 percent for the same sediments. This suggests that the EPA variable ratio method is more sensitive to the sediment properties that influence adsorption.

A comparison of the EPA variable ratio and EPA constant ratio isotherms for uranium (Figures 4.1 and 4.2) show differences in results for sediments from the same test pit. The constant ratio K_d was 28 percent greater than the variable ratio K_d for test pit 6. The constant ratio K_d was 25 percent less than the variable ratio K_d for test pit 5. The constant ratio isotherms also show less scatter, which suggests that constant ratio isotherms are less subject to the effects of variable pH and ionic strength, which are caused by sorbent phase dissolution (especially carbonates).

A retardation factor was also calculated for arsenic using the ASTM derived K_d in the mildly acid-washed system. The results were comparable to the retardation factor obtained using the variable ratio isotherm generated for this system (Figure 4.3). The results for molybdenum were consistent with those observed for uranium and arsenic. The ASTM batch test for molybdenum in the more strongly acid-washed sediment indicates less adsorption of molybdenum than the variable ratio or constant ratio isotherms.

Where direct comparisons were made between K_ds derived from ASTM batch tests and the results of the variable ratio and constant ratio isotherms, the ASTM method produced retardation coefficients that were approximately equal

or lower that would yield more conservative (higher) migration velocity predictions. The ASTM method also appeared to be insensitive to local variations in lithology. If replicate ASTM batch tests are performed on a given system (metal-pH condition), the resulting K_d may well be an adequate method for placing maximum limits on contaminant migration. The ASTM method is not sufficient for predicting actual transport rates of a contaminant species in an aquifer. If a limited number of isotherms are going to be used to constrain the adsorption behavior of a aquifer, the results of this study suggest that constant ratio isotherms are preferred.

4.7 EFFECTS OF AQUIFER MATRIX ON ADSORPTION

Spatial variations in aquifer matrix lithology could influence observed adsorptive capacity and cause the changes in uranium K_d observed for test pits 5, 6, and 7 (Figure 4.1). Lithologic components that affect adsorption and that could also vary spatially within an aquifer matrix included grain size, percentage of clay type (for example, kaolinite, illite, and smectite), total surface area, percent organic carbon content, percentage total carbon, hydrochloric acid (HCl) soluble iron, HCl soluble manganese, and acid neutralization capacity. These properties were characterized for the sediments collected from test pits 5, 6, and 7 at the Rifle site. A summary was provided in Section 3.1. Details are provided in Appendixes A through C.

The spatial variation in K_d observed for uranium at alkaline (background) pH could not be correlated with any variations in aquifer matrix properties except for organic carbon content. The organic carbon contents in test pits 5, 6, and 7 are 0.3 percent, 0.5 percent, and 0.6 percent, respectively. This is consistent with increasing K_ds observed from test pit 5 to 7 (Figure 4.1). This may suggest that organic carbon content is a significant factor in the aquifer matrix adsorptive capacity for uranium at the Rifle site. Other factors cannot be precluded, however, because of the small data set.

5.0 APPLICATION OF ADSORPTION ISOTHERM INFORMATION

The distribution coefficients or equations (as for arsenic) were applied to calculate retardation coefficients and migration velocities for the metals investigated. Retardation factors were determined assuming constant bulk densities and porosities. Velocities were calculated assuming constant hydraulic conductivity, gradient, and porosity. In reality, these parameters would vary spatially within an aquifer. Holding these hydrogeologic parameters constant allows a comparison of contaminant migration velocity variations calculated from adsorption isotherms.

5.1 MIGRATION VELOCITY PREDICTIONS

5.1.1 Uranium migration velocity

In alkaline pH conditions representative of groundwater unaffected by uranium mill tailings leachate, uranium migration velocity estimates range from 40 ft/year (ft/yr) [10 meter/year (m/yr)] to 80 ft/yr (20 m/yr) (Figure 4.1). The ASTM method yielded the most conservative (faster) migration velocities. Significant migration velocity variation occurred between sediments from different test pits, probably reflecting variations in clay quantity or type in the area represented by each test pit.

As pH decreased, the estimated migration velocity decreased remarkably (Figure 4.3). For the pH 3 system, the estimated retardation coefficient was greater than the estimated advective groundwater velocity determined from aquifer tests. This yielded a velocity ratio of less than one, or a migration rate of zero. However, if hypothetical hydraulic parameters were used (vertical hydraulic conductivity = 1/10 horizontal hydraulic conductivity, and gradient = 1) to represent leachate movement from the tailings pile, the uranium velocity estimate would be as high as 10 ft/yr (3 m/yr). Uranium migration velocities estimated for the pH 6 system were less than one-half of those estimated for alkaline conditions.

These observations suggest that the migration velocity of uranium, as controlled by the adsorptive capacity of the aquifer matrix material through which it passes, may actually increase relative to advective groundwater velocity as the dissolved uranium moves downgradient into progressively higher pH environments. It is also evident that uranium migration velocity may vary considerably within an aquifer relative to advective groundwater velocity, even if there is little variation in hydrogeological conditions.

5.1.2 Arsenic migration velocity

Arsenic adsorption in batch tests for this study resulted in nonlinear isotherms. Freundlich and Langmuir linear regression equations were derived from the observed data (Figures 4.4 to 4.6). The best-fit equation describes the mass

adsorbed as a function of equilibrium concentration of arsenic in groundwater. Using bulk density and porosity estimates, this function can be applied in the retardation equation to generate a curve describing the change in retardation factor as a function of arsenic concentration (Figure 5.1). This set of retardation factors for a range of arsenic concentrations can then be converted to a curve showing the arsenic migration velocity with respect to arsenic concentration in groundwater (Figure 5.2) under constant hydrogeologic parameters. These curves show the increase in velocity inversely proportional to the retardation factor. They also illustrate the immobility of arsenic at low concentrations in alkaline conditions. Similar curves of retardation factor and velocity with respect to concentration have been developed from the Langmuir isotherm for acidic conditions (Figure 5.3 and 5.4). Comparison of the two velocity curves for arsenic in alkaline groundwater (Figure 5.2) and in acidic groundwater (Figure 5.4) shows the extreme variation of arsenic mobility with respect to pH conditions.

5.1.3 Molybdenum migration velocity

Under background and pH 6 conditions, no significant molybdenum adsorption was observed indicating migration velocities approaching advective groundwater velocities. Molybdenum migration velocity estimates ranged from 7 to 16 ft/yr (2 to 4 m/yr) from three adsorption determination methodologies under very low pH conditions (Figure 4.7). The ASTM method yielded the most conservative (highest) molybdenum migration velocity estimate.

5.2 CONTAMINANT VELOCITY VARIATIONS: IMPACT ON GROUNDWATER CHARACTERIZATION

Commonly, flow and transport models use one K_d or parameters of one Freundlich or Langmuir-type equation to estimate velocities of metals in groundwater for the entire modeled area. In other words, one adsorption parameter for the modeled area does not represent the spatial variability expected in an aquifer lithologically and geochemically heterogeneous. This study shows that an estimate of spatial variability of adsorption capacity is necessary for more accurate contaminant travel distance predictions.

For example, the uranium retardation factor varies by 5 percent between test pits 5 and 7, which are approximately 2000 ft (610 m) apart.

This variation is significant enough to affect simulated uranium migration in the aquifer. This point is graphically illustrated in Figure 5.5. This figure shows three uranium migration distance predictions using three distribution coefficients determined from the EPA method test pit 5 sediments, EPA method test pit 7 sediments, and the ASTM method (average value determined from three test pits). Constant hydrogeologic parameters were used in the calculation of each distance. The least and greatest travel distance prediction differ by over

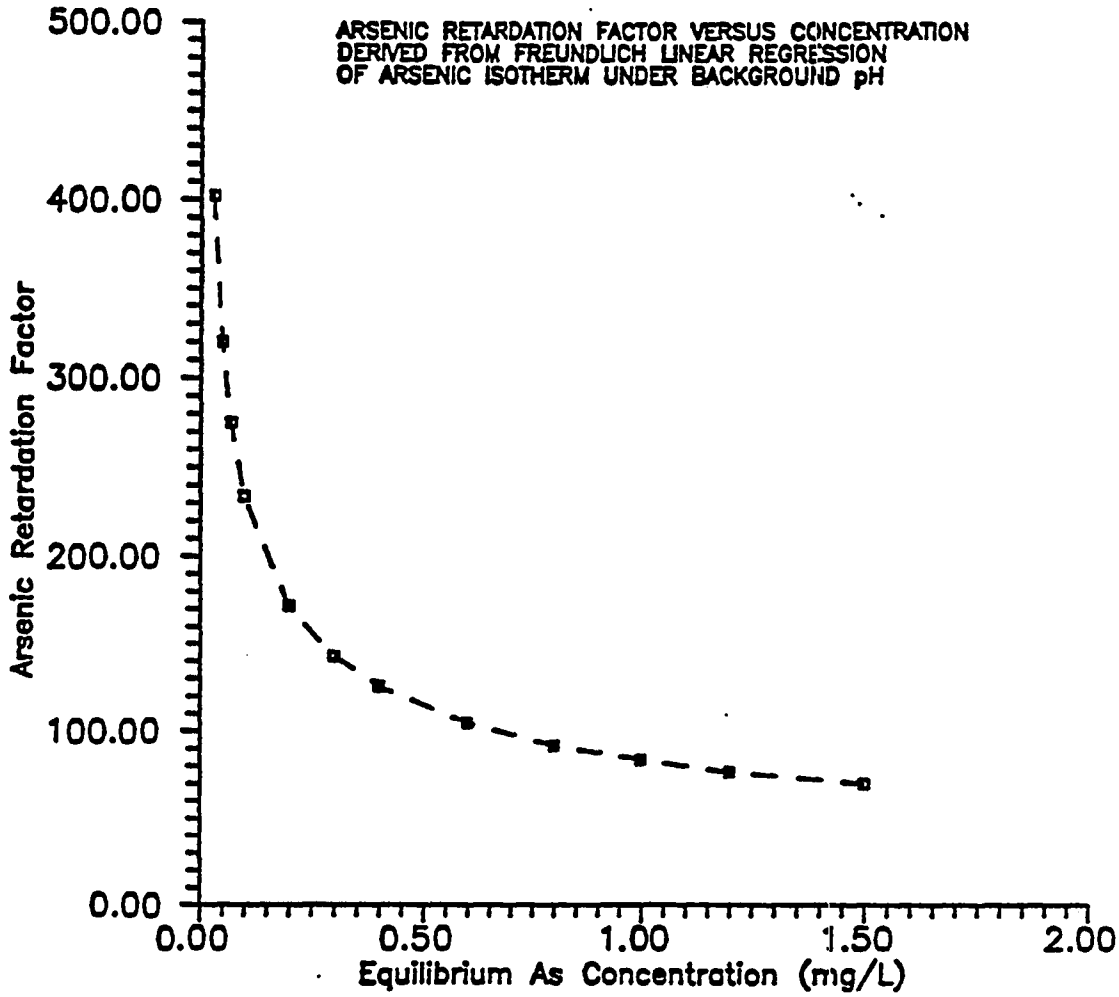


FIGURE 5.1

ARSENIC RETARDATION FACTOR VERSUS CONCENTRATION, BACKGROUND pH CONDITIONS

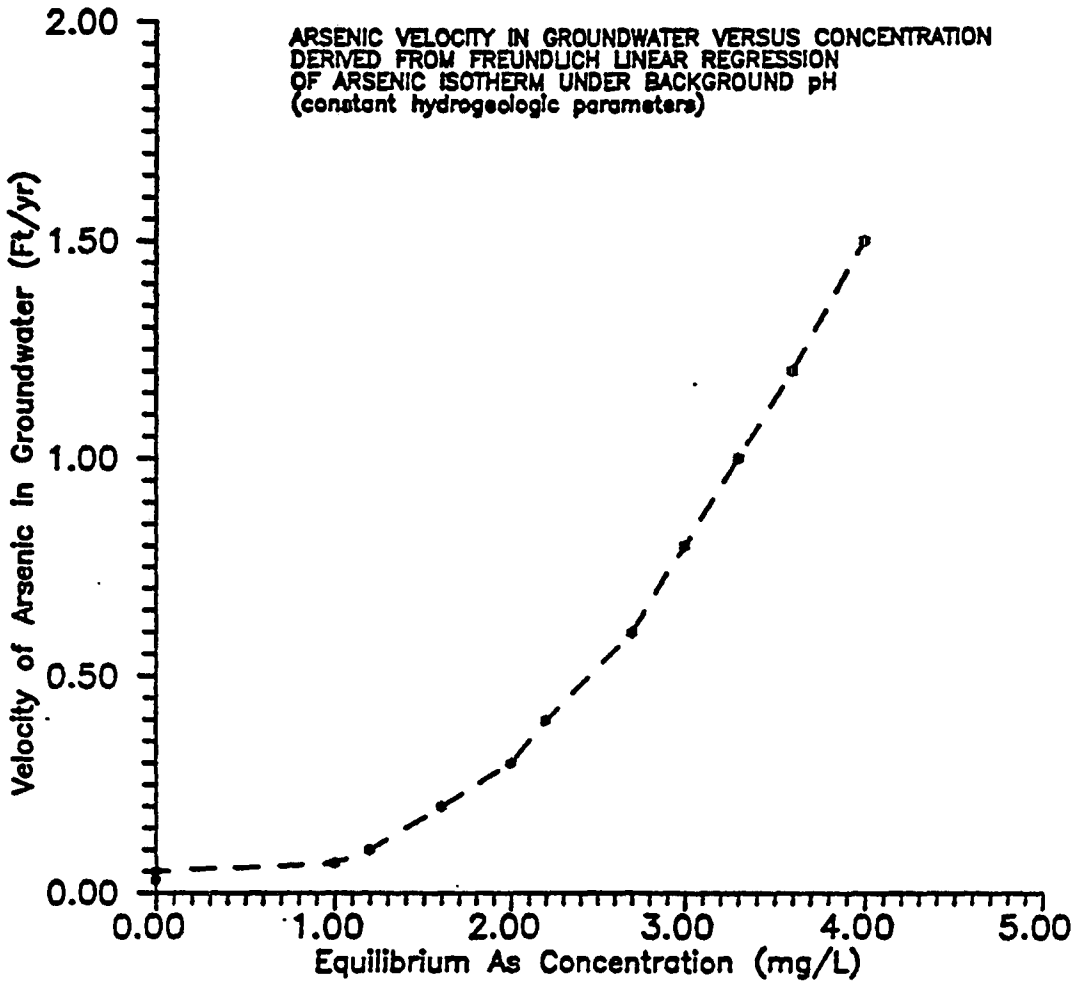


FIGURE 5.2
ARSENIC VELOCITY IN GROUNDWATER VERSUS CONCENTRATION

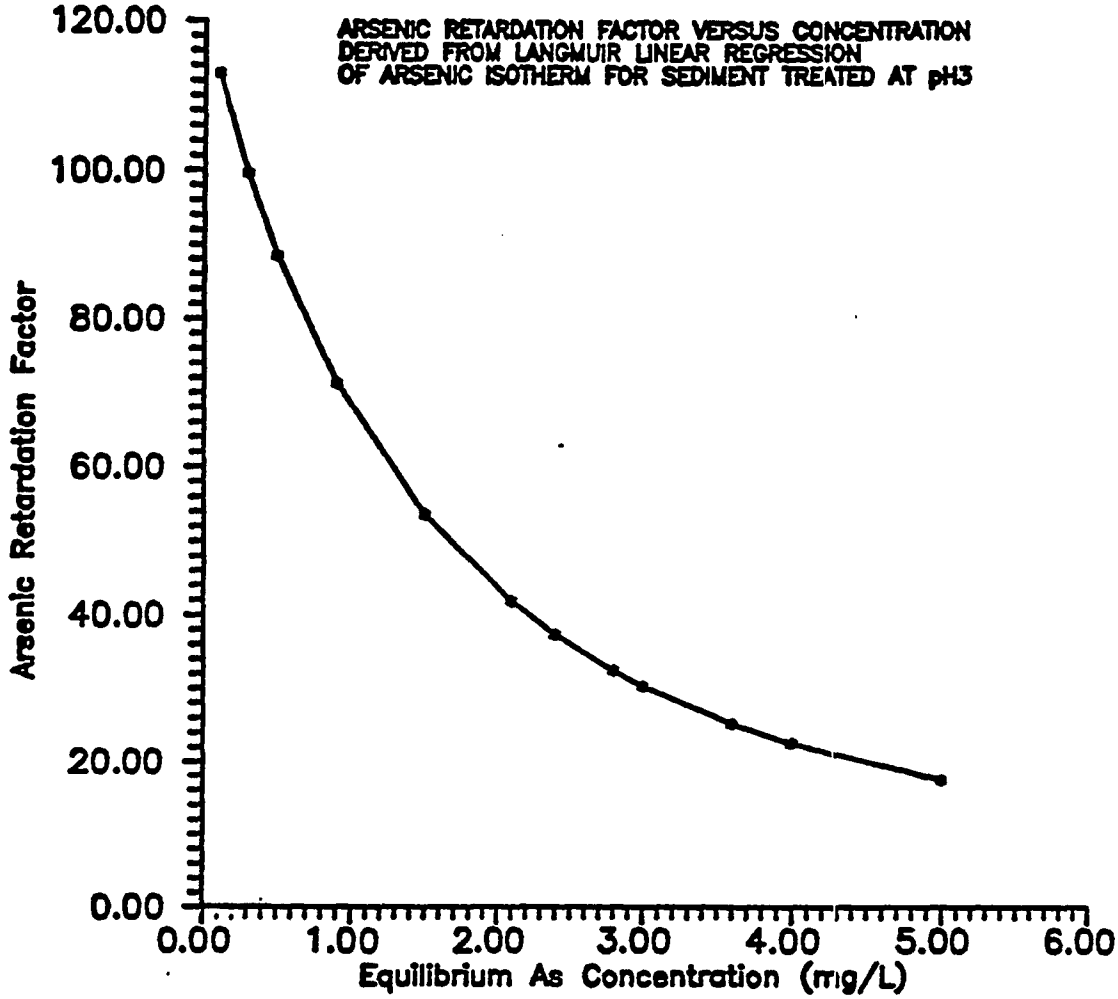


FIGURE 5.3
ARSENIC RETARDATION FACTOR VERSUS CONCENTRATION
ACIDIFIED pH CONDITION

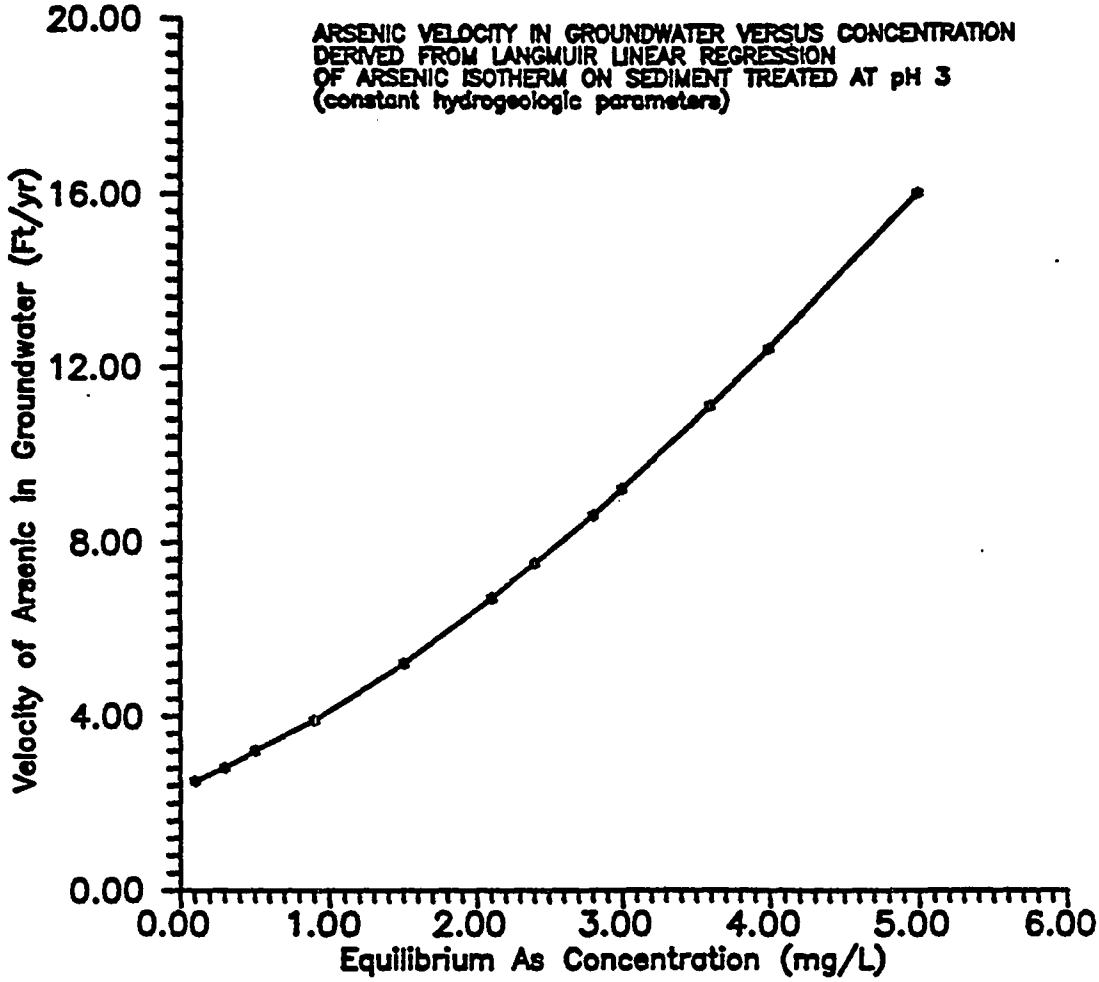


FIGURE 5.4
ARSENIC VELOCITY IN GROUNDWATER VERSUS CONCENTRATION
ACIDIFIED pH CONDITION

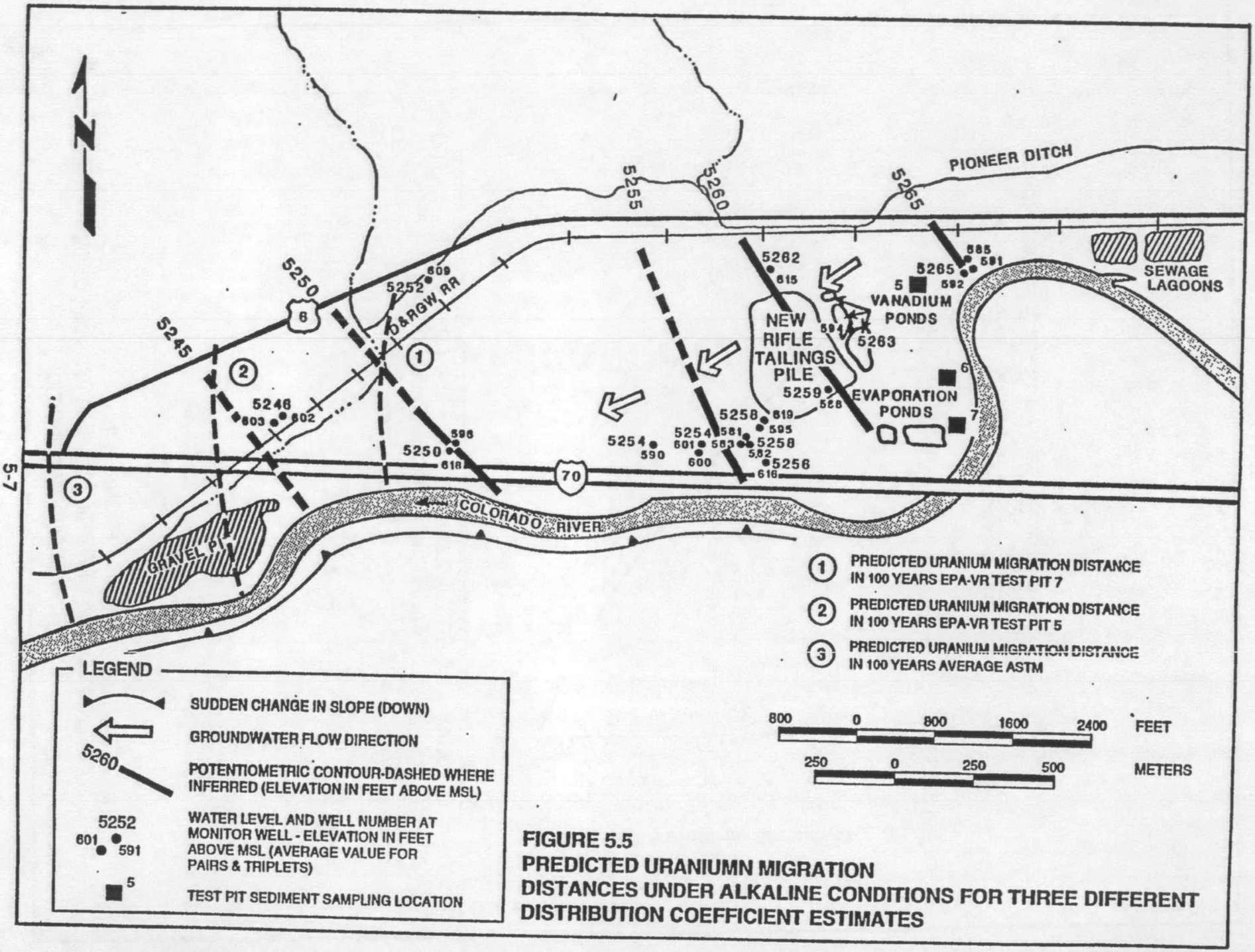


FIGURE 5.5
PREDICTED URANIUMN MIGRATION DISTANCES UNDER ALKALINE CONDITIONS FOR THREE DIFFERENT DISTRIBUTION COEFFICIENT ESTIMATES

one-half mile. In the prediction of arrival times at downgradient receptors for a risk assessment study, this would lead to differences on the order of tens of years or greater. This could affect the choice of groundwater restoration strategies (for example, passive versus active approach).

In this study, only three locations were sampled. To take the spatial variability of the retardation factor into account in a model to simulate potential remediation strategies, aquifer matrix samples should be collected over the entire modeled area. The spatial density of aquifer matrix sampling for R_d determination should be consistent with the goals of modeling and the cost impacts of the contemplated actions.

As shown in the results of this special study, contaminant migration velocities are also a function of groundwater pH. Groundwater pH varies in the subsurface at most UMTRA processing sites in relation to distance (vertical and horizontal) from the tailings piles. Groundwater pH will change with respect to time and space in an aquifer in response to source removal (surface remediation) or active manipulation of groundwater flow (e.g., extraction and land application).

In the cases of uranium and molybdenum, this special study has shown that migration velocities will increase as the pH rises. At a site in which the tailings have been removed, neutral to slightly alkaline precipitation migrates downward and alkaline background groundwater migrates through areas of the aquifer that were formerly subjected to acidic tailings leachate causing an increase in pH with time. This naturally occurring process would therefore cause migration velocities of uranium and molybdenum to increase with time after tailings removal. Likewise, in the case of arsenic, this study has shown that migration velocities decrease as the pH rises. The pH change could cause arsenic migration velocities to decrease after tailings removal.

These processes should be anticipated and addressed in groundwater restoration planning at UMTRA sites where acidic tailings leachate enters groundwater. The following UMTRA sites have acidic tailings leachate: Falls City, Grand Junction, Green River, Gunnison, Lakeview, Maybell, Mexican Hat, Monument Valley, Riverton, Shiprock, Spook, and Tuba City. Most of these sites have MCL exceedences of uranium and/or molybdenum in the uppermost aquifer. Two sites (Gunnison and Lakeview) also have MCL exceedences of arsenic in the uppermost aquifer.

