APPLICATION OF SITE-SPECIFIC ADSORPTION ISOTHERMS TO CONTAMINANT TRANSPORT PREDICTION AT THE DOE RIFLE UMTRA SITE

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ABSTRACT

For the last decade, the Department of Energy (DOE) has been remediating uranium mill tailings under the uranium mill tailings remedial action (UMTRA) Project. In the coming decade, the focus will shift to groundwater restoration at these sites. At UMTRA sites, a determination of the extent of contaminated groundwater, predictions of contaminant migration rates, and predictions of down-gradient concentrations are critical for restoration action plan design and groundwater compliance strategy formulation. This study was designed to: 1) identify methods to determine adsorption that are applicable to UMTRA Project sites; and 2) determine how changes in aquifer conditions affect metal adsorption, resulting retardation factors, and estimates of contaminant migration rates. EPA-recommended batch-type procedures and 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 site in Rifle, Colorado, were used as the adsorbents under different pH conditions. These pH conditions simulated geochemical environments under the tailings, near the tailings, and down-gradient from the tailings. Grain size, total surface area, bulk and clay mineralogy, and petrographic features of the sediments were characterized.

A subset of the hazardous constituents (that is, molybdenum, arsenic and uranium) that are of special concern to the UMTRA program were selected for investigation because of their mobility in either acidic or alkaline groundwater. In this report, only the results for arsenic and uranium will be described. Uranium forms large groundwater plumes at some UMTRA sites and arsenic is of toxicological concern at some UMTRA sites.

UMTRA SITE ENVIRONMENTS

Uranium mill tailings at many UMTRA processing sites were commonly slurried onto unlined exposures of nearby geologic units or into shallow unlined retention ponds. At many UMTRA sites, contaminant-rich acidic 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 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). 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. The migration velocities of these contaminants are attenuated relative to the advective groundwater velocity by sorption onto aquifer matrix materials.

RIFLE SITE DESCRIPTION

The Rifle site is located in a floodplain and the tailings rest on alluvial deposits containing shallow groundwater. 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). 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. Groundwater velocity is estimated to be 280 ft/yr (85 m/year), based on an average hydraulic conductivity of 70 ft/day, an effective porosity of 0.27, and an average hydraulic gradient of 0.003 (DOE, 1992).

The contaminant plume from the tailings at the Rifle site extends more than 8000 ft (2400 m) down-gradient and covers more than 400 acres (ac) [160 hectares (ha)] in the alluvium (Figure 1). The plume is characterized by concentrations of arsenic, cadmium, chromium, molybdenum, nitrate, selenium, silver, uranium, and net gross alpha activity, which exceed proposed EPA maximum concentration limits (MCL). Although there are other contaminants of concern at Rifle, this report has focused on the sorptive behavior of arsenic and uranium. Maximum concentrations of these two constituents exceed statistical maximum background concentrations and EPA MCLs in groundwater down-gradient of the tailings. Arsenic has not migrated down-gradient far enough for isopleth maps to be created; however, it is present at sufficient concentrations in the tailings area to be of toxicological concern.

AQUIFER MATRIX DESCRIPTION

At the Rifle site, sediment was collected from three test pits excavated at locations up-gradient of the known groundwater contamination (Fig. 1). The aquifer matrix sediments consisted of poorly sorted sandy to silty gravel and cobbles, which are brown to light brown. Grain-size distribution was determined by sieving and 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.