6.0 CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations resulting from this special study are summarized below.

- In general, uranium K_ds derived from the ASTM methodology are less than K_ds derived from the EPA methodology, resulting in predictions of greater uranium migration velocity.

- In general, K_ds derived from the EPA methodology are more sensitive to aquifer matrix lithologic variations as opposed to K_ds derived from the ASTM methodology.

- The predicted uranium migration velocity increases as groundwater pH increases. This suggests that after surface remediation is complete and subsurface water returns to higher pH conditions, the migration velocity of residual uranium contamination in vadose zone pore water and/or groundwater may increase with time.

- Uranium migration velocities vary by approximately 50 percent at different locations in the aquifer underlying the Rifle site. This is a function of aquifer lithologic variation.

- The predicted molybdenum migration velocity increases with respect to an increase in groundwater pH increases. This suggests that after surface remediation is complete and subsurface water returns to higher pH conditions, migration velocity of residual molybdenum contamination in vadose zone pore water and/or groundwater may increase with time.

- In neutral and slightly acidic pH environments, arsenic adsorption is described by a nonlinear isotherm; the Freundlich regression equation provided the best fit. In a highly acidic pH environment, arsenic adsorption is described by a nonlinear isotherm. The Langmuir regression equation provided the best fit. Therefore, predictions of arsenic migration must take into account groundwater pH and arsenic concentration.

- Analytical costs for the EPA method are approximately seven times the costs of the ASTM method. The ASTM method can be used as a screening tool to provide the most conservative migration distance estimates, while the EPA method should be used for more detailed assessments of adsorption.

- An assessment of aquifer matrix adsorptive capacity as a function of pH variation and lithologic variation within an aquifer is necessary for determination of the most cost-effective groundwater restoration strategy at each UMTRA site.

7.0 REFERENCES

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8.0 ACRONYMS

ASTM	American Society for Testing and Materials
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
MCL	maximum concentration limits
MK	Morrison-Knudsen
RAP	remedial action plan
SEM	scanning electron microscope
SH&B	Sergent, Hauskins, and Beckwith
UMTRA	Uranium Mill Tailings Remedial Action
UNM	University of New Mexico
XRD	x-ray diffraction

9.0 LIST OF CONTRIBUTORS

The following individuals contributed to the preparation of this special study.

Name	Contribution
C. Poore	Author
J. Blount	Author
C. Silva	Technical editing, document coordination
C. Slosberg	Word processing
R. Saar	Document reviewer

APPENDIX A

GRAIN SIZE ANALYSES OF RIFLE AND SHIPROCK SEDIMENTS

SERGENT, HAUSKINS & BECKWITH CONSULTING GEOTECHNICAL ENGINEERS
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MATERIALS ENGINEERING • MATERIALS TESTING • ENVIRONMENTAL SERVICES

March 20, 1992

Jacobs Engineering
5301 Central Ave., N.E.
Albuquerque, New Mexico 87108

SHB Job No. C92-5068

Attention: Connie Nestor

Project: Special Studies
PO #05-62350-2-92-0706

Lab No. 4421: Sandy gravel material, sampled from Test Pit No. 5 @ 0'-6.5', by Client on March 10, 1992

SIEVE ANALYSIS

	Sieve Size	Percent Passing
	6 inch	100
	3 inch	95
	2 inch	83
	1 1/2 inch	75
	1 inch	65
	3/4 inch	61
	1/2 inch	56
	3/8 inch	53
Gravel	No. 4	47
	No. 10	44 → 56% gravel
Sand	No. 40	36
	No. 100	19
Silt	No. 200	12 → 12% silt + clay

68

100-68 = 32% Sand

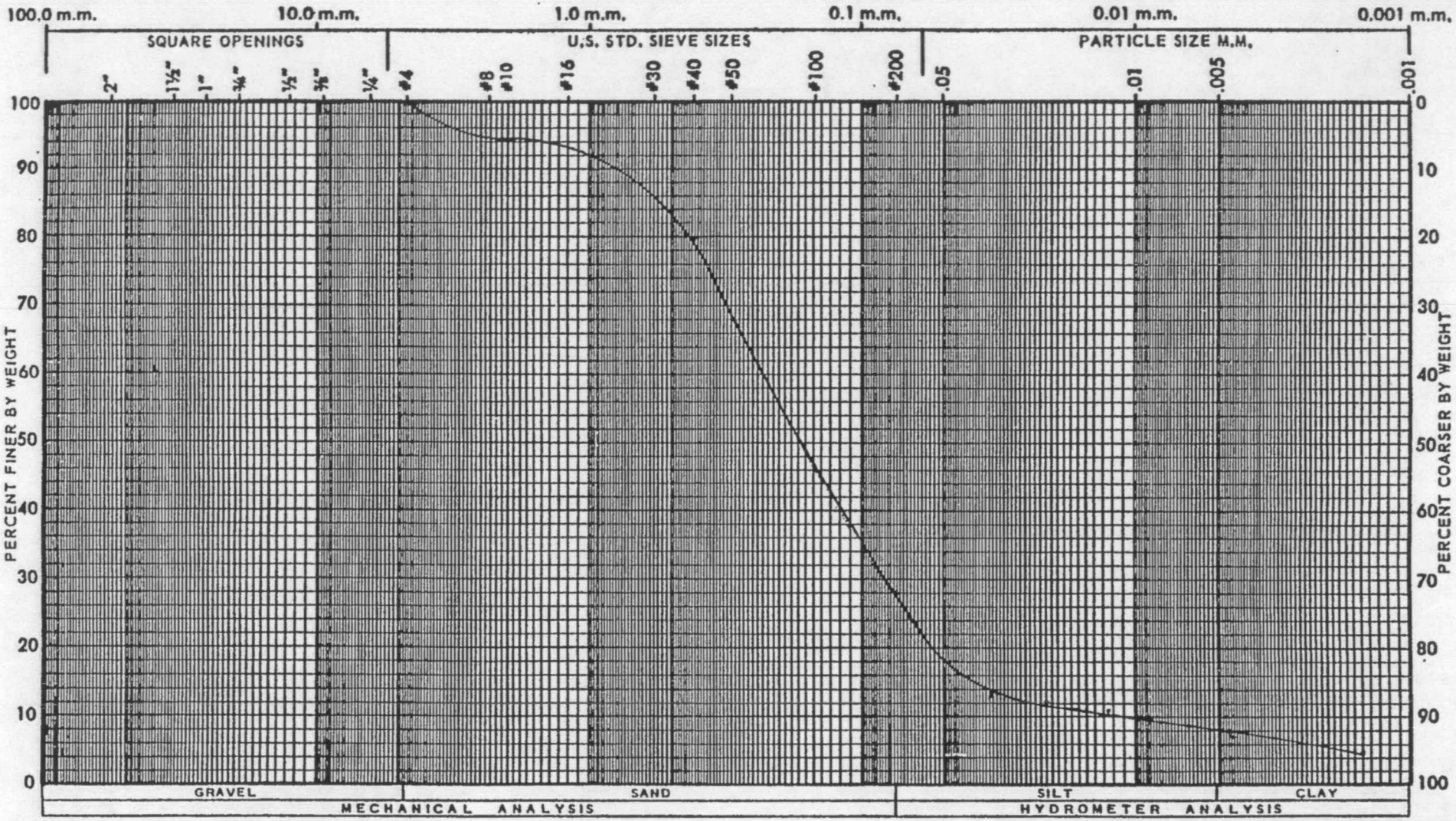
HYDROMETER:
3.8% clay
12-3.8 = 8.2% silt

be
Copies: Addressee (2)

JOB NO. C92-5068

PARTICLE SIZE DISTRIBUTION CURVE

PROJECT Special Studies LOCATION



% clay = 8% of 47 = 3.8%

CURVE	SAMPLE	LIQUID LIMIT	PLASTICITY INDEX	ACTIVITY	UNIFIED SOIL CLASSIFICATION	LAB NO.
	TP #5 @ 0'-6.5'				N/A	4421

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March 20, 1992

Jacobs Engineering
5301 Central Ave., N.E.
Albuquerque, New Mexico 87108

SHB Job No. C92-5068

Attention: Connie Nestor

Project: Special Studies
PO #05-62350-2-92-0706

Lab No. 4422: Sandy gravel material, sampled from Test Pit No. 7 @ 1.5'-6.5', by Client on March 10, 1992

SIEVE ANALYSIS

Sieve Size	Percent Passing
6 inch	100
3 inch	96
2 inch	82
1 1/2 inch	71
1 inch	57
3/4 inch	50
1/2 inch	46
3/8 inch	41
No. 4	36
No. 10	32 → ~~58~~ 68 % GRAVEL
No. 40	23
No. 100	11
No. 200	6.3 → 6.3 % silt + clay
	74.3

100 - 74.3 = 25.7 % sand

HYDROMETER:
2.2 % clay
6.3 - 2.2 = 4.1 % silt

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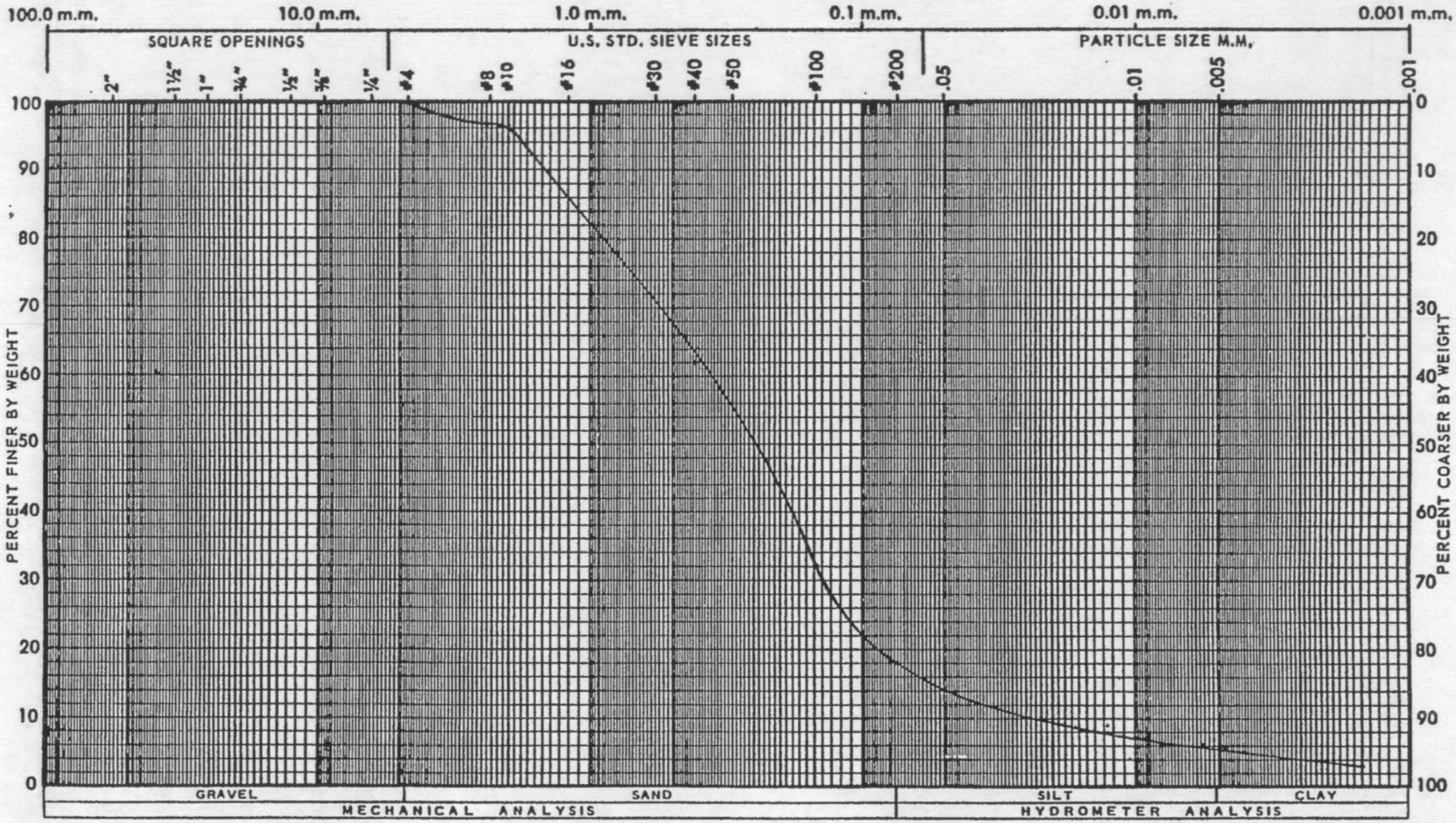
JOB NO. 692-3068

PARTICLE SIZE DISTRIBUTION CURVE

PROJECT Special Studies LOCATION



% clay = 6% of 36 = 2.2%

CURVE	SAMPLE	LIQUID LIMIT	PLASTICITY INDEX	ACTIVITY	UNIFIED SOIL CLASSIFICATION	LAB NO.
	TP #7 @ 1.5'-6.5'				N/A	4422

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March 20, 1992

Jacobs Engineering
5301 Central Ave., N.E.
Albuquerque, New Mexico 87108

SHB Job No. C92-5068

Attention: Connie Nestor

Project: Special Studies
PO #05-62350-2-92-0706

Lab No. 4423: Sandy gravel material, sampled from Test Pit No. 6 @ 1.5'-6.5', by Client on March 10, 1992

SIEVE ANALYSIS

Sieve Size	Percent Passing
6 inch	100
3 inch	97
2 inch	86
1 1/2 inch	74
1 inch	59
3/4 inch	53
1/2 inch	50
3/8 inch	48
No. 4	46
No. 10	43 → 57 % gravel
No. 40	30
No. 100	16
No. 200	9.8 → 9.8 % silt + clay

66.8

100 - 66.8 = 33.2 % sand

HYDROMETER
2.8 % clay
9.8 - 2.8 = 7 % silt

be
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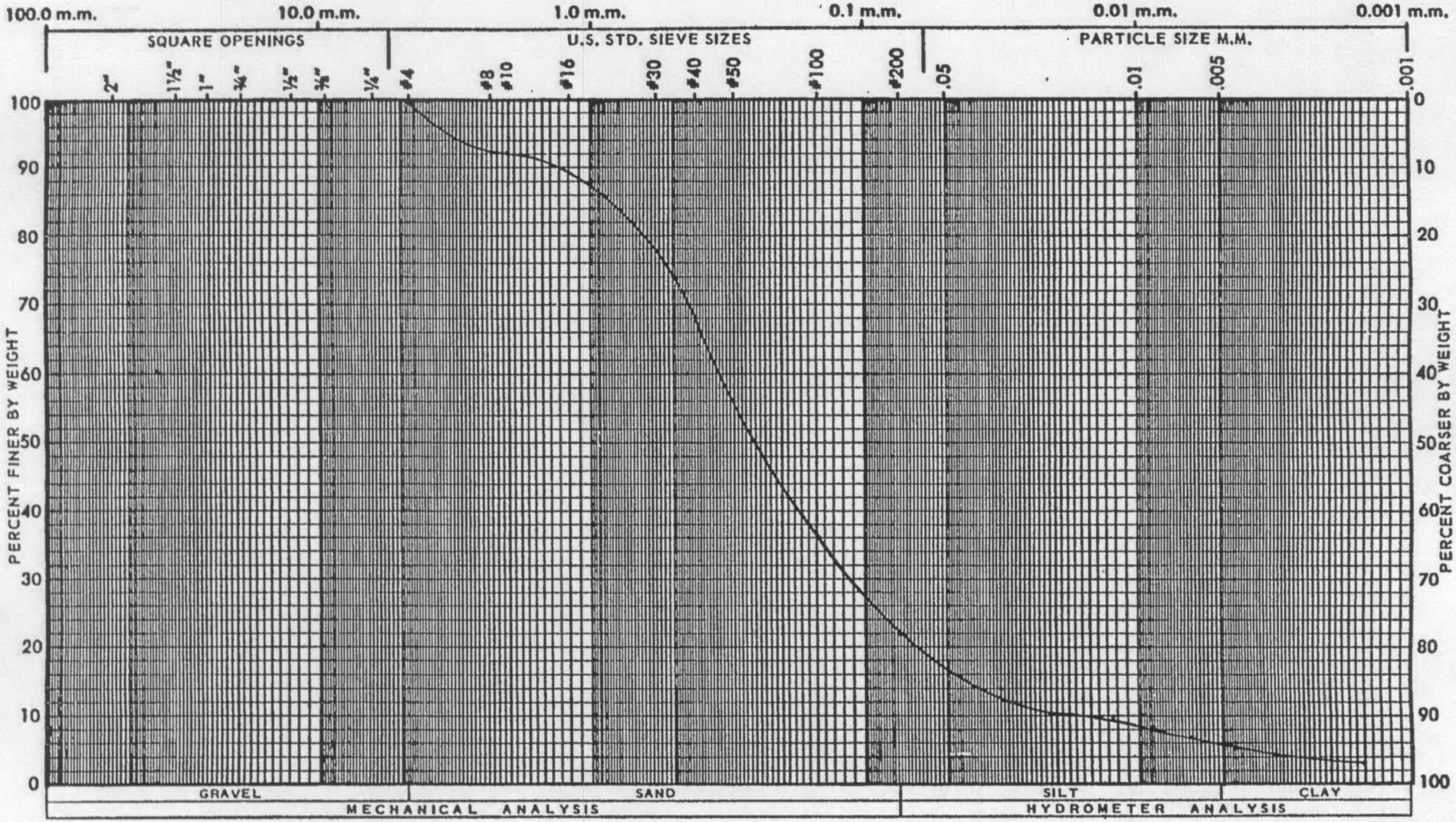
JOB NO. 692-3068

PARTICLE SIZE DISTRIBUTION CURVE

PROJECT Special Studies LOCATION



% clay = 6% of 46 = 2.8%

CURVE	SAMPLE	LIQUID LIMIT	PLASTICITY INDEX	ACTIVITY	UNIFIED SOIL CLASSIFICATION	LAB NO.
	TP #6 @ 1.5'-6.5'				N/A	4423

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B.E.T. SURFACE AREA SUMMARY

	SURFACE ID	AREA SURFACE AREA M2/G	MEASUREMENTS	MEAN M2/G
	FINE SHP	FRACTION	SUM	
	TP140	1.9476	6.2864	2.095466
*	TP340	1.7816		
	TP440	2.5572		
	RFLN			
*	TP540	3.7126	10.4242	3.474733
	TP640	3.3206		
	TP740	3.391		
	COARSE SHP	FRACTION		
	TP11040	1.354	4.3837	1.461233
	TP31040	1.4428		
	TP41040	1.5869		
	RFLN			
	TP51040	4.288	8.6553	2.8851
	TP61040	1.9347		
	TP71040	2.4326		

Gemini 2360 V1.03
Instrument ID:

mple ID: 1-40
mple Weight: 1.6795 g
evious Free Space: -2.294 cc STP
alysis Mode: Equilibration

Date: 4/15/92 Time:
Saturation Pressure: 644.52 mmHg
Evacuation Time: 1.0 min
Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	1.9476 sq. m/g
Slope:	1.945541
Y-Intercept:	-0.000116
C:	-16834.544922
Vm:	0.514026
Correlation Coefficient:	9.9955e-001

BET Single Point Surface Area: 2.2096 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.29	0.511	*
0.1226	79.03	0.589	*
0.1952	125.83	0.651	*
0.2678	172.63	0.710	*
0.3404	219.37	0.770	*

Gemini 2360 V1.03
Instrument ID:

nle ID: 3-40 Date: 4/15/92 Time:
ple Weight: 1.8373 g Saturation Pressure: 644.52 mmHg
asured Free Space: -2.294 cc STP Evacuation Time: 1.0 min
alysis Mode: Equilibration Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	1.7816	sq. m/g
Slope:	2.124597	
Y-Intercept:	0.002109	
C:	1008.394165	
Vm:	0.470211	
Correlation Coefficient:	9.9957e-001	

BET Single Point Surface Area: 2.0172 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.28	0.461	*
0.1226	79.03	0.534	*
0.1952	125.82	0.592	*
0.2678	172.60	0.648	*
0.3403	219.32	0.703	*

Gemini 2360 V1.03
Instrument ID:

nple ID: 4-40
nple Weight: 1.7631 g
asured Free Space: -2.400 cc STP
alysis Mode: Equilibration

Date: 4/15/92 Time:
Saturation Pressure: 644.52 mmHg
Evacuation Time: 1.0 min
Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	2.5572	sq. m/g
Slope:	1.478300	
Y-Intercept:	0.003334	
C:	444.417480	
Vm:	0.674931	
Correlation Coefficient:	9.9957e-001	

BET Single Point Surface Area: 2.8883 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.29	0.649	*
0.1226	79.05	0.758	*
0.1952	125.79	0.845	*
0.2677	172.56	0.927	*
0.3403	219.35	1.007	*

Gemini 2360 V1.03
Instrument ID:

ple ID: 5-40 Date: 4/14/92 Time:
ple Weight: 1.4637 g Saturation Pressure: 641.58 mmHg
asured Free Space: -1.968 cc STP Evacuation Time: 1.0 min
lysis Mode: Equilibration Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	3.7126	sq. m/g
Slope:	1.020571	
Y-Intercept:	-0.000034	
C:	-3034.035156	
Vm:	0.979876	
Correlation Coefficient:	9.9940e-001	

BET Single Point Surface Area: 4.2034 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.13	0.968	*
0.1226	78.65	1.122	*
0.1951	125.19	1.243	*
0.2676	171.71	1.356	*
0.3401	218.23	1.464	*

Gemini 2360 V1.03
Instrument ID:

nple ID: 6-40
nple Weight: 1.8720 g
asured Free Space: -2.556 cc STP
alysis Mode: Equilibration

Date: 4/14/92 Time:
Saturation Pressure: 641.58 mmHg
Evacuation Time: 1.0 min
Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	3.3206 sq. m/g
Slope:	1.139905
Y-Intercept:	0.001118
C:	1020.947815
Vm:	0.876407
Correlation Coefficient:	9.9949e-001

BET Single Point Surface Area: 3.7565 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.13	0.855	*
0.1226	78.67	0.996	*
0.1951	125.19	1.106	*
0.2676	171.71	1.208	*
0.3402	218.24	1.309	*

Gemini 2360 V1.03
Instrument ID:

le ID: [redacted]Ø TP7-40
mple Weight: 1.7680 g
asured Free Space: -2.362 cc STP
ysis Mode: Equilibration

Date: 4/14/92 Time:
Saturation Pressure: 641.58 mmHg
Evacuation Time: 1.0 min
Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	3.3910	sq. m/g
Slope:	1.116066	
Y-Intercept:	0.001268	
C:	881.472351	
Vm:	0.894988	
Correlation Coefficient:	9.9943e-001	

BET Single Point Surface Area: 3.8318 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.12	0.869	*
0.1226	78.65	1.015	*
0.1951	125.18	1.129	*
0.2676	171.68	1.234	*
0.3401	218.20	1.335	*

Gemini 2360 V1.03
Instrument ID:

nple ID: 1+40-10
nple Weight: 2.0540 g
evious Free Space: -2.294 cc STP
alysis Mode: Equilibration

Date: 4/15/92 Time:
Saturation Pressure: 644.52 mmHg
Evacuation Time: 1.0 min
Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	1.3540	sq. m/g
Slope:	2.819154	
Y-Intercept:	-0.020868	
C:	-134.094803	
Vm:	0.357362	
Correlation Coefficient:	9.9881e-001	

BET Single Point Surface Area: 1.5478 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.28	0.388	*
0.1226	79.05	0.438	*
0.1952	125.79	0.473	*
0.2677	172.56	0.506	*
0.3404	219.40	0.539	*

Gemini 2360 V1.03
Instrument ID:

ple ID: 3+40-10
ple Weight: 2.0424 g
asured Free Space: -2.809 cc STP
rlysis Mode: Equilibration

Date: 4/15/92 Time:
Saturation Pressure: 644.52 mmHg
Evacuation Time: 1.0 min
Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	1.4428	sq. m/g
Slope:	2.611534	
Y-Intercept:	0.014624	
C:	179.581268	
Vm:	0.380784	
Correlation Coefficient:	9.9975e-001	

BET Single Point Surface Area: 1.6236 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.29	0.353	*
0.1226	79.05	0.416	*
0.1952	125.81	0.468	*
0.2678	172.59	0.518	*
0.3402	219.29	0.566	*

Gemini 2360 V1.03
Instrument ID:

mple ID: 4†40-10
mple Weight: 2.1763 g
asured Free Space: -4.763 cc STP
alysis Mode: Equilibration

Date: 4/15/92 Time:
Saturation Pressure: 644.52 mmHg
Evacuation Time: 1.0 min
Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	1.5869	sq. m/g
Slope:	2.386122	
Y-Intercept:	0.001539	
C:	1551.781250	
Vm:	0.418820	
Correlation Coefficient:	9.9950e-001	

BET Single Point Surface Area: 1.7966 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.30	0.410	*
0.1226	79.04	0.478	*
0.1952	125.80	0.529	*
0.2677	172.54	0.578	*
0.3404	219.37	0.626	*

Gemini 2360 V1.03
Instrument ID:

ple ID: 5-10+40 TP
ple Weight: 1.3279 g
asured Free Space: -1.791 cc STP
rlysis Mode: Equilibration

Date: 4/14/92 Time:
Saturation Pressure: 641.58 mmHg
Evacuation Time: 1.0 min
Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area: 4.2880 sq. m/g
Slope: 0.883840
Y-Intercept: -0.000235
C: -3757.968262
Vm: 1.131727
Correlation Coefficient: 9.9935e-001

BET Single Point Surface Area: 4.8549 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.13	1.119	*
0.1226	78.65	1.299	*
0.1951	125.19	1.440	*
0.2676	171.71	1.567	*
0.3402	218.26	1.691	*

Gemini 2360 V1.03
Instrument ID:

nple ID: 6-10-+40
nple Weight: 1.7742 g
asured Free Space: -4.152 cc STP
alysis Mode: Equilibration

Date: 4/14/92 Time:
Saturation Pressure: 641.58 mmHg
Evacuation Time: 1.0 min
Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	1.9347 sq. m/g
Slope:	1.960320
Y-Intercept:	-0.001914
C:	-1023.289673
Vm:	0.510619
Correlation Coefficient:	9.9918e-001

BET Single Point Surface Area: 2.1897 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.13	0.506	*
0.1226	78.65	0.590	*
0.1951	125.20	0.653	*
0.2677	171.72	0.709	*
0.3402	218.24	0.763	*

Gemini 2360 V1.03
Instrument ID:

ple ID: 7-10-40 Date: 4/14/92 Time:
ple Weight: 1.7288 g Saturation Pressure: 641.58 mmHg
asured Free Space: -2.354 cc STP Evacuation Time: 1.0 min
rlysis Mode: Equilibration Equilibration Time: 5 sec

BET Multipoint Surface Area Report

Surface Area:	2.4326	sq. m/g
Slope:	1.554585	
Y-Intercept:	0.002950	
C:	527.977722	
Vm:	0.642040	
Correlation Coefficient:	9.9954e-001	

BET Single Point Surface Area: 2.7490 sq. m/g

Analysis Log

Relative Pressure	Pressure (mmHg)	Vol. Adsorbed (cc/g STP)	Surface Area Point
0.0501	32.13	0.619	*
0.1226	78.66	0.724	*
0.1951	125.19	0.806	*
0.2676	171.71	0.882	*
0.3402	218.24	0.958	*

APPENDIX B

PETROGRAPHIC ANALYSES OF RIFLE AND SHIPROCK SEDIMENTS

PETROGRAPHIC DESCRIPTIONS OF SEDIMENT SAMPLES FROM RIFLE, CO AND SHIPROCK, NM

for

JACOBS ENGINEERING GROUP INC.

completed by

DANIEL LARSEN, GEOLOGICAL CONSULTANT

MAY 19, 1992

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SUMMARY OF PETROGRAPHIC DESCRIPTIONS AND QUANTITATIVE ANALYSES

Six thin section grain mounts of three sediment samples (coarse and fine grained fraction of each sample) from both Rifle, CO and Shiprock, NM were described for their petrographic components and point-counted for modal analysis. Descriptive terminology used is largely taken from Folk (1980) and Blatt (1982). The method of modal analysis is adapted from Ingersoll and others (1984). Three-hundred points were counted on each slide of the fine grained fraction in order to estimate the volume percent of the various components. Only 124 to 285 points per slide of the coarse grained fraction were obtained due to the large size of grains relative to the size of the thin section. Up to 180 points were counted on each slide in order estimate the number of grains with substantial clay- and fine silt-sized coatings.

The gross composition of samples from Rifle is similar to that of the Shiprock samples. Both are largely composed of various quartz grains, sedimentary rock fragments, plagioclase and alkali feldspars, and other rock fragments. The Rifle samples are proportionally dominated by quartz and sedimentary rock fragments. The Shiprock samples contain comparatively less quartz and sedimentary rock fragments but more alkali feldspar, granitic/gneissic fragments, and volcanic rock fragments.

Quartz grains include mildly undulose and coarsely polycrystalline varieties. The mildly undulose grains generally contain numerous inclusion trails and are subangular to rounded. The polycrystalline grains commonly contain fine inclusions between subgrains and are generally subangular. The sedimentary rock fragments are mostly siltstone and very fine to coarse grained sandstone with clay matrices and/or calcite or dolomite cement. Other sedimentary rock fragments include micritic to medium crystalline limestone, clear to clay-rich chert, and iron oxide-cemented fine grained sandstone. Most sedimentary rock fragments are subrounded to rounded. Plagioclase grains are identified by polysynthetic twinning and/or intragrain zoning. Most are at least partially replaced by smectite or illite, although the fine grained fraction of both samples contains numerous unaltered oscillatory-zoned grains. The grains are generally angular to subrounded. Alkali feldspar grains are identified by the tartan twinning habit of microcline and exsolution lamellae of albitic plagioclase within most grains. Again, most grains are partially to completely replaced by smectite or illite. The grains are generally subangular to rounded. Volcanic rock fragments in the Rifle samples are predominantly basaltic lavas and silicic (rhyolite) lavas and tuffs. The grains are subangular to subrounded. In the Shiprock samples, intermediate composition (andesite and dacite) lavas and

silicic lavas and tuffs predominate. Grains in the coarse fraction of the Shiprock samples are generally angular to subrounded, but those in the fine fraction are subrounded to rounded. The granitic/gneissic rock fragments include quartz and feldspar grains similar to those described above with sparse interstitial muscovite, biotite, or chlorite. In addition, the Rifle samples include numerous fragments of a plagioclase-pyroxene-(Fe-Ti oxide) intrusive rock. The granitic/gneissic grains are angular to subrounded. Metamorphic rock fragments are sparse in most samples, but include quartz schist, metasedimentary rocks, and, less commonly, sillimanite and kyanite schist. Other grains include organic chunks, biotite and muscovite flakes, and heavy mineral grains (pyroxene, amphibole, Fe-Ti oxides, etc.).

Coatings on grains are remnants of their origin in sedimentary rock fragments. A complete gradation is observed between grains with partial coatings of clay- and silt-sized material to those completely surrounded by clay, silt, and sand grains (sedimentary rock fragments). The composition of the clay- and silt-sized fraction forming grain coatings appears to be the same as that forming the matrix of most sedimentary rock fragments. Between the two sample sites, the Rifle samples appear to contain proportionally more grains with greater than 25 per cent coating than the Shiprock samples. Moreover, the proportion of clay- and silt-rich sedimentary rock fragments in the Rifle samples appears to be greater than that in the Shiprock samples. Note that the type of material coating grains in sediment from the two sites is largely the same.

QUANTITATIVE ANALYSIS OF SEDIMENT SAMPLES

COUNTING DATA

SAMPLE	Qt	Pt	Kt	Sc	Scc	Ss	So	V	OTHER	TOTAL
RIFLE										
TP5+40-10	81	14	22	79	27	3	8	14	6	254
TP6+40-10	111	20	55	43	9	11	3	16	10	278
TP7+40-10	90	11	35	79	20	11	13	19	7	285
TP5-40	124	31	34	65	19	3	8	8	8	300
TP6-40	93	20	46	86	13	4	11	14	13	300
TP7-40	115	14	33	79	22	3	15	8	11	300
SHIPROCK										
TP1+40-10	73	5	18	13	9	10	5	4	1	138
TP3+40-10	79	11	50	17	2	4	2	11	2	178
TP4+40-10	54	3	15	32	5	4	5	5	1	124
TP1-40	158	33	51	17	2	6	1	28	4	300
TP3-40	138	35	68	25	3	4	3	20	4	300
TP4-40	165	28	43	27	7	7	1	17	5	300

SAMPLE	St	G	M	V	TOTAL
RFLTP5+40-10	193	11	3	14	221
RFLTP6+40-10	85	52	16	16	169
RFLTP7+40-10	165	30	15	19	229
RFLTP5-40	186	17	1	8	212
RFLTP6-40	150	3	23	14	190
RFLTP7-40	170	8	4	8	190
SHPTP1+40-10	58	13	0	4	75
SHPTP3+40-10	49	21	0	11	81
SHPTP4+40-10	72	8	3	5	88
SHPTP1-40	47	5	3	28	83
SHPTP3-40	81	20	3	20	124
SHPTP4-40	80	23	2	17	122

SAMPLE	CLEAN	COAT	SED.	TOTAL
RFLTP5+40-10	28	17	85	130
RFLTP6+40-10	91	39	50	180
RFLTP7+40-10	35	35	43	113
RFLTP5-40	50	28	72	150
RFLTP6-40	51	27	72	150
RFLTP7-40	38	44	68	150
SHPTP1+40-10	63	4	25	92
SHPTP3+40-10	94	10	18	122
SHPTP4+40-10	41	2	27	70
SHPTP1-40	94	34	22	150
SHPTP3-40	99	26	25	150
SHPTP4-40	93	20	37	150

PERCENTAGES

SAMPLE	Qt	Pt	Kt	Sc	Scc	Ss	So	V	OTHER	TOTAL
RIFLE										
TP5+40-10	31.9	5.5	8.7	31.1	10.6	1.2	3.1	5.5	2.4	100.0
TP6+40-10	39.9	7.2	19.8	15.5	3.2	4.0	1.1	5.8	3.6	100.0
TP7+40-10	31.6	3.9	12.3	27.7	7.0	3.9	4.6	6.7	2.5	100.0
TP5-40	41.3	10.3	11.3	21.7	6.3	1.0	2.7	2.7	2.7	100.0
TP6-40	31.0	6.7	15.3	28.7	4.3	1.3	3.7	4.7	4.3	100.0
TP7-40	38.3	4.7	11.0	26.3	7.3	1.0	5.0	2.7	3.7	100.0
SHIPROCK										
TP1+40-10	52.9	3.6	13.0	9.4	6.5	7.2	3.6	2.9	0.7	100.0
TP3+40-10	44.4	6.2	28.1	9.6	1.1	2.2	1.1	6.2	1.1	100.0
TP4+40-10	43.5	2.4	12.1	25.8	4.0	3.2	4.0	4.0	0.8	100.0
TP1-40	52.7	11.0	17.0	5.7	0.7	2.0	0.3	9.3	1.3	100.0
TP3-40	46.0	11.7	22.7	8.3	1.0	1.3	1.0	6.7	1.3	100.0
TP4-40	55.0	9.3	14.3	9.0	2.3	2.3	0.3	5.7	1.7	100.0

SAMPLE	St	G	M	V	TOTAL
RFLTP5+40-10	87.3	5.0	1.4	6.3	100.0
RFLTP6+40-10	50.3	30.8	9.5	9.5	100.0
RFLTP7+40-10	72.1	13.1	6.6	8.3	100.0
RFLTP5-40	87.7	8.0	0.5	3.8	100.0
RFLTP6-40	78.9	1.6	12.1	7.4	100.0
RFLTP7-40	89.5	4.2	2.1	4.2	100.0
SHPTP1+40-10	77.3	17.3	0.0	5.3	100.0
SHPTP3+40-10	60.5	25.9	0.0	13.6	100.0
SHPTP4+40-10	81.8	9.1	3.4	5.7	100.0
SHPTP1-40	56.6	6.0	3.6	33.7	100.0
SHPTP3-40	65.3	16.1	2.4	16.1	100.0
SHPTP4-40	65.6	18.9	1.6	13.9	100.0

SAMPLE	CLEAN	COAT	SED.	TOTAL
RFLTP5+40-10	21.5	13.1	65.4	100.0
RFLTP6+40-10	50.6	21.7	27.8	100.0
RFLTP7+40-10	31.0	31.0	38.1	100.0
RFLTP5-40	33.3	18.7	48.0	100.0
RFLTP6-40	34.0	18.0	48.0	100.0
RFLTP7-40	25.3	29.3	45.3	100.0
SHPTP1+40-10	68.5	4.3	27.2	100.0
SHPTP3+40-10	77.0	8.2	14.8	100.0
SHPTP4+40-10	58.6	2.9	38.6	100.0
SHPTP1-40	62.7	22.7	14.7	100.0
SHPTP3-40	66.0	17.3	16.7	100.0
SHPTP4-40	62.0	13.3	24.7	100.0

Symbols and Abbreviations:

Qt: total quartz (free grains, sedimentary, granitic/gneissic, and metamorphic rock fragments).

Pt: total plagioclase (free grains, sedimentary, granitic/gneissic, and metamorphic rock fragments).

Kt: total alkali feldspar (free grains, sedimentary, granitic/gneissic, and metamorphic rock fragments).

Sc: clay and silt matrix of sedimentary rock fragments.

Scc: carbonate rock fragments and cements.

Ss: chert (microcrystalline quartz).

So: other rock fragments and mineral grains in sedimentary rock fragments.

St: total sedimentary rock fragments.

V: volcanic rock fragments.

G: granitic rock fragments.

M: metamorphic rock fragments.

Clean: less than 25 % coating.

Coat: greater than 25 % coating.

Sed.: clay- and silt-rich sedimentary rock fragments.

PETROGRAPHIC DESCRIPTIONS OF SEDIMENT SAMPLES

RFLTP5+40-10: medium to very coarse grained sand

Quartz: 1) monocrystalline with undulose extinction and inclusion trails, 2) coarsely polycrystalline; both commonly have silt-clay coating, angular to rounded grains.

Plagioclase: polysynthetic twinned, clay replacement, albite-replacement?, common silt-clay coatings, angular to subrounded grains.

Alkali feldspar: 1) tartan twinning (microcline) and exsolution lamellae, 2) orthoclase; some clay or carbonate replacement, common silt and clay coatings, subrounded to subangular grains.

Sedimentary rock fragments: 1) siltstone and fine to coarse grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite cement (note some are matrix-rich), 2) micritic and silty micritic limestone (one with an echinoderm plate), 3) chert; some carbonate grains with partial silt-clay coatings, subrounded to rounded grains.

Granitic/gneissic fragments: 1) intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and biotite, muscovite, or chlorite, 2) intergrowth of oscillatory-zoned plagioclase and pyroxene; partial silt-clay coatings, subrounded to subangular grains.

Volcanic rock fragments: 1) basalt - oriented plagioclase and pyroxene grains in a black background with sparse pyroxene and plagioclase microphenocrysts, 2) silicic - sparse quartz, plagioclase, Fe-Ti oxides, and hornblende microphenocrysts in a microcrystalline background; with or without partial silt-clay coatings, subrounded to subangular.

Metamorphic rock fragments: metasedimentary and quartz-muscovite schist, subangular, partial silt-clay coatings.

Other: black organic chunk, Fe-Ti oxide, brown biotite.

RFLTP6+40-10: medium to very coarse grained sand

Quartz: 1) monocrystalline with undulose extinction and inclusion trails, 2) coarsely polycrystalline, 3) monocrystalline with straight extinction; with and without partial silt-clay coatings, angular to rounded grains.

Plagioclase: polysynthetic twinned, extensive clay replacement, albite-replacement?, with and without partial silt-clay coatings, rounded to subrounded grains.

Alkali feldspar: 1) tartan twinning (microcline) and exsolution lamellae, 2) orthoclase; some clay replacement, albite? replacement of some microcline grains, with and without partial silt-clay coatings, subrounded to subangular grains.

Sedimentary rock fragments: 1) siltstone and fine to coarse grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite cement, 2) micritic and silty micritic limestone, 3) dirty chert or mixed micrite and chert; with and without partial silt-clay coatings on chert and carbonate grains, subrounded to subangular grains.

Granitic/gneissic fragments: 1) intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and biotite, muscovite, or chlorite, 2) intergrowth of oscillatory-zoned plagioclase and pyroxene; few grains with partial silt-clay coatings, subrounded to subangular grains.

Volcanic rock fragments: 1) basalt - oriented plagioclase and pyroxene grains in a black background with sparse pyroxene and plagioclase microphenocrysts, 2) silicic - sparse quartz, plagioclase, Fe-Ti oxides, and hornblende microphenocrysts in a microcrystalline background; with or without partial silt-clay coatings, subrounded to subangular.

Metamorphic rock fragments: 1) quartz-feldspar schist with or without biotite, amphibole, muscovite, chlorite, sillimanite, epidote, and kyanite; partial silt-clay coatings, subangular.

Other: black organic chunk, Fe-Ti oxide, brown biotite.

RFLTP7+40-10: coarse to very coarse grained sand

Quartz: 1) monocrystalline with undulose extinction and inclusion trails, 2) coarsely polycrystalline; both commonly have silt-clay coating, angular to rounded grains.

Plagioclase: polysynthetic twinned, clay replacement (some grains completely replaced), albite-replacement?, common silt-clay coatings, angular to subrounded grains.

Alkali feldspar: tartan twinning (microcline) and exsolution lamellae, some clay replacement, common silt-clay coatings, subrounded to subangular grains.

Sedimentary rock fragments: 1) siltstone and fine to coarse grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite cement, 2) micritic and silty micritic limestone, 3) chert; subrounded to rounded grains.

Granitic/gneissic fragments: intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and biotite, muscovite, or chlorite, partial silt-clay coatings, subrounded to subangular grains.

Volcanic rock fragments: 1) basalt - oriented plagioclase, Fe-Ti oxide, and pyroxene grains in a black background with sparse pyroxene and plagioclase microphenocrysts, 2) silicic - sparse quartz and feldspar microphenocrysts in a microcrystalline background; with or without partial silt-clay coatings, subrounded to subangular.

Metamorphic rock fragments: metasedimentary and quartz-muscovite schist, subangular, partial silt-clay coatings.

Other: chunk of organic debris.

RFLTP5-40: coarse silt to medium grained sand

Quartz: monocrystalline with undulose extinction, inclusion trails, with and without silt-clay coatings, angular to rounded grains.

Plagioclase: 1) complexly twinned, oscillatory zoned, unaltered grains 2) polysynthetic twinned, extensive clay replacement; with and without partial silt-clay coatings, angular to subrounded grains.

Alkali feldspar: 1) tartan twinning (microcline) and exsolution lamellae, 2) orthoclase; some clay replacement, albite? replacement of some orthoclase grains, with and without partial silt-clay coatings, subrounded to subangular grains.

Sedimentary rock fragments: 1) siltstone and fine grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite cement, 2) micritic and silty to sandy micritic limestone, 3) dirty and clear chert; with and without partial silt-clay coatings on chert and carbonate grains, rounded to angular grains.

Granitic/gneissic fragments: 1) intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and biotite, 2) intergrowth of oscillatory-zoned plagioclase and pyroxene; with or without partial silt-clay coatings, subrounded to subangular grains.

Volcanic rock fragments: 1) basalt - oriented plagioclase and pyroxene in a holocrystalline or black glassy background, 2) silicic - sparse quartz, plagioclase, and biotite microphenocrysts in a microcrystalline background; with or without partial silt-clay coatings, subrounded to subangular.

Metamorphic rock fragments: few quartz-muscovite schist.

Other: brown biotite, muscovite, Fe-Ti oxides.

RFLTP6-40: coarse silt to coarse grained sand

Quartz: 1) monocrystalline with undulose extinction and inclusion trails, 2) polycrystalline; with and without silt-clay coatings, angular to subrounded grains.

Plagioclase: 1)complexly twinned, oscillatory zoned, unaltered grains 2) polysynthetic twinned, extensive clay replacement; a few grains with red oxide fracture-fill and coatings, with and without partial silt-clay coatings, angular to subrounded grains.

Alkali feldspar: 1) tartan twinning (microcline) and exsolution lamellae, 2) orthoclase; some clay replacement, with and without partial silt-clay coatings, subrounded to subangular grains.

Sedimentary rock fragments: 1) siltstone and fine grained sandstone with quartz, feldspar, and rock fragments in a silt-clay or reddish-brown oxide matrix or calcite cement, 2) micritic and silty to sandy micritic limestone and dolomite, 3) dirty and clear chert; with and without partial silt-clay coatings on chert and carbonate grains, rounded to angular grains.

Granitic/gneissic fragments: 1) intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and biotite, 2) intergrowth of oscillatory-zoned plagioclase and pyroxene; with or without partial silt-clay coatings, subrounded to subangular grains.

Volcanic rock fragments: 1) basalt - oriented plagioclase and pyroxene in a holocrystalline or black glassy background, 2) silicic - sparse quartz, plagioclase, and biotite microphenocrysts in a microcrystalline background; with or without partial silt-clay coatings, subrounded to subangular.

Metamorphic rock fragments: quartz-muscovite and quartz-biotite schist, with or without partial silt-clay coatings, subangular to subrounded.

Other: black organic chunk, brown biotite, muscovite, Fe-Ti oxide, hornblende, glass shards with partial clay replacement.

RFLTP7-40: coarse silt to medium grained sand

Quartz: monocrystalline with undulose extinction, inclusion trails, with and without silt-clay coatings, angular to subrounded grains.

Plagioclase: 1) complexly twinned, oscillatory zoned, unaltered grains 2) polysynthetic twinned, extensive clay replacement; with and without partial silt-clay coatings, angular to subrounded grains.

Alkali feldspar: 1) tartan twinning (microcline) and exsolution lamellae, 2) orthoclase; some clay replacement, with and without partial silt-clay coatings, subrounded to subangular grains.

Sedimentary rock fragments: 1) siltstone and fine grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite cement, 2) micritic and silty to sandy micritic limestone, 3) dirty and clear chert; with and without partial silt-clay coatings on chert and carbonate grains, rounded to angular grains.

Granitic/gneissic fragments: 1) intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and biotite, 2) intergrowth of oscillatory-zoned plagioclase and pyroxene; with or without partial silt-clay coatings, subrounded to subangular grains.

Volcanic rock fragments: silicic - sparse quartz, plagioclase, and biotite microphenocrysts in a microcrystalline background; with or without partial silt-clay coatings, subrounded to subangular.

Metamorphic rock fragments: quartz-muscovite schist, partial silt-clay coatings, subangular.

Other: black organic chunk and brown biotite.

SHPTP1+40-10: coarse grained sand to pebbles

Quartz: 1) monocrystalline with undulose extinction and few inclusion trails, 2) coarsely polycrystalline with inclusion trails; most without silt-clay coatings, angular to rounded grains.

Plagioclase: polysynthetic twinned, vague zoning, partial clay replacement, without partial silt-clay coatings, angular to subangular grains.

Alkali feldspar: tartan twinning (microcline) and exsolution lamellae, some clay replacement, most without partial silt-clay coatings, subrounded to subangular grains.

Sedimentary rock fragments: 1) moderately to well sorted siltstone and fine grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite cement, 2) moderately to poorly sorted, silty to coarse grained sandstone with feldspar, quartz, and volcanic fragments, 3) dirty and clear chert, 4) micritic limestone and one fossil; rounded to angular grains.

Granitic/gneissic fragments: intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and biotite, generally without partial silt-clay coatings, angular to subangular grains.

Volcanic rock fragments: 1) silicic - sparse quartz and plagioclase microphenocrysts in a microcrystalline background, 2) intermediate - feldspar laths in a microcrystalline background, 3) basalt - aphyric black or brown vesicular glass; without partial silt-clay coatings, subrounded to angular.

Metamorphic rock fragments: quartz-muscovite schist, subrounded.

Other:

SHPTP3+40-10: medium to very coarse grained sand

Quartz: 1) monocrystalline with undulose extinction with inclusion trails, 2) coarsely polycrystalline with inclusion trails; most without silt-clay coatings, angular to rounded grains.

Plagioclase: polysynthetic twinned, vague zoning, partial clay replacement, with or without partial silt-clay coatings, angular to subangular grains.

Alkali feldspar: 1) tartan twinning (microcline) and exsolution lamellae, 2) orthoclase; some clay replacement, most without partial silt-clay coatings, subrounded to subangular grains.

Sedimentary rock fragments: 1) moderately to well sorted siltstone and fine grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite or quartz cement, 2) moderately to poorly sorted, silty to coarse grained sandstone with feldspar, quartz, and volcanic fragments, 3) dirty and clear chert, 4) micritic limestone and one fossil; rounded to angular grains.

Granitic/gneissic fragments: intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and muscovite or hornblende, generally without partial silt-clay coatings, angular to subangular grains.

Volcanic rock fragments: 1) silicic - sparse quartz and plagioclase microphenocrysts in a microcrystalline background, 2) intermediate - feldspar laths in a microcrystalline background, 3) basalt - plagioclase and pyroxene microlites in a black or brown glass background; without partial silt-clay coatings, subrounded to angular.

Metamorphic rock fragments:

Other: organic chunk, a few black oxide? grains.

SHPTP4+40-10: coarse grained sand to pebbles

Quartz: 1) monocrystalline with undulose extinction with few inclusion trails, 2) coarsely polycrystalline with inclusion trails; most without silt-clay coatings, angular to rounded grains.

Plagioclase: polysynthetic twinned, vague zoning, partial clay replacement, with and without partial silt-clay coatings, angular to subangular grains.

Alkali feldspar: tartan twinning (microcline) and exsolution lamellae, some clay replacement, most without partial silt-clay coatings, subrounded to subangular grains.

Sedimentary rock fragments: 1) moderately to well sorted siltstone and fine grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite cement, 2) moderately to poorly sorted, silty to coarse grained sandstone with feldspar, quartz, and volcanic fragments, 3) dirty and clear chert, 4) medium grained iron oxide-cemented sandstone; rounded to angular grains.

Granitic/gneissic fragments: intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and biotite, generally without partial silt-clay coatings, angular to subangular grains.

Volcanic rock fragments: 1) silicic - sparse quartz and plagioclase microphenocrysts in a microcrystalline background, 2) intermediate - feldspar laths in a microcrystalline background; without partial silt-clay coatings, subrounded to angular.

Metamorphic rock fragments: quartz-muscovite metasediment, subrounded.

Other:

SHPTP1-40: coarse silt to medium grained sand

Quartz: 1) monocrystalline with undulose extinction and inclusion trails, 2) coarsely polycrystalline, with and without partial silt-clay coatings, subangular to rounded grains.

Plagioclase: 1) complexly twinned, oscillatory zoned, unaltered grains, 2) polysynthetic twinned, vague zoning, some clay replacement and albite? replacement; generally without partial silt-clay coatings, angular to subrounded grains.

Alkali feldspar: 1) tartan twinning (microcline) and exsolution lamellae, 2) orthoclase; extensive clay replacement, generally without partial silt-clay coatings, rounded to subangular grains.

Sedimentary rock fragments: 1) silty fine to medium grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite cement, 2) micritic to fine sparry limestone and a few fossils, 3) dirty and clear chert; with and without partial silt-clay coatings on chert and carbonate grains, rounded to subangular grains.

Granitic/gneissic fragments: intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and sparse muscovite; generally with partial silt-clay coatings, subrounded to angular grains.

Volcanic rock fragments: 1) intermediate - plagioclase and Fe-Ti oxide microlites in a microcrystalline background, 2) silicic - sparse quartz and plagioclase microphenocrysts in a microcrystalline background; generally without partial silt-clay coatings, subrounded to rounded.

Metamorphic rock fragments: few quartz-muscovite schist and one garnet amphibolite, subangular.

Other: pyroxene, amphibole, Fe-Ti oxides, reddish-brown organic chunks.

SHPTP3-40: coarse silt to medium grained sand

Quartz: 1) monocrystalline with undulose extinction and inclusion trails, 2) coarsely polycrystalline, with and without partial silt-clay coatings, subangular to rounded grains.

Plagioclase: 1) complexly twinned, oscillatory zoned, unaltered grains, 2) polysynthetic twinned, vague zoning, some clay replacement; generally without partial silt-clay coatings, angular to rounded grains.

Alkali feldspar: 1) tartan twinning (microcline) and exsolution lamellae, 2) orthoclase, some albite? replaced; minor to extensive clay replacement, generally without partial silt-clay coatings, rounded to subangular grains.

Sedimentary rock fragments: 1) silty fine to medium grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite cement, 2) micritic to fine sparry limestone and a few fossils, 3) dirty and clear chert 4) black oxide-cemented sandstone; with and without partial silt-clay coatings on chert and carbonate grains, rounded to subangular grains.

Granitic/gneissic fragments: intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and sparse muscovite; generally with partial silt-clay coatings, subrounded to angular grains.

Volcanic rock fragments: 1) intermediate - plagioclase and Fe-Ti oxide microlites in a microcrystalline background, 2) silicic - sparse quartz and plagioclase microphenocrysts in a microcrystalline background, 3) basalt - oriented plagioclase and Fe-Ti oxide microlites in a black background; generally without partial silt-clay coatings, subrounded to rounded.

Metamorphic rock fragments: few quartz-muscovite schist, subrounded to subangular.

Other: pyroxene, biotite, Fe-Ti oxides.

SHPTP4-40: coarse silt to medium grained sand

Quartz: 1) monocrystalline with undulose extinction and inclusion trails, 2) coarsely polycrystalline, with and without partial silt-clay coatings, subangular to rounded grains.

Plagioclase: 1) complexly twinned, oscillatory zoned, unaltered grains, 2) polysynthetic twinned, vague zoning, some clay replacement; generally without partial silt-clay coatings, angular to subrounded grains.

Alkali feldspar: 1) tartan twinning (microcline) and exsolution lamellae, 2) orthoclase; minor to extensive clay replacement, generally without partial silt-clay coatings, rounded to subangular grains.

Sedimentary rock fragments: 1) silty fine to medium grained sandstone with quartz, feldspar, and rock fragments in a silt and clay matrix or calcite cement, 2) micritic to fine sparry limestone and a few fossils, 3) dirty and clear chert; with and without partial silt-clay coatings on chert and carbonate grains, rounded to subangular grains.

Granitic/gneissic fragments: intergrowth of undulose to polycrystalline quartz with inclusion trails, clay-replaced plagioclase and microcline, and sparse muscovite; generally with partial silt-clay coatings, subrounded to angular grains.

Volcanic rock fragments: 1) intermediate - plagioclase and Fe-Ti oxide microlites in a microcrystalline background, 2) silicic - sparse quartz and plagioclase microphenocrysts in a microcrystalline background; generally without partial silt-clay coatings, subrounded to rounded.

Metamorphic rock fragments: few quartz-muscovite schist, subrounded to subangular.

Other: pyroxene, hornblende, Fe-Ti oxide.

LIST OF PHOTOMICROGRAPHS

1. RFLTP6+40-10, carbonate fragment, XP, 75x.
2. RFLTP6+40-10, sillimanite schist fragment, XP, 30x.
3. RFLTP6+40-10, quartz grain with 5 to 10% coating, PP, 75x.
4. RFLTP7+40-10, basalt, PP, 30x.
5. RFLTP7+40-10, plagioclase-rich granite (intrusive), XP, 30x.
6. RFLTP7+40-10, polycrystalline quartz, XP, 30x.
7. RFLTP7+40-10, grains with partial to complete coating, PP, 30x.
8. RFLTP5-40, grain with partial coating, PP, 150x.
9. SHPTP3+40-10, microcline (alkali feldspar), XP, 30x.
10. SHPTP1+40-10, quartz grain with < 5% coating, PP, 75x.
11. SHPTP4+40-10, sandstone rock fragment, PP, 75x.
12. SHPTP4+40-10, iron oxide-cemented sandstone fragment, PP, 30x.
13. SHPTP4+40-10, granitic rock fragment, XP, 75x.
14. SHPTP4+40-10, intermediate composition volcanic fragment, PP, 75x.
15. SHPTP4+40-10, undulose quartz grains, XP, 30x.
16. SHPTP4+40-10, calcite-cemented sandstone fragment, XP, 75x.
17. SHPTP3-40, chert (microcrystalline quartz), XP, 75x.
18. SHPTP3-40, orthoclase? with extensive clay replacement, XP, 150x.
19. SHPTP3-40, plagioclase with clay replacement, XP, 150x.
20. SHPTP3-40, grain with nearly complete coating, PP, 150x.
21. SHPTP4-40, plagioclase with oscillatory zoning, unaltered, XP, 75x.
22. SHPTP4-40, silicic volcanic fragment, PP, 150x.
23. SHPTP4-40, grain with partial coating, PP, 75x.
24. SHPTP4-40, carbonate fossil fragment, XP, 150x.

XP: cross-polarized light.
PP: plane-polarized light.
150x: magnification.

REFERENCES

Blatt, H., 1982, Sedimentary Petrology. W.H. Freeman and Co., New York, 564 p.

Folk, R.L., 1974, Petrology of Sedimentary Rocks. Hemphill, Austin, 182 p.

Ingersoll, R.V., T.F. Bullard, R.L. Ford, L.P. Grimm, J.D. Pickle, and S. Sares, 1984, The effect of grain size on detrital modes: a test of the Gazzi-Dickinson point-counting method. Journal of Sedimentary Petrology, vol. 54, p. 103-16.

APPENDIX C

X-RAY DIFFRACTION ANALYSES OF RIFLE AND SHIPROCK SEDIMENTS

Report On Jabcobs Engineering Sediments

Whole rock XRD of the Rifle, Colorado samples indicates the presence of quartz, plagioclase, calcite and some mica (illite?). Also some of the samples (esp. RFL-TP7 -40) contain either nitrammite or natrophosphate. The presence of these two minerals suggests contamination from fertilizers used in agricuture. Other techniques would have to be used (thin section, wet chemistry, etc.) for positive identification.

Whole rock XRD of the Shiprock, New Mexico samples indicates the presence of quartz, plagioclase, and calcite.

XRD of the fine fraction from the Rifle and Shiprock samples contain kaolinite, illite, and smectite. The samples from Rifle contain proportionately more illite than the Shiprock samples. The samples from Shiprock contain proportionately more smectite than the Rifle samples. Both sites have proportionately the same amount of kaolinite (table 1).

Table 1

40 FRACTION	Kaolinite	Illite(mica)	Smectite
RFLTP5	XX	XXX	XX
RFLTP6	XX	XX	XXX
RFLTP7	XX	XX	XX
SHPTP1	XX	XX	XXXX
SHPTP3	XX	X	XXX
SHPTP4	XX	X	XXX

The coarse fractions have similar relationships. Many of the grains in the coarse fraction are aggregates of clay, silt, and sand.

READING DEFRACTOGRAMS.
Black = air dried
Green = glycolated
Red = 300 degree centigrade
Blue = 500 degree centigrade

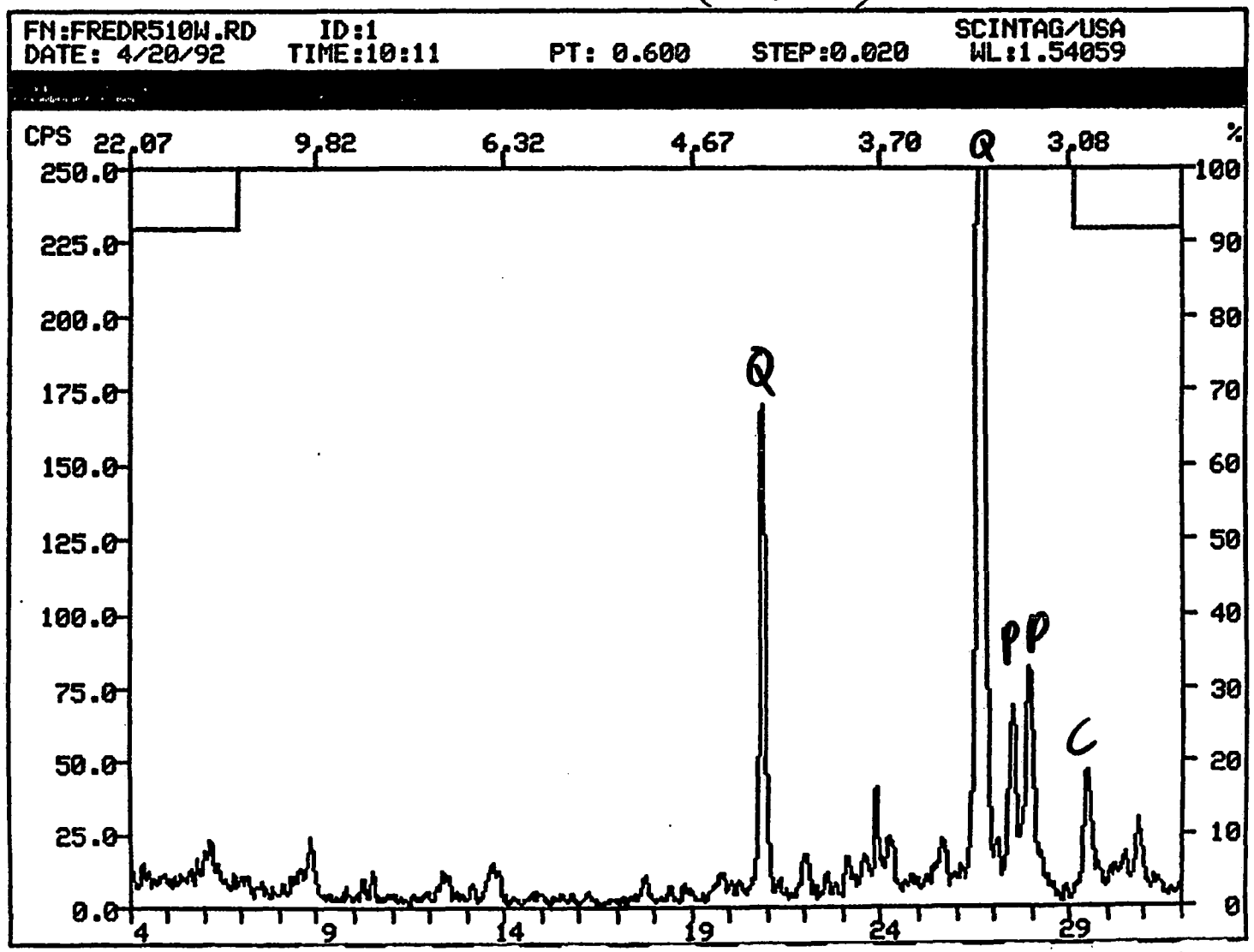
The defractograms for the whole rock samples are on two pages, which can be taped together to form one page.

Clay types intermixed – assoc. w/ sed. rock frags.

"Smectite" could be mixed-layer clay dominated by smectite

RFL 11 ...

RIFLE TP 5 (+40-10)



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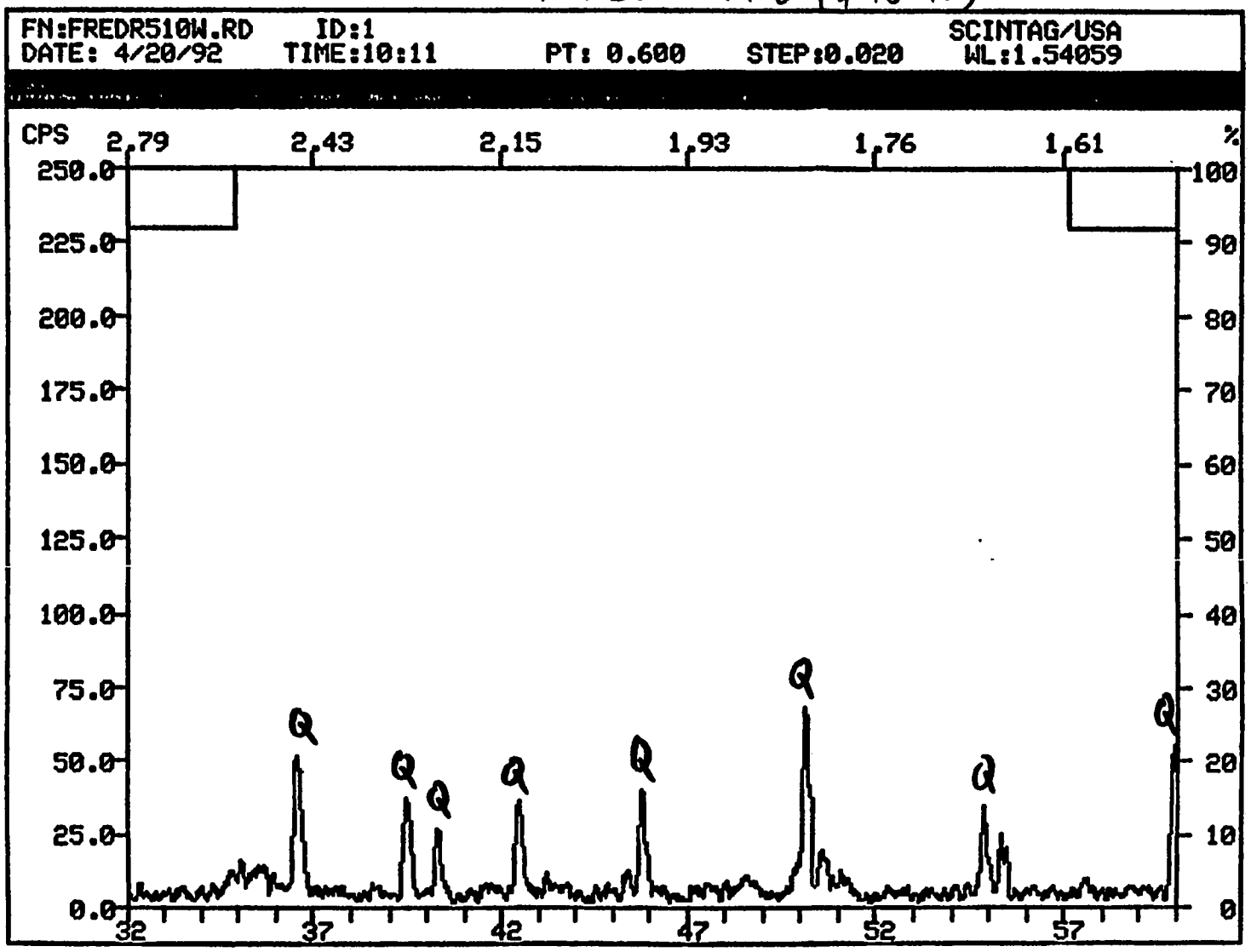
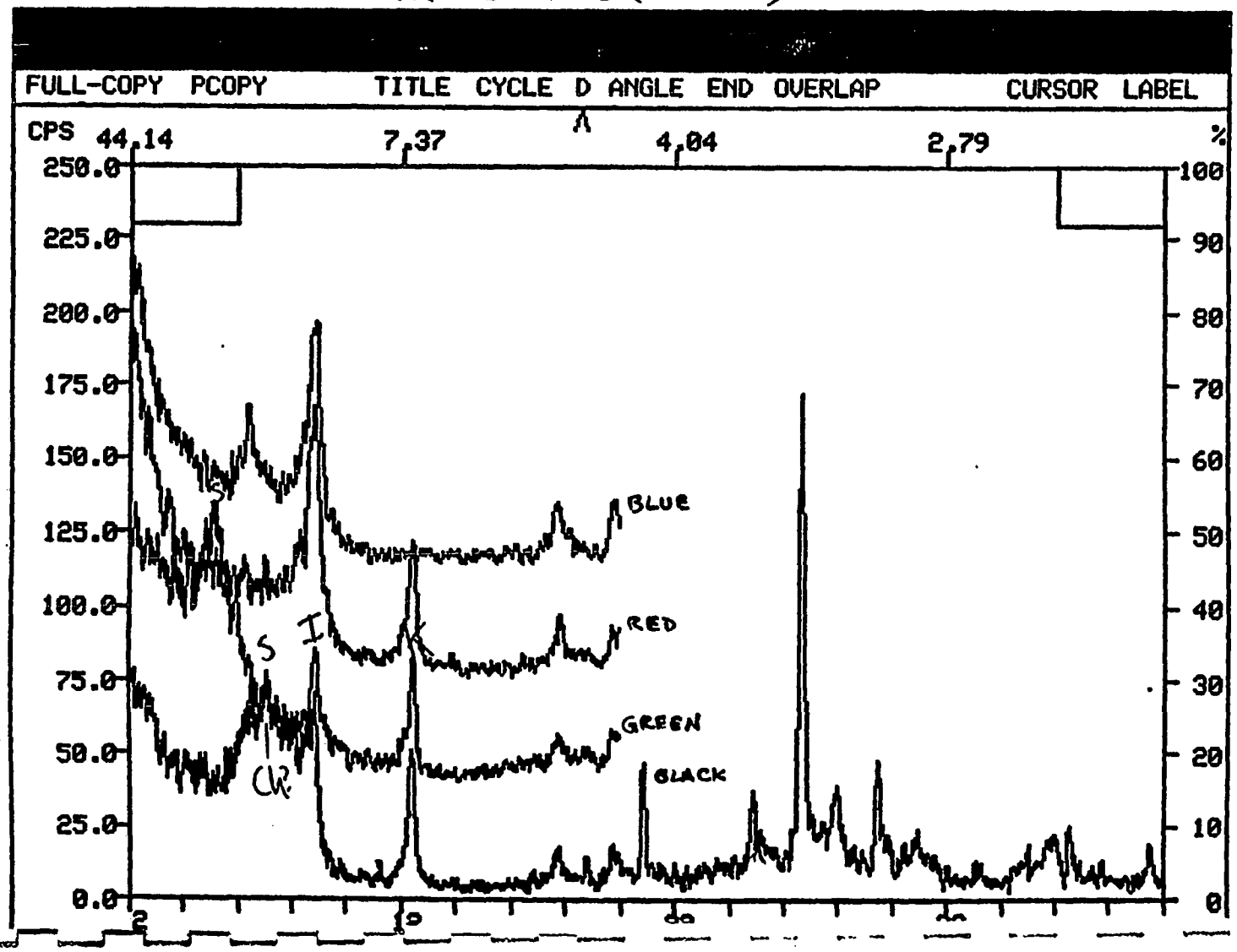


KFL IP 9 1 10-1

RIFLE TP5 (440-10)



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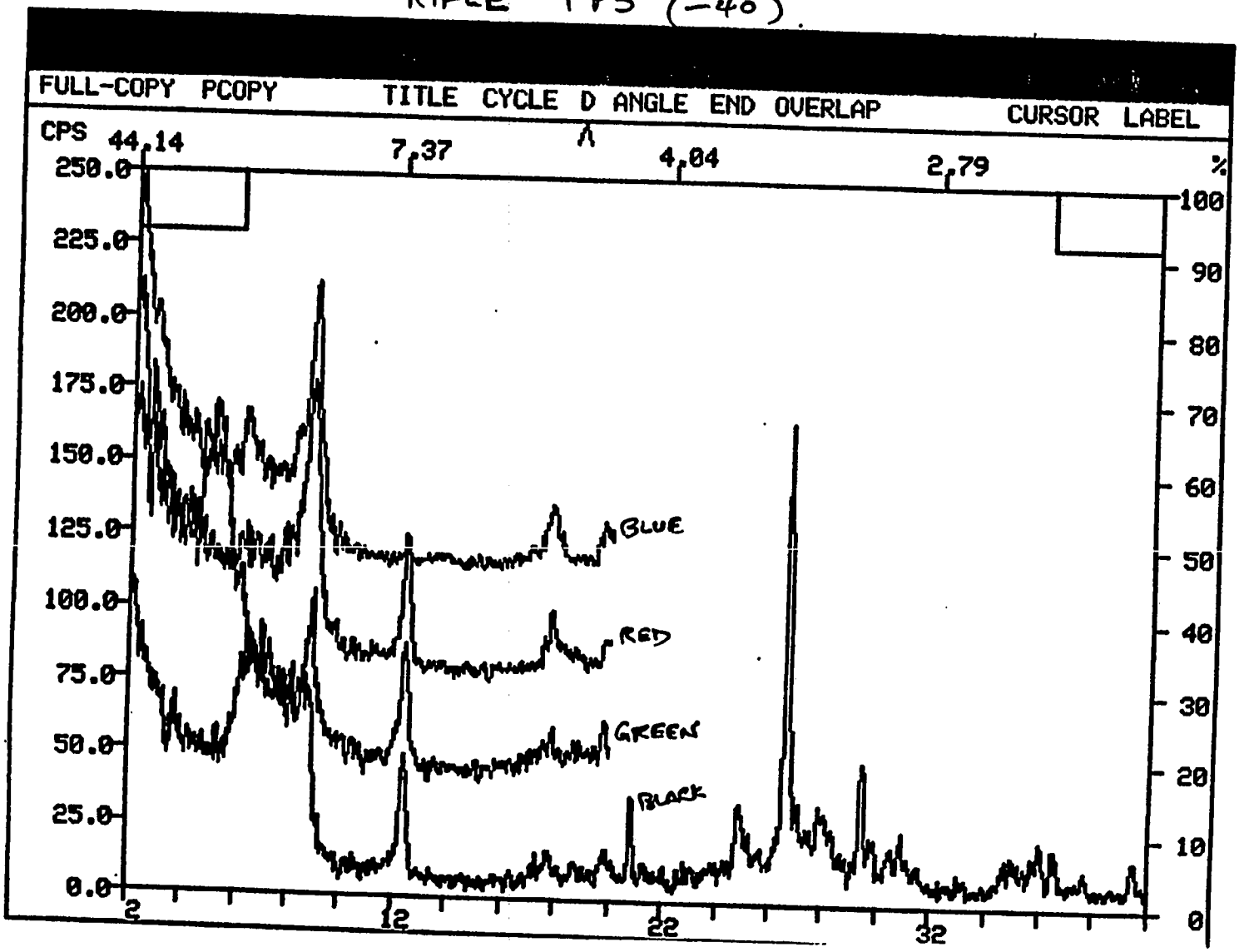
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0.0
100
90
80
70
60
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40
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0
2
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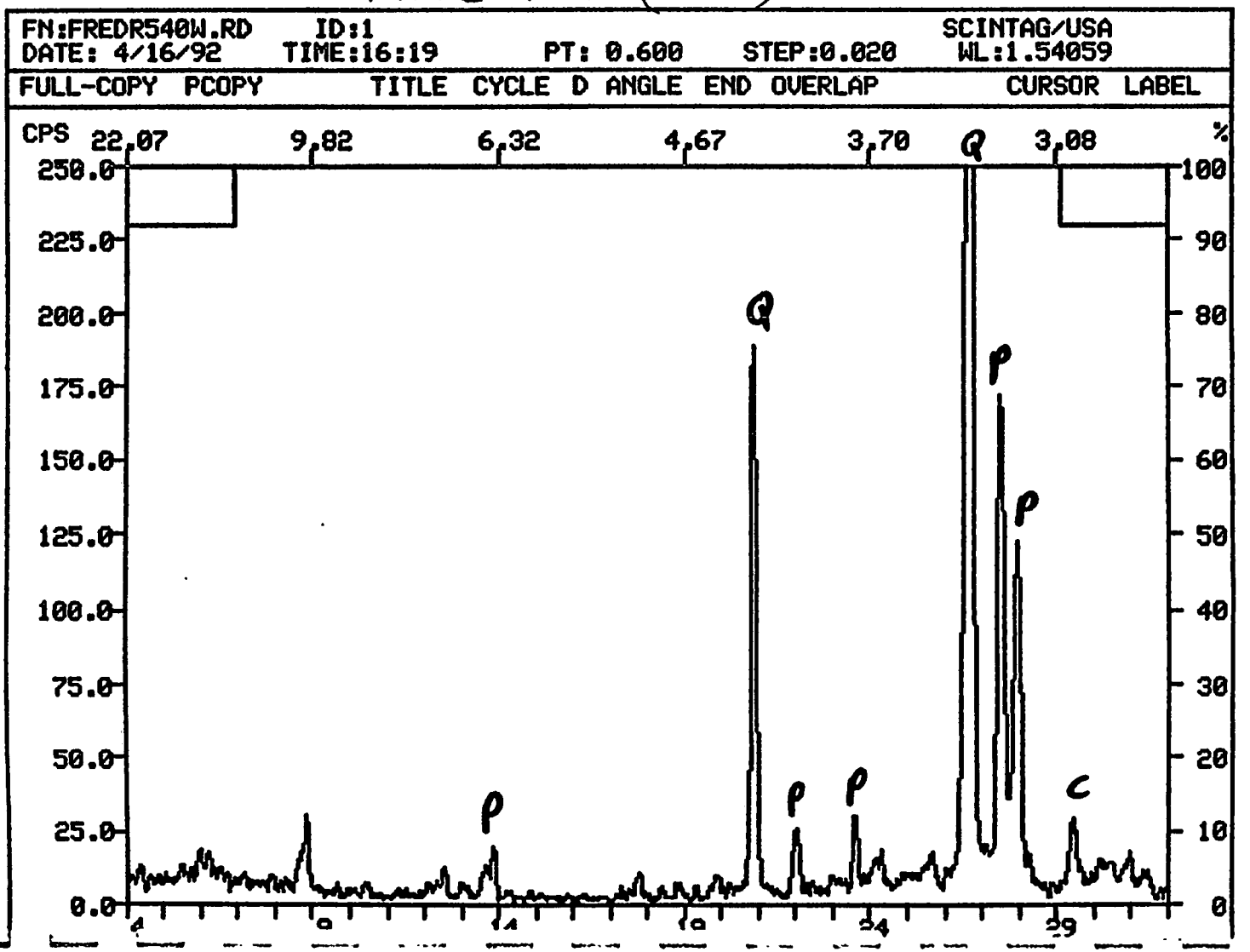
22
32
BLUE
RED
GREEN
BLACK

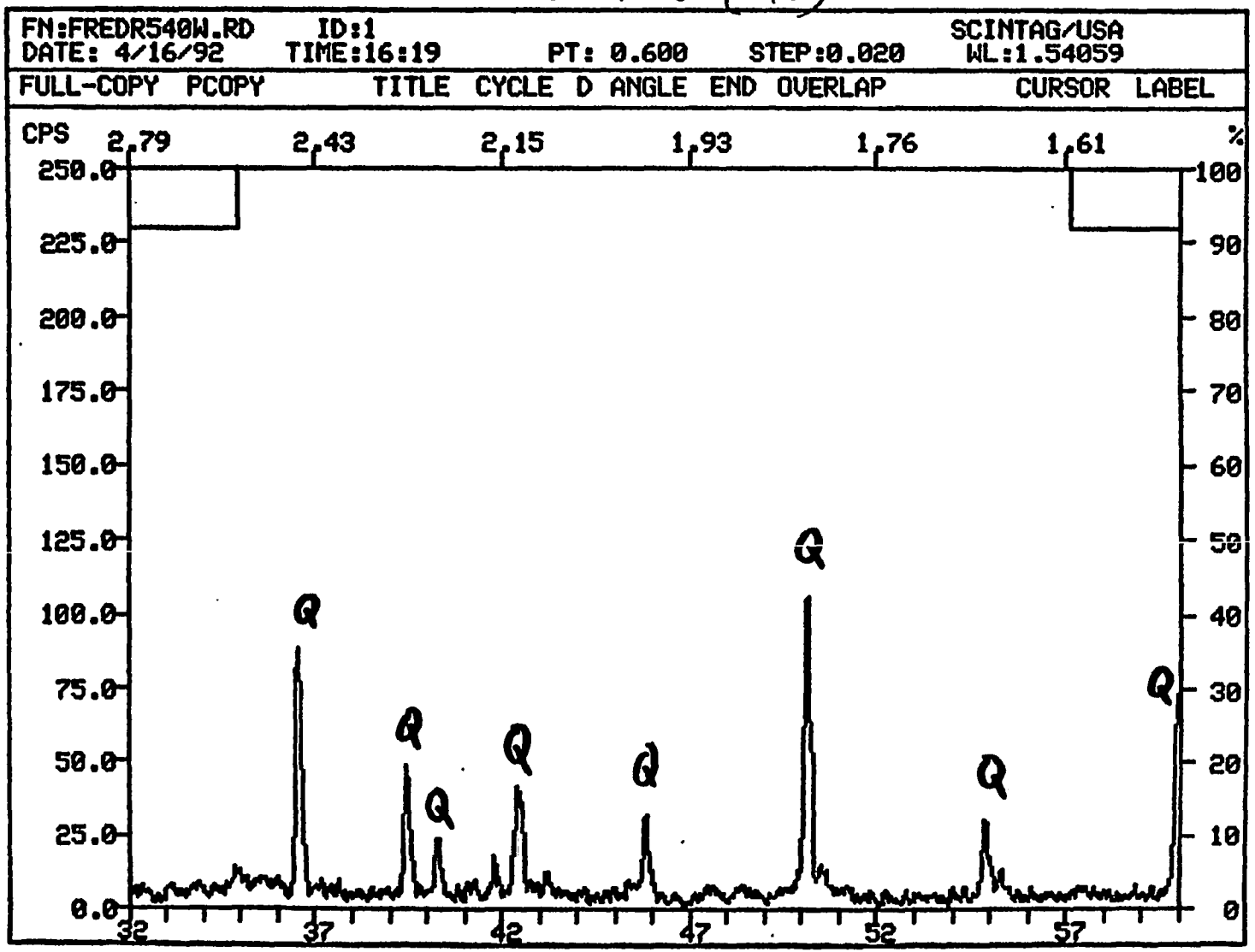
RFL TP5 -40

RIFLE TP5 (-40)



Good CC

RIFLE TP5 (-40)



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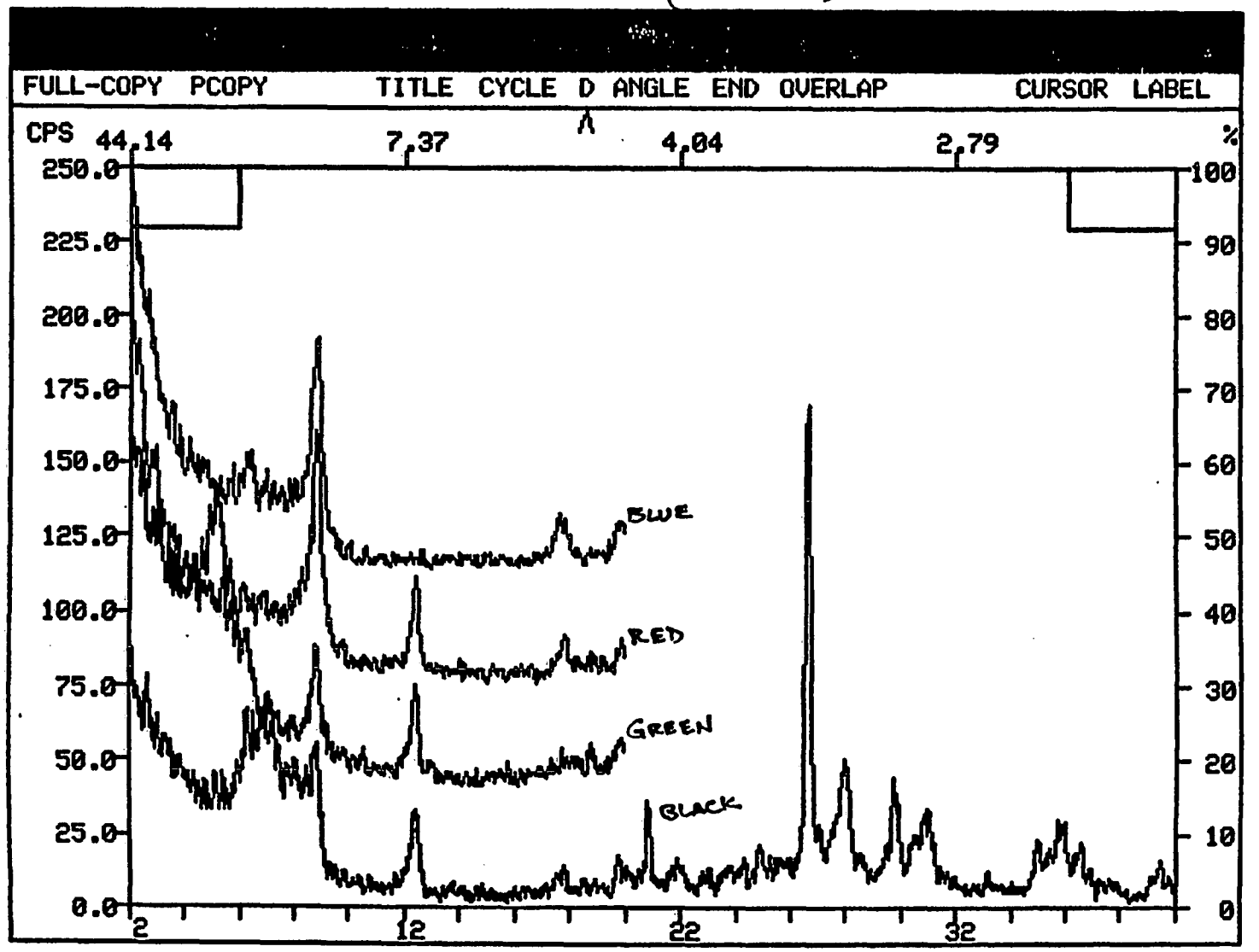

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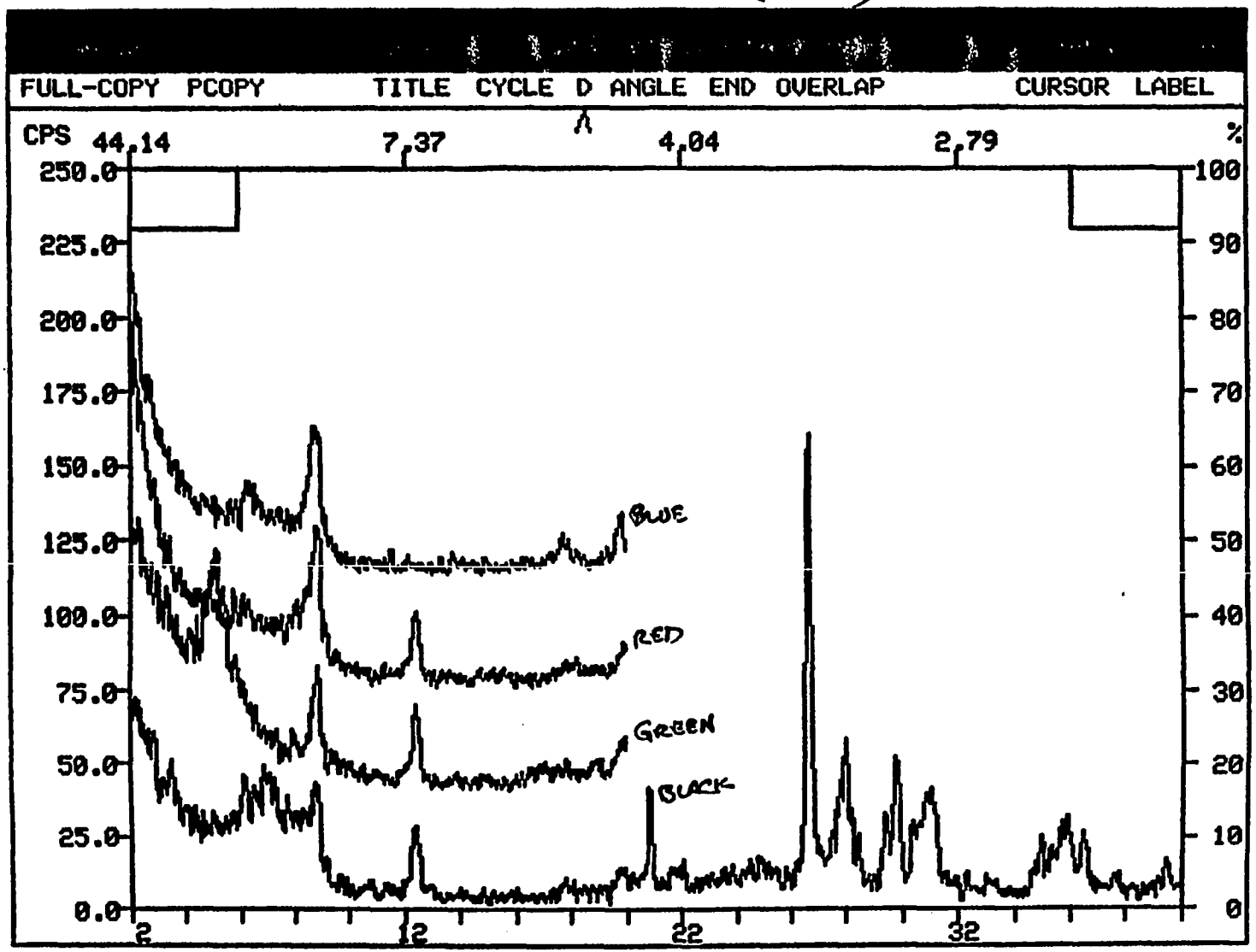
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150.0
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25.0
0.0
100
90
80
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10
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12
22
32
BLUE
RED
GREEN
BLACK

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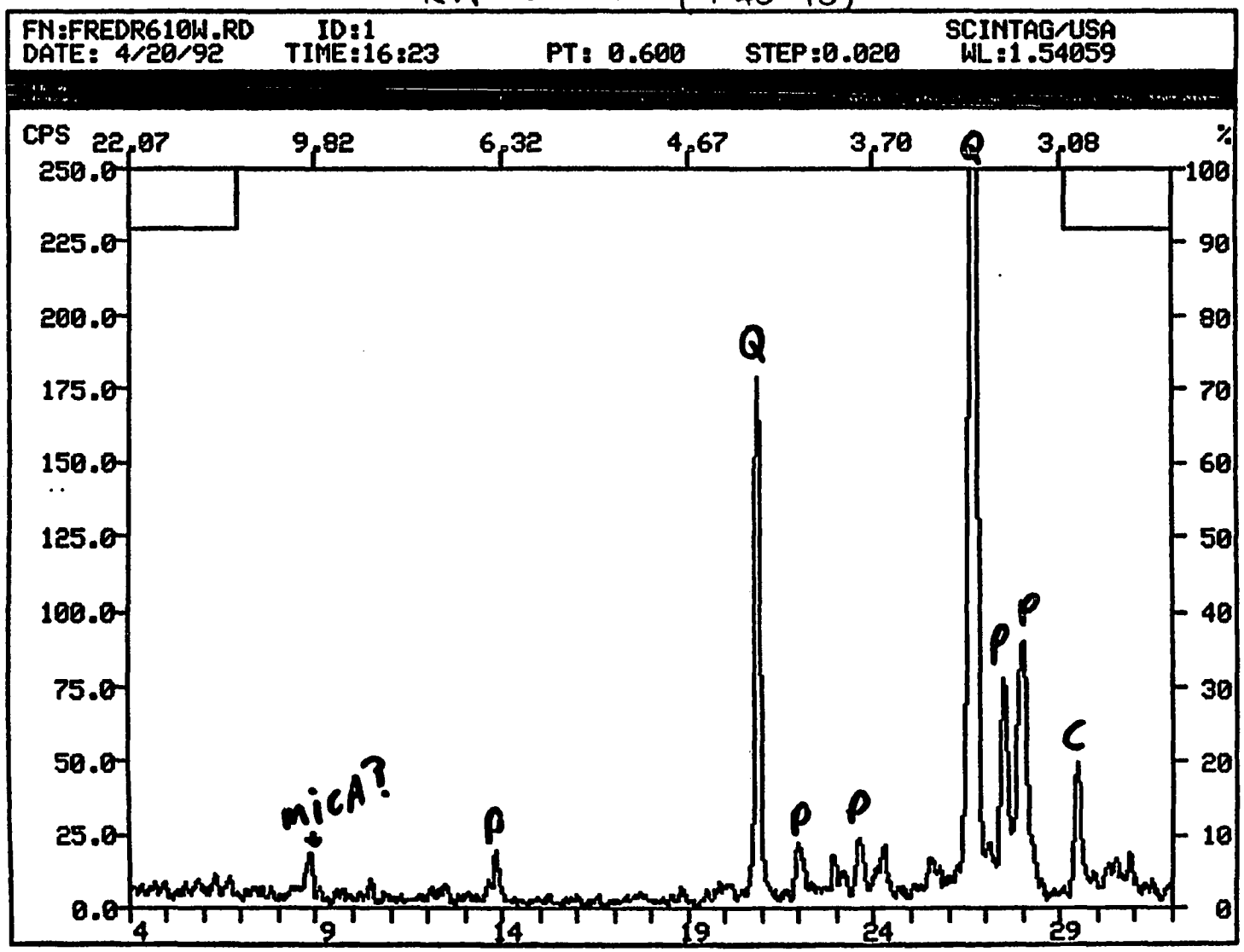

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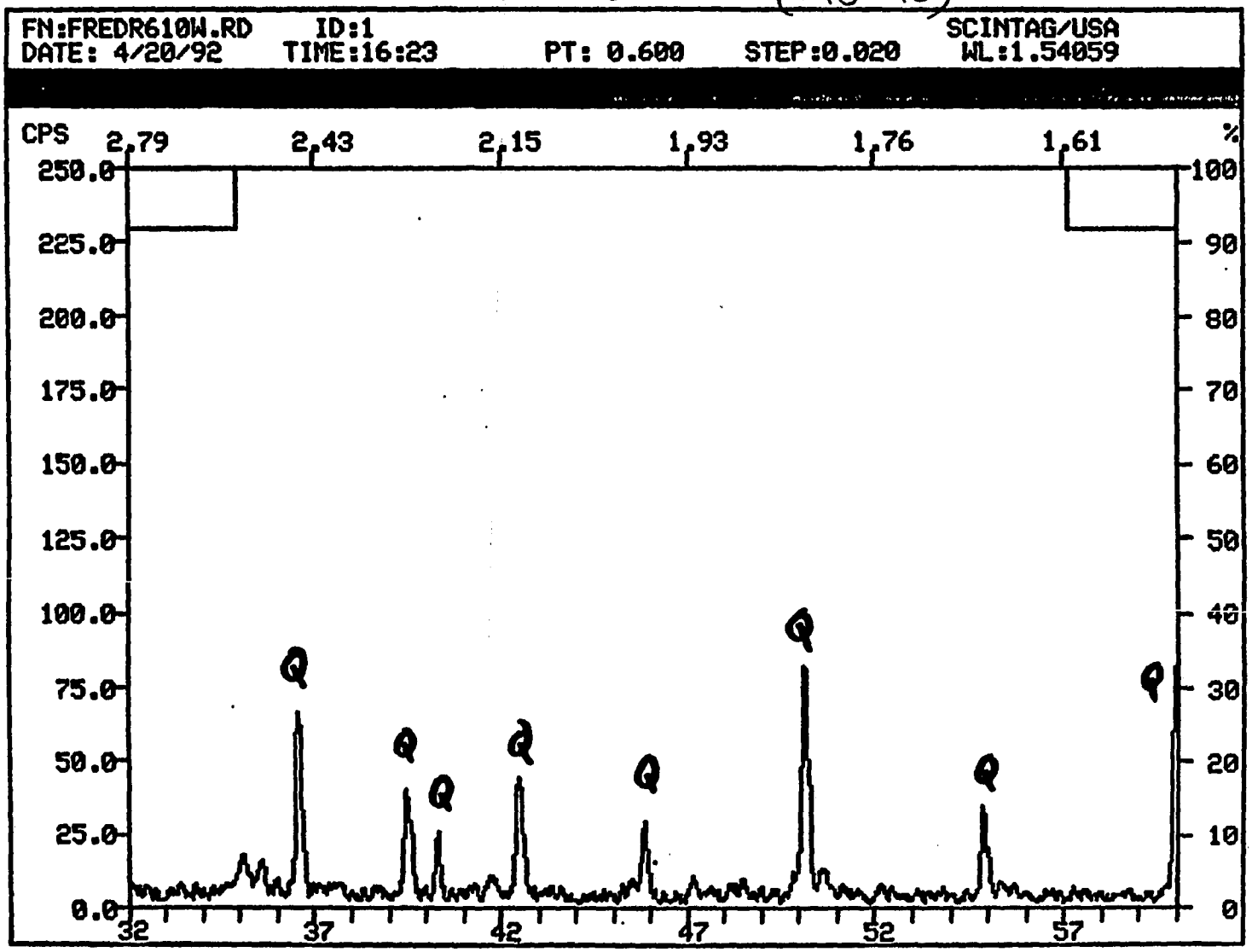

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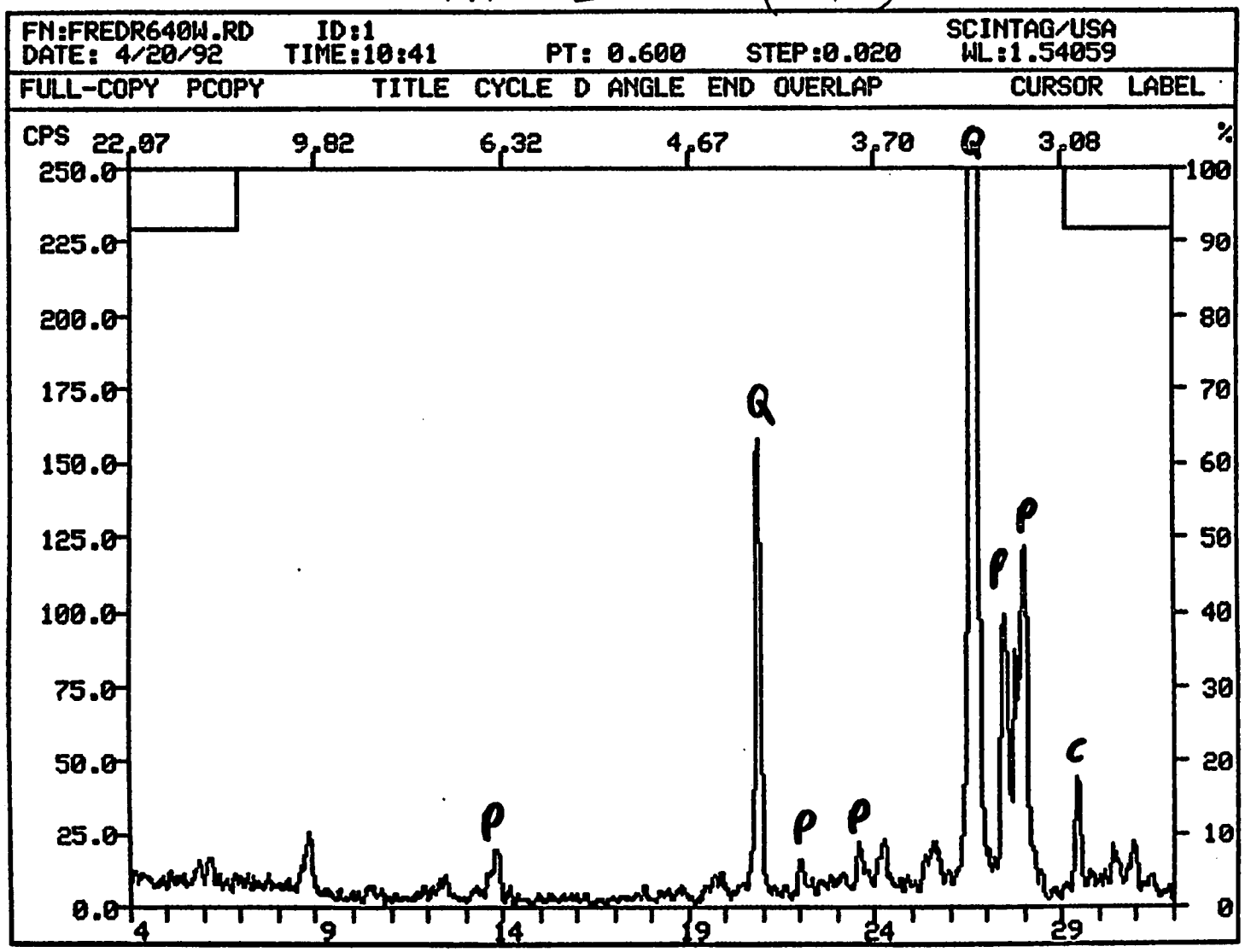
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3.70
3.08
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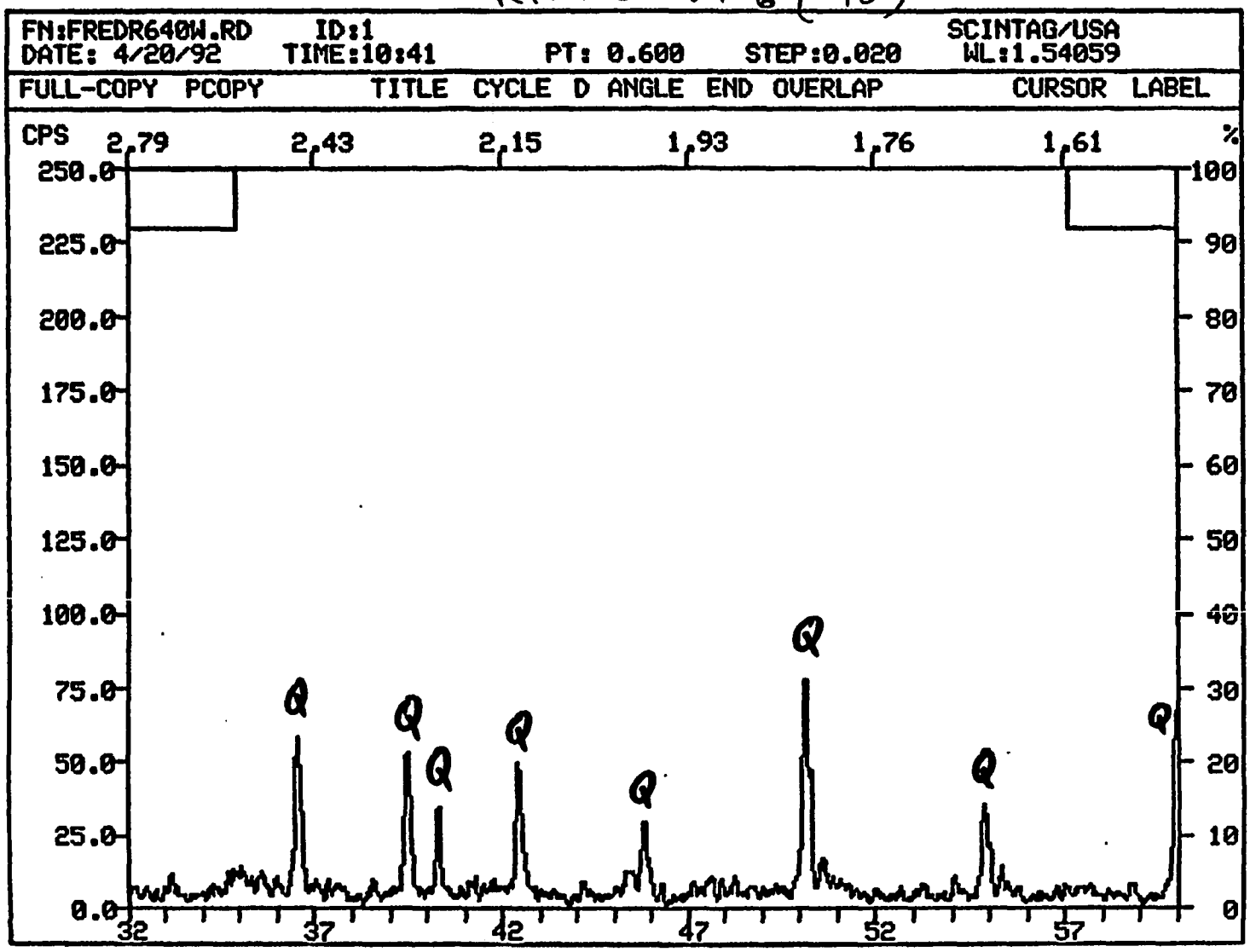
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
100
90
80
70
60
50
40
30
20
10
0
4
9
14
19
24
29
Q
Q
P
P
P
P
P
C

RIFLE TP6 (-40)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%
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2.15
1.93
1.76
1.61
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200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
100
90
80
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40
30
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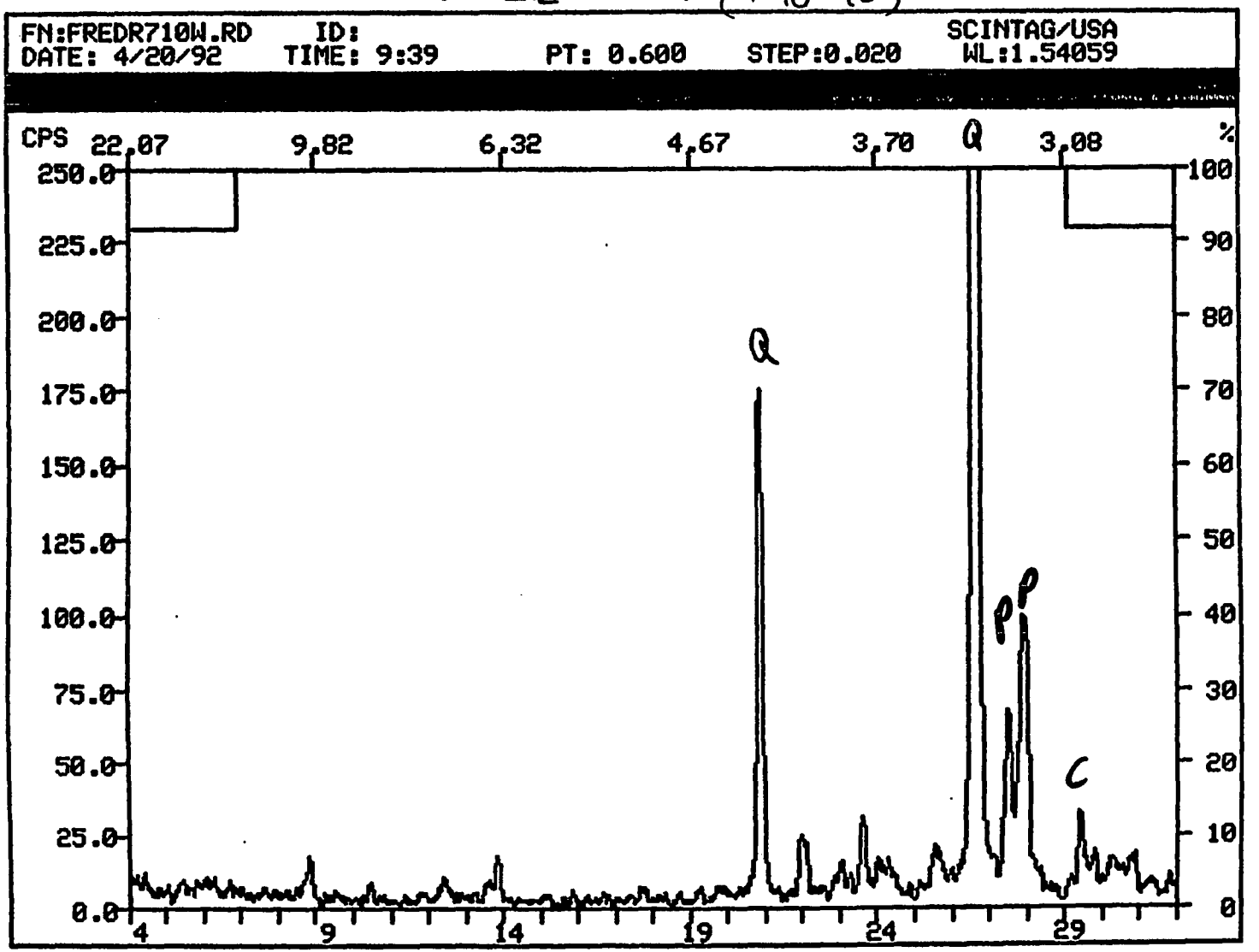
10
0
32
37
42
47
52
57
Q

RIFLE TP 7 (+40-10)



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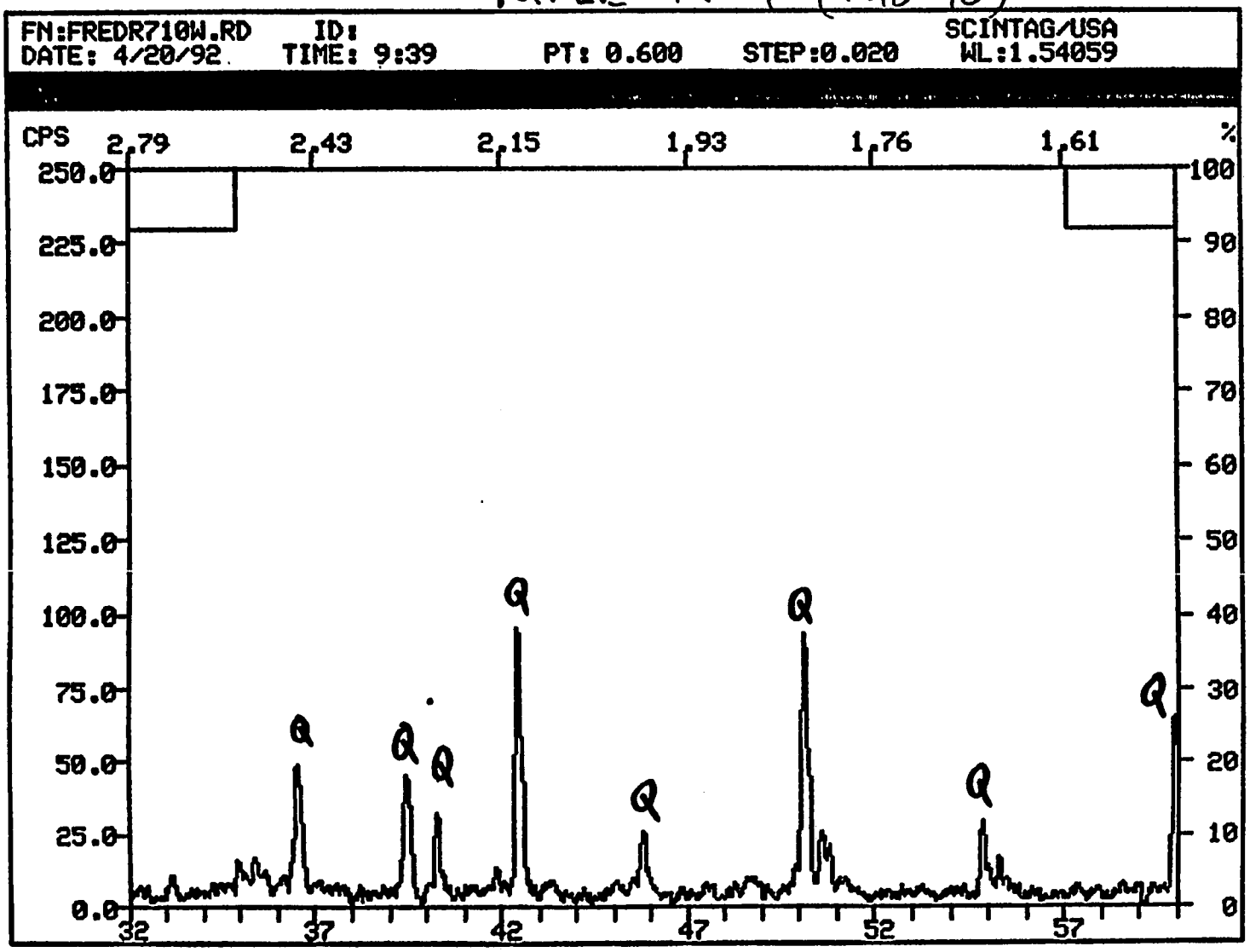

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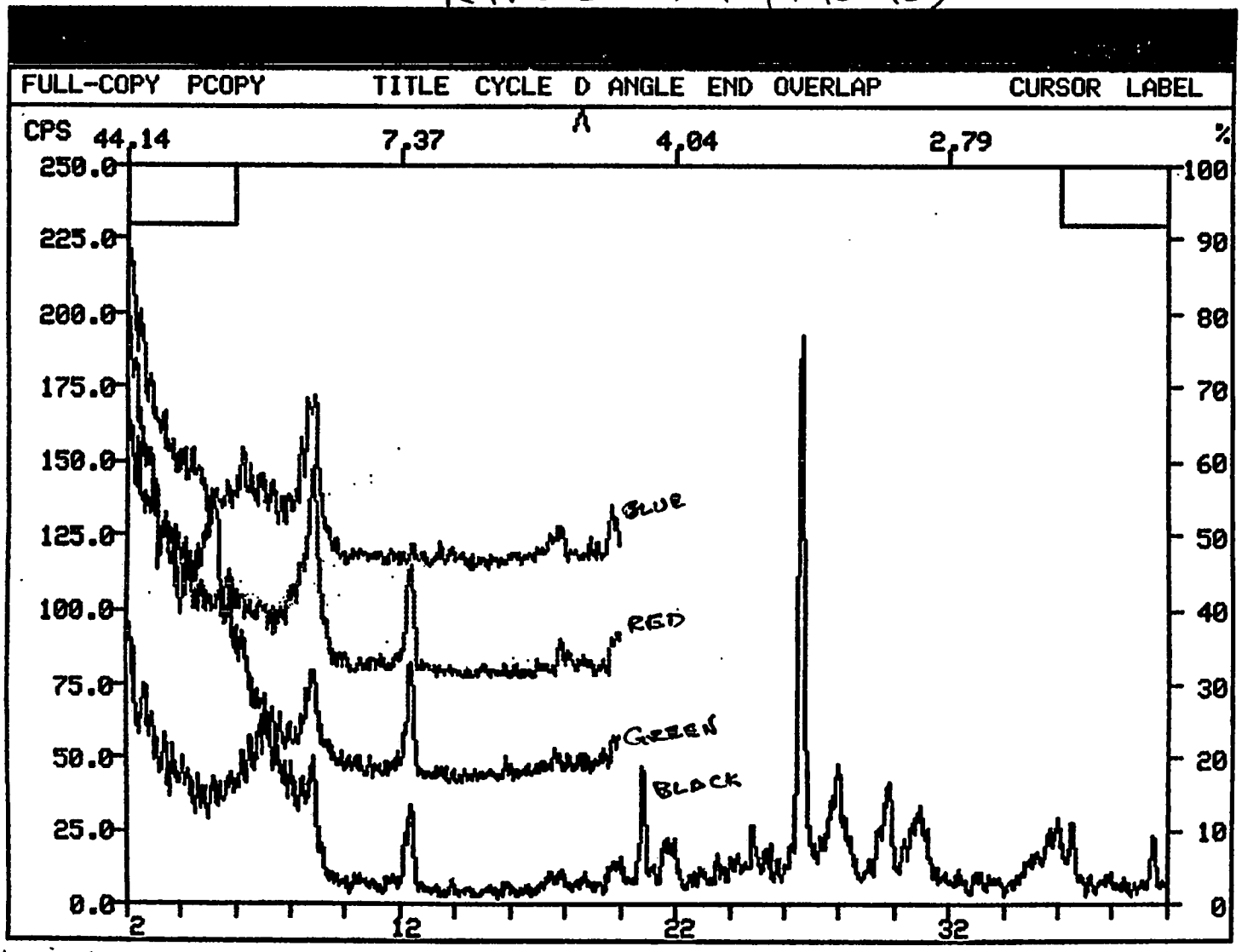

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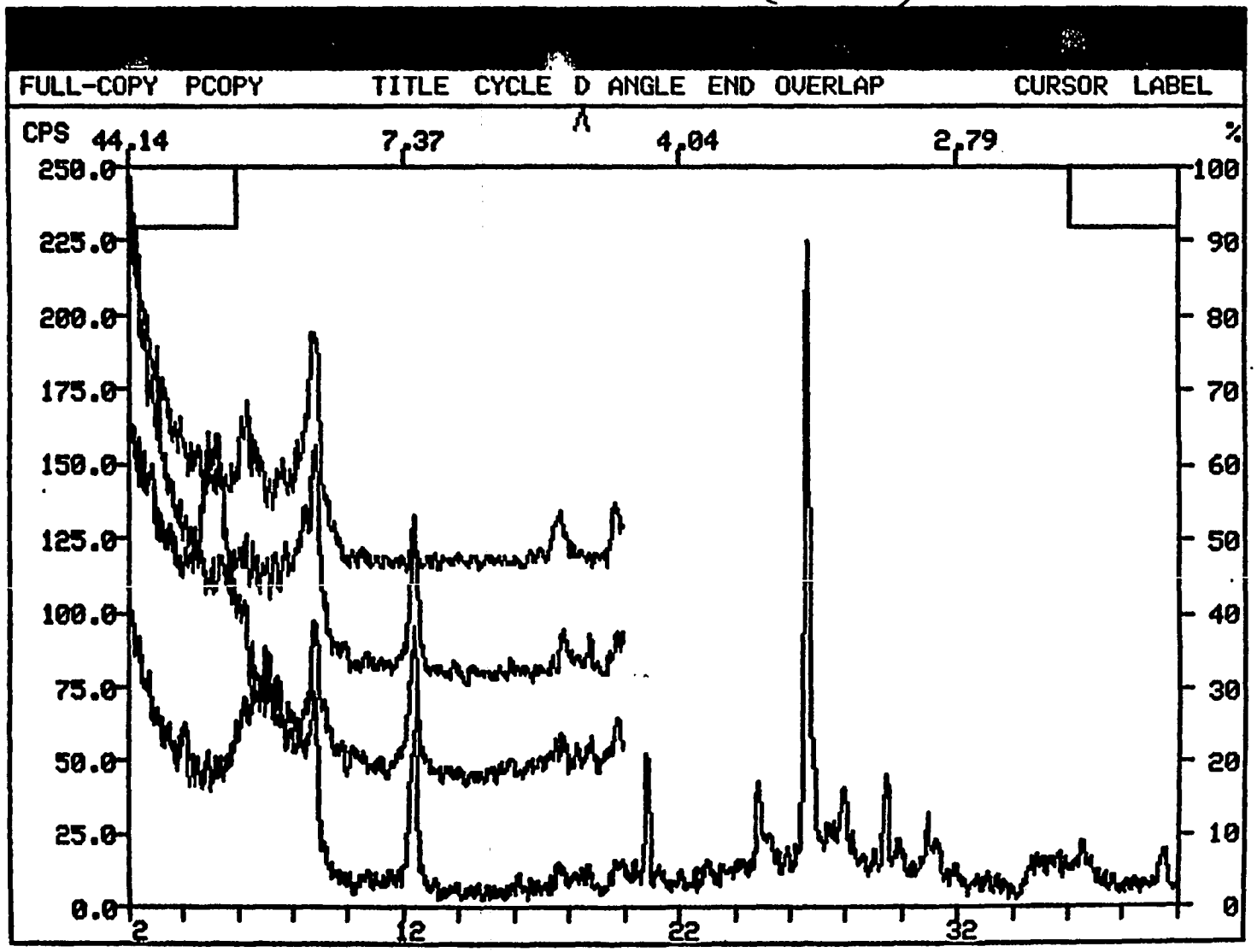

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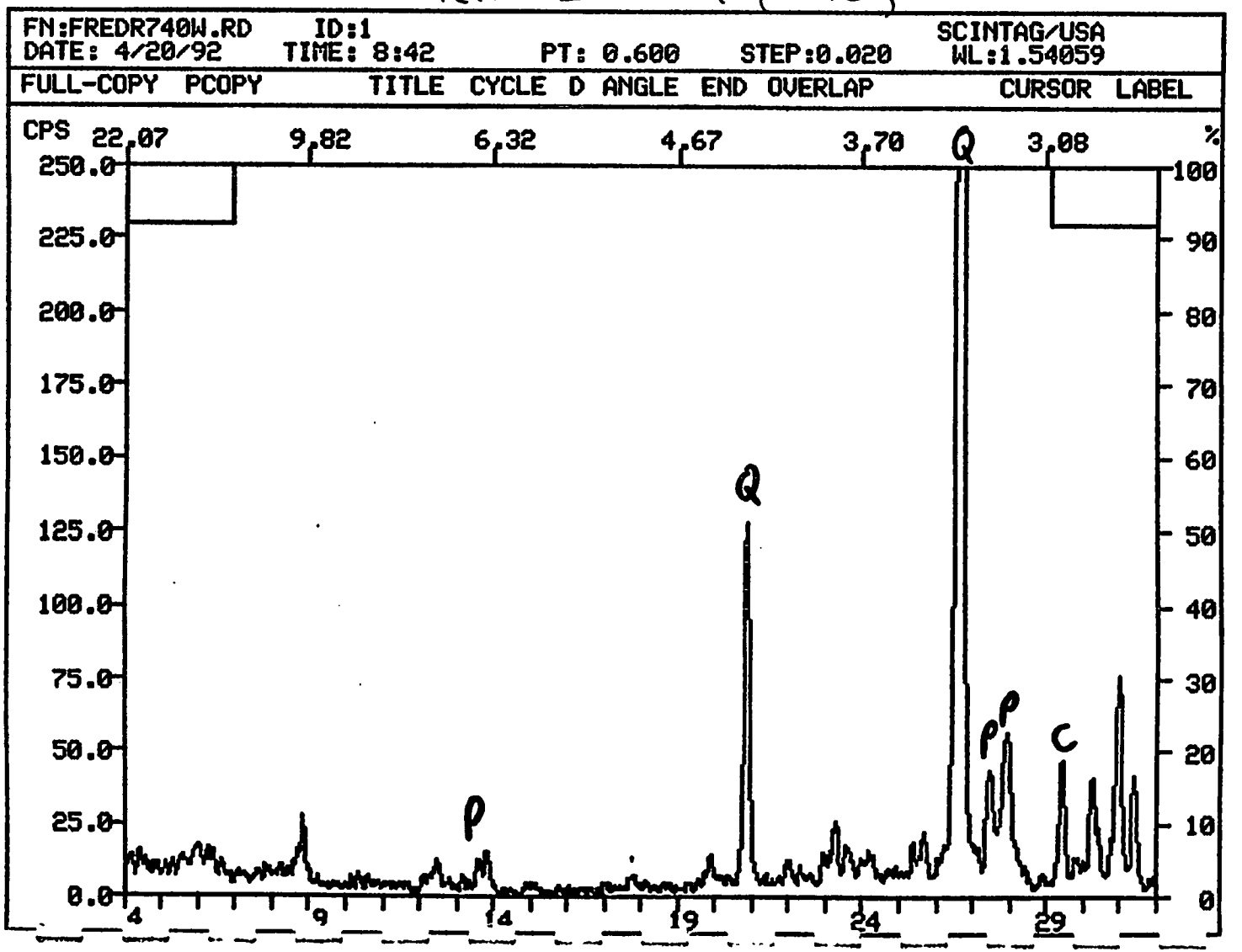
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6.32
4.67
3.70
3.08
%
250.0
225.0
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
100
90
80
70
60
50
40
30
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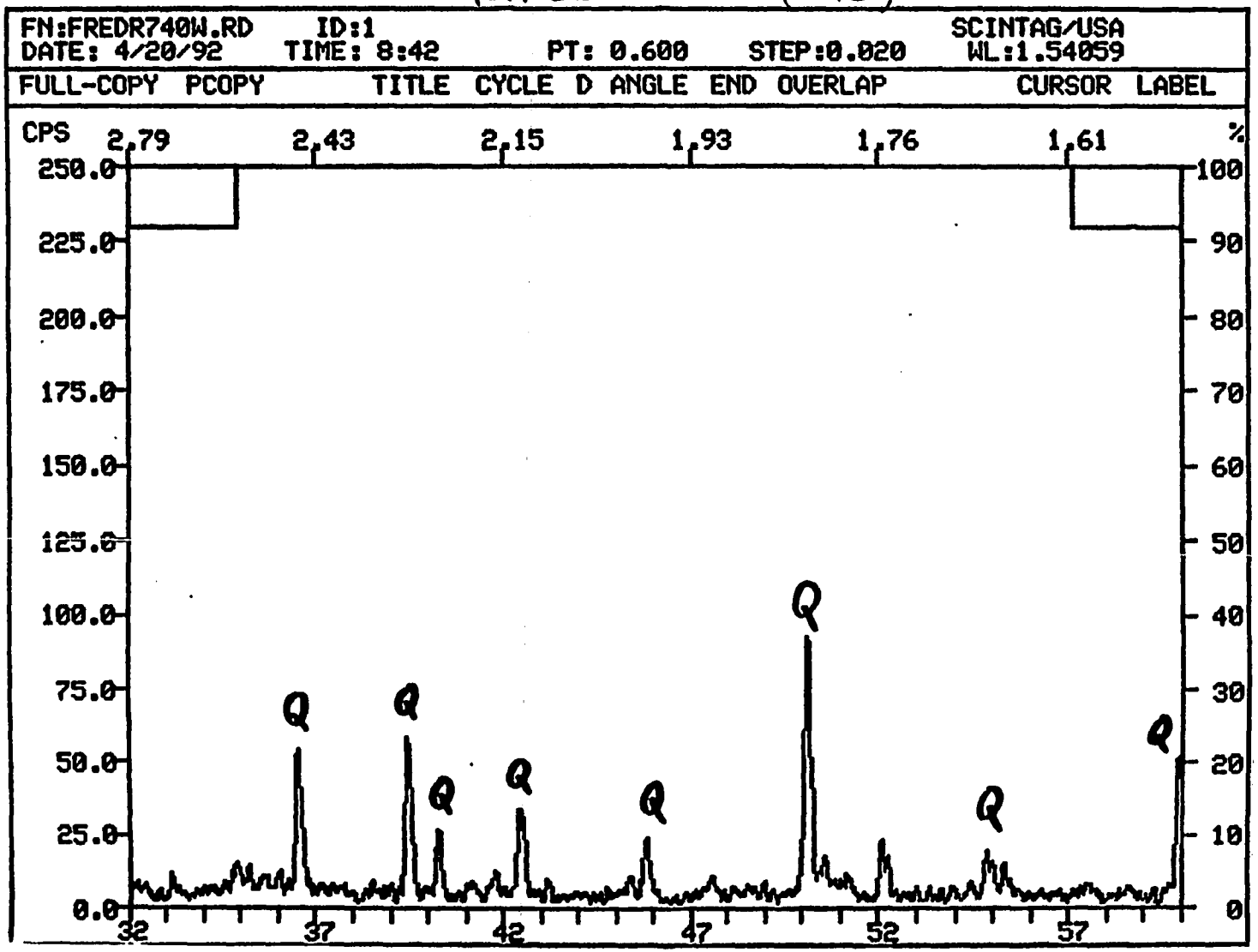
10
0
4
9
14
19
24
29
Q
Q
P
P
P
C

RIFLE TP 7 (-40)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CPS
%
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2.43
2.15
1.93
1.76
1.61
250.0
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APPENDIX D

ADSORPTION ISOTHERM DETERMINATION GENERAL PROCEDURES

EPA-RECOMMENDED METHODOLOGY

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1.0 LABORATORY PROCEDURES—EPA-RECOMMENDED METHODOLOGY AND ASTM METHODOLOGY

1.1 CHEMICAL CHARACTERIZATION OF SEDIMENT

Untreated and acid-washed sediments (-40 mesh) from the Rifle test pits were chemically investigated at the TAC Hydrology Laboratory, and by Pittsburgh Mineral and Environmental Technology, Inc (PMET). PMET performed analyses of gypsum content percentage, percent calcite, acid neutralization, hydrochloric acid soluble iron, hydrochloric acid soluble manganese, organic carbon, and total carbon (Table D.1). The percent moisture, percent total hydrochloric acid soluble material, and percent magnetic mineral determinations were performed at the Hydrology Laboratory. The percent calcite determination from Pittsburgh Minerals was made using optical methods rather than wet chemistry. These values appear substantially high, considering that the percent calcite in the sample cannot be greater than the percent total hydrochloric acid soluble materials determination made at the Hydrology Laboratory. Rather, the true calcite content is probably closer to the acid neutralization potential, [recalculated to express percent calcium carbonate ($CaCO_3$)] made by PMET. These values agree reasonably well with the Hydrology Laboratory percent total hydrochloric acid soluble materials when corrected for soluble iron.

1.2 SEDIMENT PREPARATION

Two types of acid-leached sediment were produced. The first was sediment leached with acid solutions whereby the pH was never allowed to drop below

Table D.1 PMET chemical characterization of Rifle sediments

Parameter	TP-5 (-40)	TP-5 (-40)[a]	TP-6 (-40)	TP-7 (-40)
Gypsum (%)	<1	<1	<1	<1
Calcite (%)	14.91	7.95	12.92	11.92
Acid Neutralization[b]	59.0	45.5	51.6	61.5
Hydrochloric Acid Soluble Iron (%)	2.7	2.7	2.8	2.7
Hydrochloric Acid Soluble Manganese (ppm)	380	370	360	450
Organic Carbon (%)	0.33	0.33	0.50	0.62
Total Carbon (%)	1.00	0.75	1.11	1.37

[a]Acid leached at pH 5.
[b]Results expressed as tons calcium carbonate equivalent/thousand tons of material.

about 5.0. For the second type, the pH was controlled so that it did not fall below 2.7. The essential difference between the two types of leached sediment was the carbonate content.

1.1.1 First type of acid-leached sediment

The first quantity of acid-leached sediment (known as RFL-TP-5-40-AW-I) was prepared as follows:

1. 6.281 kilograms of Rifle Test Pit No. 5 -40 mesh sediment was placed in a new, 20-gallon [76-liter (L)], plastic bucket. The bucket was cleaned with Radiwash, dilute hydrochloric acid rinsed, and deionized water rinsed.

2. Four gallons (15 L) of deionized water were added to the sediment. The bucket contents were then slurried using a rotary mixer. Agitation was kept as light as possible, yet enough to keep the contents—especially the fine materials—in suspension.

3. 0.76 normal sulfuric acid (H_2SO_4) was then slowly and intermittently added dropwise. The pH was steadily lowered, but never allowed to drop below about 4.9. When the pH stabilized at about 5.29, the leachate was decanted (July 6, 1992), and replaced with deionized water. Sulfuric acid was again added, until approximate equilibrium was achieved. This process was repeated a third time until a pH not above about 5.3 could be sustained for 1 day (July 16, 1992). The pH of the final decant solution was 5.29.

4. The leachate was decanted, and the sediment was rinsed and equilibrated with Rifle background water (RFL-01-592) adjusted to pH 6.0. Immediately, a sharp pH rise occurred (which cannot be readily explained). Because of this, the sediment was rinsed with Rifle background water adjusted to pH 6.8. The sediment was rinsed two more times with the pH 6.8 Rifle water, decanted, transferred to a clean sample tray, air dried, and reconstituted (July 18, 1992).

1.1.2 Second type of acid-leached sediment

When it became apparent that carbonates remained after the first type of acid treatment, a one-third split of the first quantity of acid-washed sediment was

made. This split was treated with much stronger sulfuric acid solutions, with the pH never allowed to drop below about 2.8 (with approximate equilibrium with the leachate achieved). The second quantity of acid-leached sediment (known as RFL-TP-5-40-AW-II) was prepared as follows:

1. A one-third split of the initial acid-washed sediment was transferred to the original 20-gallon (76-L) bucket. Two gallons (8 L) of water were then added, and the materials slurried (July 22, 1992).

2. 0.8 normal sulfuric acid was then vigorously added, but the pH was never allowed to drop below approximately 2.7. The solution pH was continually monitored.

3. After a pH of approximately 3.0 could be sustained for 24 hours (whereby an approximate equilibrium was achieved), the sediment was first slurried with about 3 gallons (11 L) of deionized water, and then washed and equilibrated with Rifle background water adjusted to pH of about 4.9. Again a sharp pH rise with time was observed, to about 5.75.

4. The sediment was decanted, transferred to a clean tray, air dried, and reconstituted.

Stock solution preparation

Stability in Storage

The Rifle water was supplied to the laboratory in 13, 5-gallon (19-L) polyethylene carboys. The carboys were immediately refrigerated at 8°C, which was the measured groundwater temperature. To assess the homogeneity of the water, pH, conductivity (Ec), and ORP (Eh) were performed on seven randomly chosen carboys. The results are presented in Table D.2.

Table D.2 Stock groundwater parameters

Carboy #	pH	Ec (mS/cm)	Eh (mV)
1	7.28	2.34	451
2	7.30	2.38	450
3	7.30	2.38	448
4	7.36	2.40	446
5	7.32	2.37	444
6	7.33	2.39	445
7	7.29	2.37	445

Temperature of analyses was 22°C.

Alkalinity data on the above carboys were also taken with a value of 542 mg calcium carbonate ($CaCo_3$)/100 milliliters (mL) found, with a total error of less than 1 percent found between carboys. Because alkalinity was not considered a robust measure for homogeneity (as discussed below), it was not presented in Table D.2.

Before laboratory work, several tests to assess the stability of the Rifle water were performed. It was noted immediately that, upon warming to room temperature and/or allowing contact with air, the Rifle water precipitated a slight yellow-brown precipitate. Also, fresh unopened carboys displayed the same precipitate after about 3 weeks, inspite of refrigeration. The formation of these precipitates was accompanied by an increase in the pH to near 8.0. Furthermore, a sample of the fresh Rifle groundwater was placed in a stoppered flask where carbon monoxide gas was introduced, lowering the pH to 6.84. This water remained stable for weeks. Thus, it appears that the Rifle water, while residing in the well, was in equilibrium with a higher carbon monoxide partial pressure than atmospheric, and could dissolve more carbonate.

Room temperature, air exposed, "decomposed" Rifle water, unfiltered and filtered (0.45 micron) were measured for parameters. The following results were obtained (Table D.3).

Table D.3 Stock groundwater parameters—different types of

	pH	Ec mS/cm	Alkalinity[a]
Raw Rifle water (unfiltered)	7.31	2.38	542
Decomposed RFL-592 (unfiltered)	7.78	2.19	542
Decomposed RFL-592 (filtered)	8.18	2.19	434
Acidified RFL-592	5.85	2.41	42
Acidified RFL-592	2.80	3.11	--

[a]Alkalinity expressed as mg calcium carbonate per 1.00 liter titrated to pH 4.25.

Additionally, 0.10 grams of the yellow-brown precipitate was removed from 1.8 L of Rifle water. Since this precipitate had settled, the original quantity of water it was derived from was probably much greater. After reviewing these results, it was concluded that instability of the RFL-592 water was insignificant.

The Rifle groundwater was modified with the addition of sulfuric acid for sorption tests at pH values below 7. This acidified groundwater showed small amounts of gypsum precipitate, and initially produced carbon monoxide gas bubbles. An attempt was made to equilibrate these acidified, carbon monoxide-rich waters with atmospheric gases, either by aging, or sparging with air. Parameters for these waters appear in Table D.3.

The question of stability of contaminant spiked, raw RFL-592 water was partly addressed when 1000 milligram/liter (mg/L) stock solutions were prepared, initially using a matrix of the Rifle groundwater. This was attempted to match the matrix of all subsequent dilutions needed for an isotherm. At 1000 mg/L, at a pH of about 7.5, it was observed that molybdenum, copper, and cadmium precipitated with time. Because of this, contaminant stock solutions were prepared using salts dissolved in deionized water to produce 1000 mg/L solutions. These 1000 mg/L stock solutions could then be used to prepare dilute solutions of the contaminant of interest, with matrices essentially matched in all cases. The following paragraphs describe stock solution preparations used at the Hydrology Laboratory for the study:

Molybdenum: 1.830 grams of E&M ammonium molybdate assaying 83 percent molybdate (MoO_4) was dissolved in 30 mL of deionized water, and one pellet (0.1 gram) of sodium hydroxide (NaOH) added to ensure dissolution. This solution was diluted to 1 L using a class A volumetric flask, and mixed. The nominal assay of this solution was 1010 mg/L molybdenum.

Copper: 3.977 grams of Fischer reagent grade hydrated copper sulfate ($CuSO_4 \bullet 5H_2O$), 98.8 percent purity, were dissolved in deionized water, diluted to 1000 mL volume, and mixed, giving 1000 mg/L.

Uranium: 1.179 grams of alpha products U_3O_8, 99 percent purity, were weighed into a 100-mL beaker, and dissolved in 5 mL of 1:1 nitric acid with a small amount of hydrochloric acid added. This solution was then evaporated to about 1 to 2 mL, and diluted to a total volume of 990 mL with deionized water to give 1000 mg/L uranium.

In most cases the uranium concentrations were determined using the inductively coupled plasma/mass spectrophotometer (ICP/MS) technique, which provides accurate results. In the early stages of the special study, however, some uranium concentrations were determined with a fluorometric technique that has less accuracy than the ICP/MS technique.

The ICP/MS analyses of uranium resulted in stock solution concentrations of 10.5 mg/L. However, contract laboratory QA/QC spiked solutions demonstrated uranium recovery results of 103 percent to 105 percent. Therefore, the calculated 10 mg/L for the uranium stock solutions is accurate.

Uranium in stock solutions analyzed by the fluourometric technique resulted in concentrations of less than 10 mg/L (8.1 to 9.8 mg/L). However, because the results of the ICP/MS analyses confirmed the 10 mg/L uranium in the same stock solution, this discrepancy is probably due to the fluorometric technique. This interpretation is supported by low spike recovery results obtained by the fluorometric technique. Therefore, a correction factor was applied to the equilibrium uranium concentrations determined by the fluourometric technique. The correction factor was derived by first determining the percentage difference between the contract laboratory and calculated uranium concentrations of the stock solution. Then the contract laboratory equilibrium concentration was increased by the same percentage.

<u>Cadmium</u>: 2.282 grams of E&M reagent grade cadmium sulfate ($3CdSO_4 \cdot 8H_2O$) of 99.1 percent purity were dissolved in deionized water and brought up to a total volume of 991 mL with deionized water, giving 1000 mg/L Cd.

<u>Arsenic</u>: Two different 1000 mg/L stock solutions were utilized for the study:

a. For alkaline systems, 1.000 grams (estimated for report only) (actual notes lost), of E&M arsenic oxide (As_2O_3), 100 percent purity, were dissolved in 5 mL of 50 percent sodium hydroxide (NaOH) solution, and brought up to a volume of 1000 mL to give 1000 mg/L arsenic.

b. For acidic systems, a commercial (Mallinckrodt) stock standard of 1000 mg/L arsenic in very dilute sulfuric acid (H_2SO_4) solution was used.

The stability of unpreserved dilutions of the above stock standards with raw Rifle groundwater was investigated two ways: 1) through the use of procedural (no soil) blanks, and 2) the monitoring of unpreserved contaminant spiked solutions. The following was noted:

Molybdenum, uranium, and arsenic: At the 10 mg/L level or less, unpreserved, Rifle groundwaters spiked with these contaminants showed no instability over the pH range of about 5.8 to 8.0.

Copper, Cadmium: At the 10 mg/L level or less, Rifle groundwater spiked with these contaminants appeared stable at pH values near 7.0. These unpreserved solutions may have been metastable, as suggested from modelling results.

Batch testing procedures

1. Individual batch tests were conducted in 250-mL-wide mouth Nalgene bottles. Accordingly, the following schedule (Table D.4) of soil and solution masses was devised and used throughout the study (of which six or more were chosen for a particular isotherm):

   In following the above schedule for soil and solution masses, each bottle was filled with very nearly the same air space (about 40 mL, as the bottles held 290 mL total). Also, ratios were kept in integral fractions, to facilitate data handling. Since all of the weights, except for the smallest

soil weights, contained at least three significant figures, the implied precision of the ratios was also three significant figures. This exceeded, usually by a large degree, the analytical precision of the assays for the contaminants. All soil and solution masses were made with a Mettler PJ-3000 electronic balance that could read to 10 milligrams. This balance was regularly calibrated with a Class S weight set.

Table D.4 Soil:solution ratios and masses used in adsorption experiments

Ratio	Soil mass (grams)	Solution mass (grams)
1:1	170.0x	170.0x
1:2	100.0x	200.0x
1:3	70.0x	210.0x
1:4	62.5x	250.0x
1:6	40.0x	240.0x
1:8	32.0x	256.0x
1:10	25.0x	250.0x
1:15	16.0x	240.0x
1:20	12.5x	250.0x
1:40	6.25	250.0x
1:60	4.17	250.0x
1:100	2.50	250.0x
1:200	1.25	250.0x
1:500	0.50	250.0x

2. All materials were 10 mesh or finer.

3. Individual batch test points were prepared as follows:

   a. For variable ratio, constant concentration isotherms, the soil was first weighed into a Nalgene bottle tared to 0.00 grams, with the

appropriate weight from the above schedule dispensed. A bulk solution of the contaminated Rifle water was then prepared by making an appropriate dilution of a 1000 mg/L stock solution (see below). This solution was well mixed and added to the bottle in the appropriate quantity as designated above.

b. Constant ratio, variable concentration batch tests were weighed in a similar manner as above, but individual aliquots of solution were prepared by spiking an appropriate mass of the contaminant, in micrograms, into a total volume equal to that needed for the solution mass.

4. Bottles were quickly capped, gently agitated, and placed on the rotary mill for 24 hours. The ratios of 1:1 and 1:2 could be mixed adequately. A rotation time of 24 hours was found adequate, as described below. The rotation rate was 29 RPMs, with a very stable temperature of 24.5°C maintained during rotation. Bottles remained closed systems for the period of rotation.

5. After 24-hour rotation was complete, samples were removed and allowed to settle for 2 to 6 hours, so as to facilitate filtering. If parameters were not required, and only one metal was needed for analysis, 60 to 80 mL were filtered though a 0.45 micron Gelman filter funnel, bottled, preserved with about 0.5 percent nitric acid (HNO_3), and archived. Contaminant levels were ultimately assayed by a contract laboratory, which was sent about 30 mL of solution. If

parameters were required, unfiltered solutions could only be used for these analyses because filtering would disturb carbon dioxide levels in the solutions, causing large pH shifts upwards.

Equilibration time check

Unlike the ASTM method of batch testing (see below), which assumes equilibration after a specified period of shaking or rotation time, the EPA batch testing method requires that the time for equilibration be experimentally determined. Since EPA batch testing documents suggested 24 hours would be sufficient to complete the sorption process, this time was initially chosen. To evaluate equilibration time, individual uranium and molybdenum batch tests (points on an EPA isotherm) were rotated for 36, 48, and 72 hours and compared to results obtained for a 24-hour rotation. The data are presented in Table D.5.

Quality control procedures

1. Blanks, Procedural Blanks, Stock Solution Checks:

To monitor the quality of the experiment, blanks and standards were prepared for each isotherm. The following describes these samples:

- **Stock solution check:** an aliquot of the initial solution (e.g., 10 ppm for molybdenum and uranium) would be taken during the preparation of batch tests, immediately acidified, and ultimately analyzed.

Table D.5 Equilibration time experiment results

Equilibration Check #1: Uranium sorption.

Batch Test Description:

Sorbate: Rifle Test Pit 6, -40 mesh, raw.

Solution: Rifle 592-01 raw, spiked with uranium to 10.05 ppm.

Ratio: 1:2

	Rotation Period				
	0 Hours	24 Hours	36 Hours	48 Hours	72 Hours
U, mg/L:	10.05	7.0	7.5	8.1	7.7

Equilibration Check #2: Molybdenum sorption.

Batch Test Description:

Sorbate: Rifle Test Pit 5, -40 mesh, Acid Washed I.

Solution: Rifle 592-01, acidified to pH 6.0 with H_2SO_4, and spiked with Mo to 10.2 ppm.

Ratio: 1:4

	Rotation Period			
	0 Hours	24 Hours	36 Hours	48 Hours
Mo, mg/L:	10.2	10.3	9.5	9.5

- **Procedural blank:** a batch test containing 250 mL, with no soil (ratio = 0) was always run with an isotherm. This type of sample differed from the stock solution check in that it was rotated for 24 hours and then filtered and acidified. This was designed to check for instability of the spiked solutions.

- **Desorption/background blank:** an intermediate soil:solution ratio was chosen and prepared with contaminant-free RFL-592 matrix water. This was to check for background levels of the contaminant not added as a spike.

2. Reproducibility Experiments:

Reproducibility experiments where either individual batch tests or entire isotherms were rerun one or more times were conducted to evaluate the following:

- Reproducibility of the sorption process.
- Consistency of Hydrology Laboratory procedures.
- Precision and accuracy of contract laboratory analyses.

Reproducibility of the sorption phenomena itself can only be strictly evaluated if no uncertainty resides elsewhere in the procedure. Thus, the reproducibility experiments have to be viewed as a test of all three parameters above, combined. Furthermore, factors 1 and 2 above are to some extent mutually dependent on one another.

1.3 ASTM PROCEDURES

The ASTM batch testing procedure (ASTM, 1987) uses a single soil:solution ratio of 1:4 to calculate a distribution coefficient (kd). In the special study, the "modified ASTM method" of batch testing was used, as described below:

1. Two-hundred grams of soil weighed into a 1000-mL Nalgene Ehrlenmeyer flask, and 800 grams of solution added. The flasks were covered with parafilm.

2. Samples were agitated using a wrist-action shaker for 1-hour intervals, twice daily, for 3 days (when it is assumed sorption is complete and equilibration is achieved). Because of the inability to effectively seal flasks, they were not closed systems. If sample quantity was limited, 100 grams of soil and 400 grams of sediment in a 500-mL flask were used.

3. After final shaking, samples were allowed to settle for a short period, and filtered through a 0.45 micron filter funnel. Samples were then preserved with nitric acid (HNO_3) or sulfuric acid (H_2SO_4) and split for analysis and archiving.

4. Stock solution checks, procedural blanks, and desorption blanks were prepared similar to the EPA method to monitor the process.

2.0 REFERENCES

ASTM (American Society for Testing and Materials), 1987. "Standard Test Method for Distribution Ratios by the Short-Term Batch Method," in Annual Book of ASTM Standards, Philadelphia, Pennsylvania.

EPA (U.S. Environmental Protection Agency), 1991. "Batch-Type Procedures for Estimating Soil Adsorption of Chemicals," Technical Resource Document, EPA/530-SW-87-006-F, Risk Reduction Engineering Laboratory Office of Research and Development, Cincinnati, Ohio.

APPENDIX E

ADSORPTION ISOTHERM DETERMINATION GENERAL PROCEDURES (EPA, 1991)

CHAPTER 14

CONSTRUCTION OF ADSORPTION ISOTHERMS (CURVES)

An adsorption isotherm or curve is a graphic representation showing the amount of solute adsorbed by an adsorbent as a function of the equilibrium concentration of the solute. This relationship is quantitatively defined by some type of partition function or adsorption isotherm equation that is statistically applied to the adsorption data to generalize the adsorption data.

In studies concerned with the adsorption of gases by solids, more than 40 equations have been used to describe the data. Historically, only a few of the equations have been found to be applicable to solid-liquid systems. Only the two most commonly used and simplest of these adsorption equations will be discussed here—the Freundlich and Langmuir isotherms. Neither may be appropriate for a given system. The reader may wish to consult a paper by Kinniburgh (1986) on the applicability of other adsorption equations.

The Freundlich Equation

Probably the oldest, most widely used adsorption equation for solid-liquid systems is the Freundlich adsorption equation, named after H. Freundlich (Freundlich, 1909),

$$\frac{x}{m} = K_f C^{1/n} \qquad [15]$$

where x is the amount or concentration of the solute adsorbed, m is the mass of the adsorbent, C is the equilibrium concentration of the solute, and K_f and $1/n$ are constants.

The Freundlich equation was originally proposed as an empirical expression without a theoretical foundation. However, some investigators have referred to the Freundlich constant (K_f) as being related to the capacity or affinity of the adsorbent; the exponential term may be an indicator of the intensity of adsorption or how the capacity of the adsorbent varies with the equilibrium solute concentration (see Suffet and McGuire, 1980).

Other investigators attempted to show that the Freundlich equation has a theoretical basis. A number of derivations of the Freundlich equation were based on the Gibbs adsorption equation (Chakravarti and Dhar, 1927; Rideal, 1930; Freundlich, 1930; Halsey and Taylor, 1947; see Hayward and Trapnell, 1964; Kipling, 1965). Zeldowitsch (1935) demonstrated that the Freundlich equation could be explained in terms of a nonhomogeneous surface. Sips (1948) established in a rigorous fashion a general relationship between surface heterogeneity and the Freundlich equation, a derivation Sposito (1980) partially adapted to his system to derive a Freundlich-type expression for trace-level exchange reactions.

The Freundlich equation is frequently used, probably because it is simple. It contains two constants; both are positive-value numbers that can be solved statistically when expressed in logarithmic form:

$$\log(x/m) = \log K_f + 1/n \log C \qquad [16]$$

By taking the logarithms of both sides of equation 15, the constants K_f and $1/n$ may be solved, via equation 16, as a simple linear regression,

$$y_i = a + bx_i \qquad [17]$$

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where $\log(x/m)_i = y_i$
$\log K_f = a$
$1/n = b$
$\log C_i = x_i$

The technique for solving a linear regression can be found in any introductory statistics textbook and is also a common feature of most moderately priced electronic calculators. (Note: linear regressions are sometimes referred to as the line of best fit or method of least squares.) For the sake of completeness, the constants may be solved (with n* as the number of pairs of data points) using

$$b = \frac{1}{n} = \frac{n(\sum \log C_i \times \log x/m_i) - (\sum \log C_i)(\sum \log x/m_i)}{n(\sum (\log C_i)^2) - (\sum \log C_i)^2} \qquad [18]$$

The following example is given to illustrate the application of the Freundlich equation. Previous work showed that the adsorption of arsenate by kaolinite could be characterized by using a 1:10 soil: solution ratio (chapter 9) and that the system reached a steady state after 24 hours. Under these experimental conditions, 17 dilutions of a stock KH_2AsO_4 solution were mixed with an NBS rotary extractor with kaolinite for 24 hours. Table 13 contains all the data needed to construct an isotherm and also includes the

Table 13 Data reduction for arsenic adsorption at 25°C by a kaolinite clay sample (volume of solution, 200 mL)

Initial conc (mg/L)	Equilibrium conc (mg/L)	Adsorbent wt (g)	Amount adsorbed (µg/g)	pH	EC (dS/m)
4.89	1.20	20.42	36*	8.30	160
10.0	3.56	20.42	64	8.26	168
15.2	6.76	20.42	84	8.26	170
19.9	10.1	20.42	98	8.19	185
19.9	10.1	20.42	98	8.23	185
19.9	10.3	20.42	96	8.25	185
29.9	17.6	20.42	123	8.16	205
40.3	25.0	20.42	153	8.03	221
49.4	33.4	20.42	160	8.02	240
80.5	58.4	20.42	221	7.77	305
80.5	59.5	20.42	210	7.80	313
80.5	58.9	20.42	216	7.83	305
98.8	76.3	20.42	225	7.69	350
121.0	92.6	20.42	284	7.56	385
137.7	109.4	20.42	283	7.50	413
160.3	128.3	20.42	320	7.27	434
160.3	129.7	20.42	306	7.26	430

* Sample calculation:

$$\frac{x}{m} = \frac{(\text{Initial conc.} - \text{equil. conc.}) \times \text{volume of solution}}{\text{weight of adsorbent}}$$

$$= \frac{(4.89\ \text{mg/L} - 1.20\ \text{mg/L}) \times 0.200\ \text{L}}{20.42\ \text{g}} = 0.036\ \text{mg/g} = 36\ \mu\text{g/g}$$

linite for 24 hours. Table 13 contains all the data needed to construct an isotherm and also includes the pH and electrical conductivity (EC) of each solution, determined as recommended at the ends of chapters 5 and 6.

In this example (table 13),

$$\log K_f = 1.536 \qquad 1/n = 0.452$$

and thus

$$\frac{x}{m} = 34.328 \ (As)^{0.452} \qquad [19]$$

where As is the equilibrium concentration of arsenic in solution (mg/L). The units mg/L are equivalent to µg/mL, and therefore the units of K_f are $mL^{1/n}\mu g^{(1-1/n)}/g^{-1}$ from

$$x/m\,(\mu g/g) = K_f\,(\mu g^{(1-1/n)}\,mL^{1/n}/g)\ As\ (\mu g^{1/n}/mL^{1/n})$$

The $1/n$ term has no units. The selection of the units for x/m and the equilibrium solute concentration will determine the units of K_f in a given situation. When $1/n < 1$, the units used must be considered when adsorption constants are compared from different sources (see Bowman, 1981; Hassett et al., 1983).

Thus, equation 19 becomes a predictive equation capable of describing the adsorption data. The reader may wish to use the data given in table 13 to verify equation 19. For example, equation 19 should not be used to predict x/m at equilibrium concentrations greater than 130 mg/L; to do so requires the collection of data in this higher concentration range. The validity of this cautionary note becomes apparent when one considers that the Freundlich equation predicts infinite adsorption at infinite concentrations; hence, any soil or clay would have an unlimited capacity to retain chemicals dissolved in water. Not only would an infinite capacity be thermodynamically inconsistent, but experience has shown that the extent of adsorption is ultimately limited by the surface area (or some portion of the surface) of the adsorbent. Thus, there are two drawbacks in using the Freundlich equation: (1) it cannot be extrapolated with confidence beyond the experimental range used in its construction, and (2) it will not yield a maximum capacity term, which in many cases is a convenient single-value number that estimates the maximum amount of adsorption beyond which the soil or clay is saturated and no further net adsorption can be expected.

The Langmuir Equation

The Langmuir equation has given rise to a number of Langmuir-type expressions that have been widely used to describe adsorption data for solid-liquid systems. The most commonly used expression may be generalized as

$$\frac{x}{m} = \frac{K_L M C}{1 + K_L C} \qquad [20]$$

where x is the amount or concentration of the solute adsorbed, m is the mass of the adsorbent, C is the equilibrium concentration of the solute, and K_L and M are constants.

Langmuir (1918) derived an expression similar to equation 20 to describe the adsorption of gases on solids (flat surfaces of glass, mica, and platinum). He generalized that the Freundlich equation was unable to describe the adsorption of gases when the range of pressures was large. Langmuir's original derivation was based on the premise that during the adsorption of gases, a dynamic equilibrium is established in which the rate of condensation (adsorption) is equal to the rate of evaporation (desorption). Derivations of the Langmuir and Langmuir-type equations for gas-solid interactions are given elsewhere (Langmuir, 1918; Hayward and Trapnell, 1964; Ponec et al., 1974). Langmuir-type expressions for ion exchange reactions in soils have also been derived (Sposito, 1979; Elprince and Sposito, 1981).

The applicability of Langmuir-type equations to solid-liquid systems has been a controversial topic in recent years (see Harter and Baker, 1977; Veith and Sposito, 1977; Barrow, 1978; Sposito, 1982). However, this controversy is concerned not with the ability of the equation to simply describe the adsorption data, but with interpretations of adsorption mechanisms and energetics that are based on the results of applying Langmuir-type expressions.

Some investigators have concluded that the Langmuir constant (K_L) is somehow related to the bonding energy between the adsorbed ion and the adsorbent, but that specific functional relationship is uncertain. The constant M in equation 20 is generally accepted as the adsorption maximum of the adsorbent with respect to the specific solute and is interpreted as the maximum amount or concentration that an adsorbent can retain.

Langmuir-type equations are frequently used because of their ease of application. Like the Freundlich equation, such equations contain only two constants, both of which are positive-value numbers that can be statistically solved when equation 20 is cast in a linear form. Two linearized expressions are possible:

$$\frac{C}{x/m} = \frac{1}{K_L M} + \frac{C}{M} \qquad [21]$$

$$\frac{1}{x/m} = \frac{1}{K_L M C} + \frac{1}{M} \qquad [22]$$

The linearized form of equation 21 is sometimes referred to as the "traditional linear Langmuir equation," and equation 22 is called the "double-reciprocal Langmuir equation." The latter is more suitable for situations in which the distribution of equilibrium concentrations tends to be skewed towards the lower end of the range of the equilibrium concentrations. As indicated above, linearized Langmuir-type expressions such as equations 21 and 22 are equivalent to a simple linear regression,

$$y_i = a + bx_i$$

where the traditional linear Langmuir equation is

$$\begin{aligned} y_i &= (C/x/m)_i \\ a &= 1/K_L M \\ b &= 1/M \\ x_i &= C_i \end{aligned}$$

and the double-reciprocal form is

$$\begin{aligned} y_i &= (1/x/m)_i \\ a &= 1/M \\ b &= 1/K_L M \\ x_i &= 1/C_i \end{aligned}$$

The techniques for solving either equations 21 or 22 are the same as those used to solve the linear form of the Freundlich equation (eq. 16). From the data set given in table 13, application of the linear Langmuir-type equations yields:

Traditional Linear Langmuir

$$a = \frac{1}{K_L M} = 0.0792 \qquad [23]$$

$$b = \frac{1}{M} = 0.0028 \qquad [24]$$

and thus

$$\frac{x}{m} = \frac{3.568 \times 10^{-2}(353.856)C}{1 + 3.568 \times 10^{-2}(C)} \qquad [25]$$

Double-Reciprocal Langmuir

$$a = \frac{1}{M} = 0.0050 \qquad [26]$$

$$b = \frac{1}{K_L M} = 0.0297 \qquad [27]$$

and thus

$$\frac{x}{m} = \frac{0.1702\,(198.098)C}{1 + 0.1702(C)}$$

In this example, the units for the adsorption maximum are the same as for x/m (µg/g), and the units for K_L are liters per milligram:

$$x/m\,(\mu g/g) = \frac{K\,(L/mg)\,M\,(\mu g/g)\,C\,(mg/L)}{1 + K\,(L/mg)\,C\,(mg/L)} \qquad [28]$$

The selection of units for x/m and the equilibrium solute concentration determines the units for M and K_L.

Equations 25 and 28 are predictive expressions that can describe the adsorption of arsenic by kaolinite. The reader should work through these examples to verify the results. In the previous examples, the isotherm constants were derived by linear regression. Kinniburgh (1986) recommended that isotherm constants be solved by nonlinear regression (nonlinear least squares) to obtain more accurate values than those derived by linear regression. A short BASIC program using a nonlinear least-squares method for determining Langmuir constants was written by Persoff and Thomas (1988).

CHAPTER 15

SELECTION OF ADSORPTION EQUATIONS

Three isotherm regressions were used to describe the example data set given in table 12. Given the selection of different models, one equation usually will describe the results with the greatest accuracy. No clear consensus has been reached on which equation (Freundlich or Langmuir-type) is the most reliable for simply fitting data. Barrow (1978) objected to the application of Langmuir-type expressions, but his objection was based on theoretical considerations. Singh (1984) compared five adsorption equations and found that the Freundlich equation was the most accurate in describing the adsorption of SO_4^{2-} by soils. Polyzopoulos et al. (1984) compared four adsorption equations in a study concerned with phosphate adsorption by soil. They found that Langmuir-type or Freundlich expressions described the data with comparable success.

Generally the choice of an equation is based on the coefficient of determination (r^2) obtained in a given case and the equation's simplicity (Polyzopoulos et al., 1984). The Freundlich and Langmuir equations each contain only two constants and are easily solved.

The coefficient of determination (sometimes called the goodness of fit) is a measure of how closely the regression line fits the data, and may be calculated using equation 29:

$$r^2 = \frac{\sum(\hat{y}_i - \bar{y})^2}{\sum(y_i - \bar{y})^2} \qquad [29]$$

where $\hat{y}_i$ is the value of the dependent variable predicted by the regression, y_i is the value actually measured, and y is the arithmetic mean of all y_i. The value of r^2 will always be between 0 and 1, inclusive. If all of the points are close to the regression line or, in this example, if all of the adsorption data plot closely to the statistically constructed adsorption isotherm, the corresponding r^2 will be close to 1. The application of equations 16, 21, and 22 to the data set in table 12 yielded dissimilar r^2 values:

Freundlich	0.996
traditional linear Langmuir	0.954
double-reciprocal Langmuir	0.916

When the coefficient of determination is used as a criterion, the Freundlich equation best described the adsorption data, although the traditional linear Langmuir expression would also yield satisfactory results. Figure 41 clearly shows that the double-reciprocal linear Langmuir equation did not fit the adsorption data well and that the traditional linear form tended to overpredict adsorption in the upper part of the isotherm. Obviously the high r^2 value associated with the Freundlich equation is reflected by the closeness of fit of the isotherm with the data.

Obtaining a reliable fit of adsorption data with the chosen equation (so that r^2 values are close to 1) is a major concern in the construction of adsorption isotherms. However, in some cases, a low r^2 value will be obtained regardless of the equation used, raising concerns that the adsorption constants actually have little meaning. Probably the simplest statistical test for such situations is to use t-statistics to examine whether the sample correlation coefficient (r) is significantly different from a population correlation coefficient (ρ) where $\rho = 0$. This test appears in most introductory statistics textbooks and will not be discussed here.

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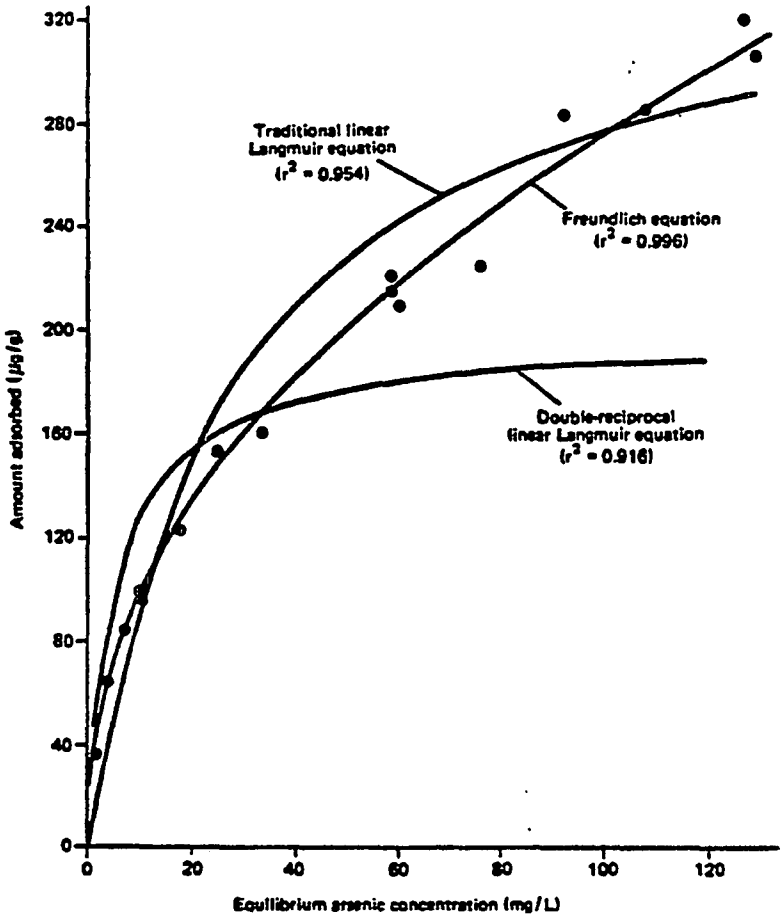

Figure 41 Adsorption of arsenic by a kaolinite clay sample at 25°C, described by the traditional linear Langmuir, double-reciprocal Langmuir, and Freundlich equation. The mean pH of the soil-solute suspensions was 7.8.

CHAPTER 16

APPLICATION OF BATCH-ADSORPTION DATA

Adsorption data are used in describing the partitioning of chemicals between soils and water, and have been used successfully as input parameters in many models describing the movement of chemicals in soil (Dragun, 1988). Batch-adsorption data have also been applied successfully to groundwater systems. For example, Curtis et al. (1986) found that the rates of movement of halogenated organic solutes in a sandy aquifer in Canada were in good agreement with those predicted from adsorption data. In a study described by CH2M Hill, Inc. (1986), data on the distribution and concentration of organic solutes at a field site in Indiana were in good agreement with data predicted from laboratory adsorption studies.

Miller et al. (1989) found that isotherms generated with a batch technique were very similar to those derived from flow-through column experiments for the adsorption of anions by soils. Adsorption tended to be greater in the flow systems, possibly because of precipitation or reduced competition between the solutes and desorbed antecedent species.

This chapter is a brief introduction to the application of batch-adsorption data in calculations of solute movement through compacted landfill liners. These calculations are used particularly for estimating the minimum thickness of liner required to prevent pollutant movement beyond a certain depth of the liner for a specified period of time. As leachate moves through a liner, the movement of chemical solutes in the leachate may be retarded if they are adsorbed by the liner. We may define R as the ratio of the velocity of the leachate to that of the solute,

$$R = V_{leachate}/V_{solute} \qquad [30]$$

The R term is called the retardation function or factor. When the solute is not retained by the liner, R equals 1: the solute moves at the same velocity as the leachate. Increasing degrees of adsorption yield larger values for R. The retardation factor may also be defined by an empirical relationship (Freeze and Cherry, 1979, and references cited therein) as

$$R = 1 + \frac{\rho_b (K_d)}{\theta} \qquad [31]$$

where ρ_b is the dry bulk density of the liner, K_d is a distribution coefficient, and θ is the volumetric water content of the liner. The distribution coefficient is a parameter that describes the partitioning of solutes between the leachate and liner soil materials at equilibrium. The distribution coefficient may be defined as

$$\frac{dS}{dC} = K_d \qquad [32]$$

where S is equal to x/m (the amount adsorbed per mass of adsorbent), and C is the equilibrium concentration of the solute. In other words, equation 32 is the slope of an adsorption isotherm.

Before equation 31 can be used, a functional relationship for dS/dC must be determined. The possible solutions range from simple assumptions to complex numerical solutions. The simplest case is one in which the adsorption of the solute conforms to a Freundlich equation (chapter 14) isotherm where the $1/n$ term is unity,

$$\frac{x}{m} = S = K_f C^{1/n} = K_f C \qquad [33]$$

Such an isotherm is termed linear; a plot of S versus C is a straight line. The slope of this type of plot yields K_d,

$$\frac{dS}{dC} = K_f \text{ or } K_d \qquad [34]$$

hence,

$$R = 1 + \frac{\rho_b K_d}{\theta} \qquad [35]$$

The retardation factor is unitless; if K_d is in milliliters per gram, then the units of the term

$$\rho_b\,(\text{g/cm}^3)\; K_d\,(\text{mL/g})/\theta\,(\text{cm}^3/\text{cm}^3)$$

cancel because 1 cm^3 = 1 mL.

When a linear isotherm is used, the Freundlich constant (K_f) reduces to the simple partition constant (K_d), a single-value number used to calculate solute-adsorbate partitioning at any equilibrium concentration of the solute. Because of its mathematical simplicity, this approach (the linear isotherm assumption) has been widely used and may be valid for many dilute systems. When the adsorption isotherm of a solute is a nonlinear function ($1/n \neq 1$), the retardation factor is concentration-dependent:

$$\frac{dS}{dC} = \frac{d}{dC}(K_f C^{1/n}) = \frac{K_f}{n} C^{(1/n)-1} \qquad [36]$$

$\frac{1}{n} K_f C^{\frac{1}{n}-1}$

hence,

$$R(C) = 1 + \frac{\rho_b K_f C^{(1/n)-1}}{\theta n} \qquad [37]$$

Equation 37 is complicated by the fact that the numerical value of R depends on the concentration of the solute. Solute movement may be seriously underestimated if, when dealing with nonlinear isotherms, investigators assume that a constant retardation factor is valid for a given system.

Rao (1974) developed an empirical technique to estimate a weighted-mean adsorption partition coefficient ($\bar{K}_d$) for the Freundlich equation. In this technique, the rate of adsorption with respect to concentration ($\partial S/\partial C$) is normalized by the total amount of solute in a given concentration range,

$$\bar{K}_d = \frac{\int_0^{C_0} \frac{dS}{dC}\,dC}{\int_0^{C_0} dC} = \frac{\int_0^{C_0} \frac{K_f C^{(1/n)-1}}{n}\,dC}{\int_0^{C_0} dC} = \frac{K_f C_0^{1/n}}{C_0} = K_f C_0^{\,(1/n)-1} \qquad [38]$$

The solute concentration C_0 is the highest concentration (before contact with the adsorbent). If K_f is in units of $\text{mL}^{1/n}\,\mu\text{g}^{(1-1/n)}/\text{g}$, then $\bar{K}_d$ may be expressed in milliliters per gram, since

$$K_f C_0^{\,(1/n)-1} = \frac{\text{mL}^{1/n}\,\mu\text{g}^{1-1/n}}{\text{g}} \times \frac{\mu\text{g}^{(1/n)-1}}{\text{mL}^{(1/n)-1}} = \frac{\text{mL}}{\text{g}}$$

A weighted-mean retardation factor ($\bar{R}$) may be calculated as

$$\bar{R} = 1 + \frac{\rho_b K_f C_0^{(1/n)-1}}{\theta} \qquad [39]$$

In a study concerned with pesticide adsorption by a soil sample, Davidson et al. (1980) found that the error introduced by assuming linear adsorption isotherms was not serious at low concentrations (<10 mg/L) but became significant at higher concentrations. Van Genuchten et al. (1977) proposed an alternative method for isotherm linearization that the reader may wish to examine.

To demonstrate possible applications of these concepts, the following examples are presented to illustrate how batch-adsorption data are used to estimate clay liner thickness.

In this hypothetical example, the metallic waste described in appendix B is to be placed into a disposal basin lined with Cecil clay loam (see appendix A). The soil, which was graded, blended, and compacted, has a saturated hydraulic conductivity of 10^{-7} cm/sec. The major concern of the company operating the disposal facility is the possible uncontrolled movement of a leachate plume containing high concentrations of lead in solution. In a preliminary analysis, this company conducted batch-adsorption experiments using a $Pb(NO_3)_2$ salt and samples of the Cecil soil (table 14). The question posed is, what must the minimum thickness of the liner be to attenuate the lead from solution over a 5-year operating life and a 30-year post-closure period?

Several approaches can be used to answer this question. For each approach, the mean pore velocity of the leachate through the liner must be calculated by using Darcy's law as

$$V = K_{sat} i / n_e \qquad [40]$$

where K_{sat} is the saturated hydraulic conductivity of the liner, i is the hydraulic gradient (dH/dZ), and n_e is the effective (water-conducting) porosity of the liner.

If we assume saturated conditions, subject to steady-state flow through an isotropic liner over time t, and neglect the effects of dispersion and diffusion, equation 40 can be combined with equation 31 to yield

$$Z = t K_{sat} i / R n_e \qquad [41]$$

where Z is the estimated vertical distance of migration of the solute in centimeters, and t is time in seconds.

Equation 41 treats solute movement as a piston-flow problem: a chemically uniform slug of leachate moving downward. This equation is simple and may readily be used to estimate the minimum thickness of a liner. The application of the equation is simplified by assuming that the isotherm is linear. In this example (table 14 and figure 42), a linear regression of the data through the origin (Steel and Torrie, 1960) yielded

$$\frac{x}{m} = S = 342 \text{ (Pb)}$$

Moreover, the liner is assumed to have the following properties:

$$\begin{aligned} n_e &= 0.09 \text{ cm}^3/\text{cm}^3 \\ r &= 0.36 \text{ cm}^3/\text{cm}^3 \\ \rho_b &= 1.7 \text{ g/cm}^3 \\ K_{sat} &= 1 \times 10^{-7} \text{ cm/sec} \\ i &= dH/dZ = 1 \text{ cm/cm, and that} \\ 1.1038 \times 10^9 \text{ sec} &= 35 \text{ years} \end{aligned}$$

With these assumptions, the retardation factor becomes

$$R = 1 + \frac{1.7\,(342)}{0.36} = 1{,}619$$

and solving equation 40 becomes

$$Z = (1.1038 \times 10^9)\,(1 \times 10^{-7})\,(1)/1619(0.09) = 0.8\ \text{cm}$$

On the basis of this approach, the compacted liner would have to be at least 1 cm thick to adsorb lead over a 35-year period. But although the application of a linear isotherm yields a reasonable coefficient of determination ($r^2 = 0.95$), inspection of figure 42 indicates that this approach overestimates lead adsorption at high lead concentrations and underestimates adsorption at lower concentrations. The adsorption of lead (table 14) is more accurately described by a Freundlich equation,

$$\frac{x}{m} = S = 291(\text{Pb})^{0.492}$$

As a second level of refinement, the nonlinearity of the isotherm is considered using equation 38 to estimate a weighted-mean retardation factor (Davidson et al., 1980). An appropriate value for C_0 was determined from a laboratory extract of the metallic waste sample (appendix B), which suggests that the maximum amount of lead that initially will come in contact with the liner is approximately 15 mg/L Pb. A revised retardation factor is derived from equation 38:

$$\bar{R} = 1 + \frac{1.7(291)15^{(0.492-1)}}{0.36} = 348$$

and the minimum thickness, based on the weighted-mean retardation factor, is

$$Z = (1.1038 \times 10^9)\,(1 \times 10^{-7})\,(1)/348(0.09) = 3.5\ \text{cm}\ .$$

Thus, when the nonlinearity of the isotherm is considered, the minimum thickness of the liner is estimated to be about 4 cm. As a third level of refinement, the chemical composition of the leachate was considered. The first two estimates were based on lead adsorption from a pure $Pb(NO_3)_2$ solution. Laboratory ex-

Table 14 Lead adsorption data for a $Pb(NO_3)_2$ salt and the Cecil clay (volume of solution, 200 mL; adsorbent weight, 10.18 g)

Initial conc (mg/L)	Equilibrium conc (mg/L)	Amount adsorbed (x/m) as µg/g	pH	EC (dS/m)
2.07	0.05	61	4.79	27
5.11	0.11	100	4.74	33
5.11	0.11	100	4.75	35
6.22	0.16	121	4.74	34
7.28	0.22	141	4.73	33
10.2	0.41	198	4.68	39
10.2	0.43	195	4.67	40
12.4	0.65	235	4.66	45
14.6	0.94	273	4.62	45
14.6	0.94	273	4.62	43

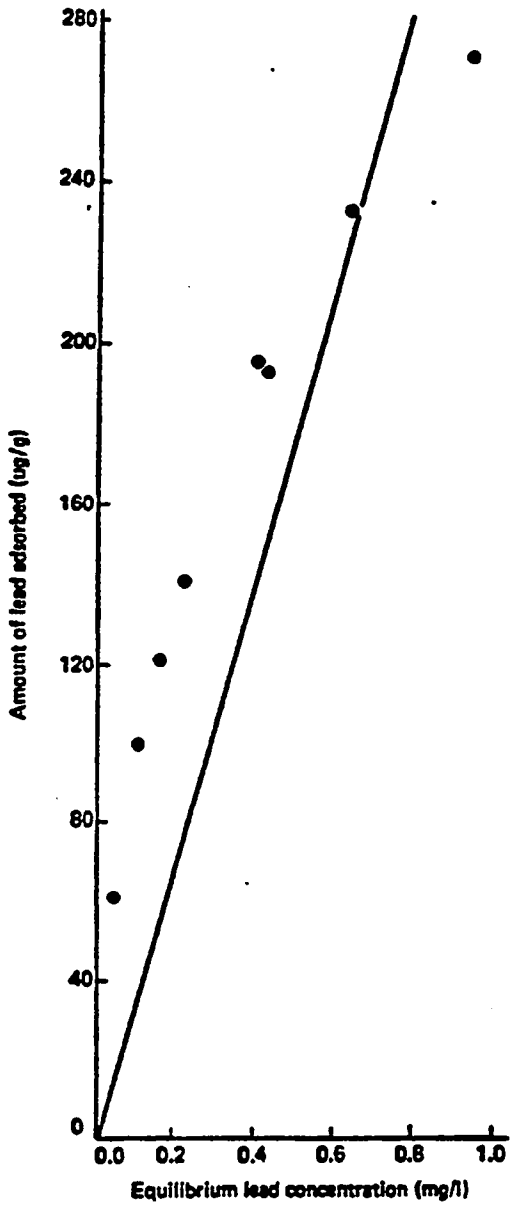

Figure 42 Lead adsorption by Cecil clay loam at pH 4.5 and at 25°C, described by a linear Freundlich equation forced through the origin.

tracts, of the waste also contained large concentrations of zinc (appendix B). The adsorption of lead from the extracts was significantly less than that from the pure $Pb(NO_3)_2$ solution, presumably because of competitive interactions between Zn^{2+} and Pb^{2+} for adsorption sites. The net effect is that lead could be more mobile in the presence of zinc. The adsorption of lead by Cecil from the laboratory extract of the waste can be described by

$$\frac{x}{m} = S = 70\,(Pb)^{0.481}$$

If the minimum liner thickness is recalculated using these isotherm constants and equations 38 and 40, the thickness is estimated to be about 15 cm, again assuming that the initial lead concentration in the leachate is 15 mg/L. Clearly, migration distance estimates based on adsorption data from pure, single-solute tests may underestimate the minimum thickness of liners because these estimates fail to account for competitive interactions that may significantly reduce adsorption. At the next level in refining the estimated liner thickness, the effects of dispersion and diffusion are considered. In saturated homogeneous materials that are subjected to steady-state flow conditions along a flow path z, the change in solute concentration as a function of time may be generalized (Ogata, 1970; Bear, 1972; Boast, 1973; Freeze and Cherry, 1979) as

$$\frac{\partial C}{\partial t} = D_z \frac{\partial C^2}{\partial z^2} - V_z \frac{\partial C}{\partial z} - \frac{\rho_b}{\theta} \frac{\partial S}{\partial t} \qquad [42]$$

where
- C = concentration of the solute,
- D_z = effective diffusion-dispersion coefficient (distance/time) along the flow path z,
- V_z = mean convective flow velocity (distance/time) along the flow path z,
- ρ_b = bulk density (wt/vol) of the material,
- θ = volumetric water content (vol/vol),
- S = amount of solute adsorbed per mass of adsorbent (x/m), and
- t = time

Equation 41 can be rearranged as

$$R\frac{\partial C}{\partial t} = D_z \frac{\partial C^2}{\partial z^2} - \bar{V}_z \frac{\partial C}{\partial z} \qquad [43]$$

where R is the retardation factor

The analytical solution to this second-order differential equation (Ogata, 1970) is given by

$$\frac{C}{C_0} = \frac{1}{2}\left[\operatorname{erfc}\left(\frac{z - Vt^*}{2(D_z t^*)^{0.5}}\right) + \exp\left(\frac{Vz}{D_z}\right)\operatorname{erfc}\left(\frac{z + Vt^*}{2(D_z t^*)^{0.5}}\right)\right] \qquad [44]$$

where
- C/C_0 = ratio of the solute concentration at time t and distance z to the intial solute concentration C_0,
- erfc = complementary error function,
- V = average linear pore water velocity (cm/sec),
- D_z = vertical dispersion coefficient (cm^2/sec),
- t^* = retarded time (actual time divided by the retardation factor of R or R), and
- z = vertical distance of migration (cm).

Furthermore, $D_z = a\bar{V} + D^*$, where a is the dispersivity (cm) and D^* is the effective diffusion coefficient in porous media (cm^2/sec).

In the following examples, the three previous liner thickness estimations were recalculated using equation 43. The only additional information needed to conduct this analysis was a dispersivity value. The dispersivity has been found to be scale-dependent and is estimated to be about 10% of the distance measurement of the analysis (Gelhar and Axness, 1981). A diffusion coefficient of Pb^{2+} in soil of 1×10^{-6} cm^2/sec was used in this analysis (Daniel et al., 1988). In figure 43, the relative concentration (C/C_0) is shown as a function of distance of migration after 35 years. Case A represents the first situation, in which the adsorption of lead, a $Pb(NO_3)_2$ salt, was assumed to be depicted by a linear isotherm. Case B corresponds to the second calculation, in which a weighted-mean retardation factor was used with the $Pb(NO_3)_2$ solute-

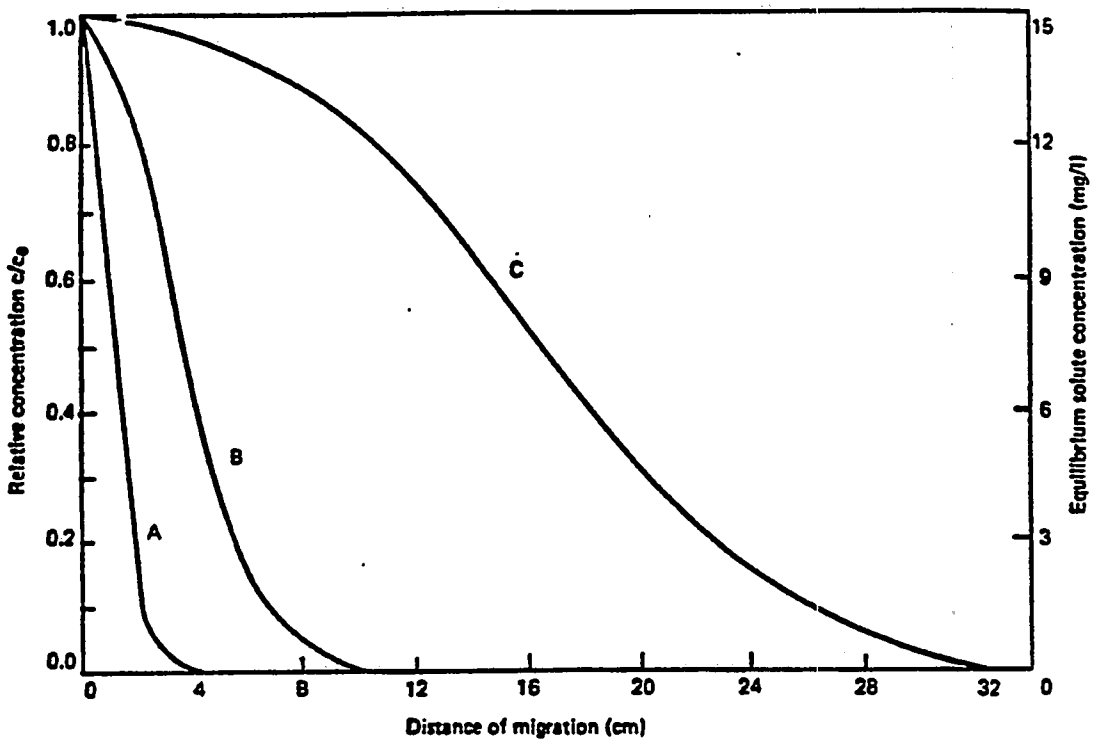

Figure 43 Predicted distance of lead migration in Cecil clay loam after 35 years, based on three approaches: case A (linear isotherm assumption, $Pb(NO_3)_2$ salt); case B (weighted-mean retardation factor, $Pb(NO_3)_2$ salt); and case C (weighted-mean retardation factor, multicomponent waste extract).

soil system. Case C represents the adsorption of lead from the multicomponent-waste extract, coupled with the corresponding weighted-mean retardation factor. Case C, which takes into account dispersion, indicates that lead may move farther than predicted by an elementary piston-flow model (eq. 40). The effects of diffusion on the predicted migration distances were negligible (not shown).

An element of interpretation is involved in evaluating graphs (see fig. 43) for the purpose of estimating liner thickness. A judgment must be made as to which C/C_0 ratio, for practical considerations, translates into the minimum significant concentration. In this hypothetical example, the regulatory agency decided that a lead concentration of <0.05 mg/L (the U.S. drinking water standard for lead) would be an operational definition of the compliance concentration.

If the initial lead concentration is 15 mg/L, the lead concentration of <0.05 mg/L is predicted to occur at a depth of 5 cm in case A and at 10 cm in case B. The results for case C represent the fourth level of refinement in this analysis, yielding the most accurate liner thickness estimate. After 35 years, the concentration of lead in solution would be reduced to <0.05 mg/L at a depth of 35 cm on the basis of these calculations. Consequently, the minimum liner thickness would be 35 cm. The actual thickness necessary in a field application must be somewhat greater to allow for nonequilibrium conditions and the normal engineering safety factors. The application of batch-adsorption data provides an estimation of boundary conditions, i.e., the minimum thickness.

In summary, the minimum liner thickness for a hypothetical liner varied from 1 to 35 cm, depending on the approach (table 15). Liner thickness estimates can be refined further if the adsorption data can be integrated with other information, such as the solubility of solid phases, oxidation-reduction equilibria, cosolvent effects, and the design and performance of on-site earthen liners. This information would include

seepage rate through the cover, fraction of seepage that will pass through the liner, and other water flux information that would allow calculation of the distribution of a pollutant in soil as a function of time and space.

Table 15 Approaches for estimating minimum liner thicknesses on the basis of adsorption

Flow model	Isotherm treatment	Solute system	Minimum liner thickness (cm)
Piston flow*	linear	single solute	1
Piston flow	nonlinear	single solute	4
Advection dipersion†	linear	single solute	5
Advection dispersion	nonlinear	single solute	10
Piston flow	nonlinear	mixture‡	15
Advection dispersion	nonlinear	mixture	35

* Represented by equation 41.
† Represented by equation 44.
‡ Laboratory extract.

APPENDIX F

ADSORPTION ISOTHERM CALCULATIONS FOR RIFLE, COLORADO, SITE

Adsorption Isotherm
Arsenic Background pH
Freundlich Best Fit Calculation

OBSERVED DATA		FREUNDLICH EQUATION			
C	x/m	log Ci	log Ci x log x/mi	$(\log Ci)^2$	(log x/mi)
0.03	2.0	-1.52	-0.46	2.31	0.30
0.041	3.9	-1.39	-0.82	1.93	0.59
0.1	7.6	-1	-0.88	1	0.88
0.6	14.0	-0.22	-0.25	0.048	1.15
1.1	18.0	0.04	0.05	1.6×10^{-3}	1.26
1.4	24.0	0.15	0.21	0.023	1.38
Σ 3.27	69.5	Σ -3.94	-2.15	5.31	5.56

$$\frac{1}{n} = \frac{6(-2.15) - (-3.94)(5.56)}{6(5.31) - (-3.94)^2} = \frac{9.0}{16.34} = 0.55$$

$$\log Kf = \frac{\sum \log x/mi}{n*} - \left(\frac{1}{n}\right)\left(\frac{\sum \log Ci}{n*}\right)$$

$$= \frac{5.56}{6} - (0.55)\left(\frac{-3.94}{6}\right) = 1.29$$

Kf = 19.4

$$\frac{x}{m} = 19.4\ C^{0.55}$$

THEORETICAL	
C	x/m
0.03	2.8
0.05	3.7
0.07	4.5
0.1	5.5
0.3	10.0
0.6	14.6
0.8	17.2
1.0	19.4
1.2	21.4
1.5	24.2

Adsorption Isotherm
Arsenic Background pH
Freundlich Equation
Rd(C) and Velocity (C) Calculations

Freundlich Best Fit: $\frac{x}{m} = 19.4\ C^{0.55}$

$$Rd = 1 + \frac{P_b\ Kf\ C^{\frac{1}{n} - 1}}{\theta n} = 1 + \frac{(2.1)(19.4)\ C^{0.55 - 1}}{0.27(1.8)}$$

Rd	C	(ft/yr) Velocity	C
402	0.03	–	0.03
320	0.05	–	0.05
275	0.07	1	0.07
234	0.1	1.2	0.1
143	0.3	2.0	0.3
105	0.6	2.7	0.6
92	0.8	3.0	0.8
84	1.0	3.3	1.0
77	1.2	3.6	1.2
70	1.5	4	1.5
172	0.2	1.6	0.2
126	0.4	2.2	0.4

$$V_{AS} = \frac{Vw}{Rd} = \frac{280}{Rd}\ ft/yr$$

Adsorption Isotherm Special Study
Arsenic pH 6 treated sediment

OBSERVED DATA		FREUNDLICH EQUATION			
C	x/m	log Ci	log x/mi	log Ci x log x/mi	$(\log Ci)^2$
0.023	4.0	-1.64	0.60	-0.98	2.69
0.1	7.6	-1	0.88	-0.88	1
0.56	14.4	-0.25	1.16	-0.29	0.063
0.98	20.4	-8.77×10^{-3}	1.31	-0.011	7.69×10^{-5}
1.4	24.0	0.15	1.38	0.21	0.023
1.5	30.0	0.18	1.48	0.27	0.032
1.7	30.0	0.23	1.48	0.34	0.053
		Σ -2.34	8.29	-1.34	3.86

$$\frac{1}{n} = \frac{7(-1.34) - (-2.34)(8.29)}{7(3.86) - (-2.34)^2} = \frac{10.02}{21.54} = 0.47$$

$$\log Kf = \frac{8.29}{7} - (0.47)\left[\frac{-2.34}{7}\right] = 1.34$$

$$Kf = 21.94$$

$$\frac{x}{m} = 21.9\ C^{0.47}$$

THEORETICAL	
C	x/m
0.02	3.5
0.05	5.4
0.08	6.7
0.1	7.4
0.2	10.3
0.4	14.2
0.6	17.2
0.8	19.7
1.0	21.9
1.4	25.6
1.5	26.5
1.7	28.1
0.3	12.4
1.3	24.8

Adsorption Isotherm Special Study
Arsenic pH 3
Langmuir Regression

OBSERVED DATA				
C	x/m	$(Ci)^2$	$\frac{Ci}{x/mi}$	$(Ci)\left[\frac{Ci}{(x/mi)}\right]$
5.09	29.1	25.91	0.17	0.87
3.58	24.2	12.82	0.15	0.54
2.79	22.1	7.78	0.13	0.36
2.12	18.8	4.49	0.11	0.23
0.93	10.7	0.86	0.087	0.08
0.098	9.0	9.6×10^{-3}	0.011	1.1×10^{-3}
0.27	2.3	0.073	0.12	0.03
14.88	116.2	Σ 51.94	0.78	2.11

$$\frac{1}{M} = \frac{n * \left[\sum Ci\left[\frac{Ci}{x/mi}\right]\right] - (\sum Ci)\left[\sum \frac{Ci}{x/mi}\right]}{n * (\sum Ci^2) - (\sum Ci)^2}$$

$$\frac{1}{M} = \frac{7(2.11) - (14.88)(0.78)}{7(51.94) - (14.88)^2} = \frac{3.16}{142.2} = 0.022$$

$$\frac{1}{K_L M} = \frac{\sum \frac{Ci}{x/mi}}{n *} - \left[\frac{1}{m}\right]\left[\frac{\sum Ci}{n *}\right] = \frac{0.78}{7} - (0.022)\left[\frac{14.88}{7}\right]$$

$$\frac{1}{K_L M} = 0.065$$

$$\frac{x}{m} = \frac{C}{0.065 + 0.022\ C}$$

need derivative
of this expression

$$Rd = 1 + \frac{P_b\left[\frac{C}{0.065 + 0.022\ C}\right]}{\theta}$$

LANGMUIR REGRESSION	
C	x/m
5.0	28.6
4.0	26.1
3.6	25.0
3.0	22.9
2.8	22.1
2.4	20.4
2.1	18.9
1.5	15.3
0.9	10.6
0.5	6.6
0.3	4.2
0.1	1.5

Adsorption Isotherm Special Study
Derivation of Rd function
from Langmuir Regression fit
Arsenic adsorption on pH3-treated Sediment

$$\frac{d}{dc}\frac{C}{0.065 + 0.022\,C} = \frac{d}{dc}\left[(0.065 + 0.022\,C)^{-1}\,C\right] =$$

(product rule)

$$\frac{d}{dc}\left[(0.065 + 0.022\,C)^{-1}\right]C + 1(0.065 + 0.022\,C)^{-1}$$

(chain rule)

$$= -1(0.065 + 0.022\,C)^{-2}\,(0.022)\,C + (0.065 + 0.022\,C)^{-1}$$

$$= \frac{1}{0.065 + 0.022\,C} - \frac{0.022\,C}{(0.065 + 0.022\,C)^2}$$

$$\frac{d\frac{x}{mi}}{d\,C} = R(C) = 1 + \frac{Pb}{\theta}\left[\frac{1}{0.065 + 0.022\,C} - \frac{0.022\,C}{(0.065 + 0.022\,C)^2}\right]$$

$$V(C) = \frac{V}{R(C)}$$

Rd	C	Velocity (ft/yr)
17.5	5.0	16
22.6	4.0	12.4
25.3	3.6	11.1
30.4	3.0	9.2
32.5	2.8	8.6
37.4	2.4	7.5
41.9	2.1	6.7
53.6	1.5	5.2
71.3	0.9	3.9
88.5	0.5	3.2
99.6	0.3	2.8
113.0	0.1	2.5

Variable definitions used in Adsorption Isotherm Calculations

Variable	Units	Description
C	mg/L	equilibrium concentration of a metal in groundwater
x	μg/g	amount of solute (metal) adsorbed
m	g	mass of adsorbent (aquifer matrix)
$\frac{1}{n}$	-	constant in Freundlich equation
K_f	-	Freundlich constant
P_b		bulk density of aquifer matrix
Θ	-	effective porosity
Σ	-	summation
R_d	-	retardation coefficient
V_{AS}	ft/yr	velocity of arsenic in groundwater
V_W	ft/yr	velocity of groundwater
V(c)	-	velocity as a function of metal concentration in groundwater
R(c)	-	retardation coefficient as a function of metal concentration in groundwater
n*	-	number of pairs of data points
$\frac{x}{m}$		$\frac{\text{(initial conc.-equil. conc.) x vol. of solution}}{\text{weight of adsorbent}}$
K_L		Laugmuir constant
M		Laugmuir constant