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. Only the two finer fractions were used in the
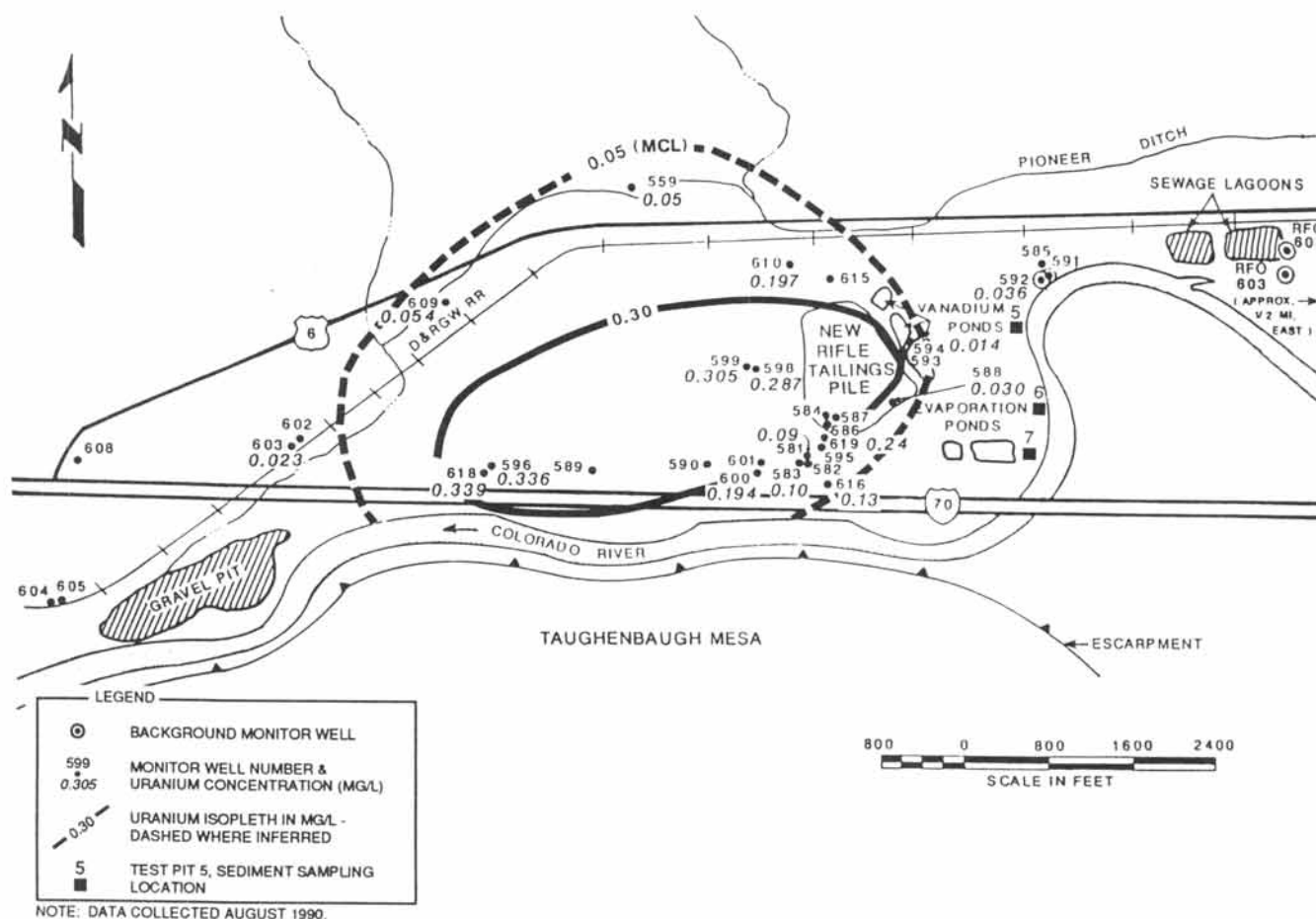
Fig. 1. Uranium concentrations in alluvial groundwater, new rifle site.

experiments because coarser fractions are much less likely to show significant sorption and because of time constraints.

The -40 (fine sand and finer) and +40/-10 (fine to coarse sand) fractions from each test pit are largely the same in terms of percent and composition of mineral and rock fragments. These sieve fractions were derived from non-indurated alluvial gravel, 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. 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. In both size fractions approximately 15 to 30 percent of the grains are coated.

The scanning electron microscope (SEM) observations show that clay overgrowth occur as complete coverings or as small patches on the grains. X-ray diffraction (XRD) analyses of aquifer sediment sample bulk mineralogy indicate the presence of quartz, plagioclase feldspar, carbonate, illite, kaolinite, and smectite.

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

washing had minimal effect on carbon content (as distinct from the carbonate content).

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).

BATCH TEST METHODOLOGIES

We used two common methodologies to determine sediment adsorption. One method is recommended by the EPA (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 intersect the origin).

ISOTHERM EXPERIMENTAL CONDITIONS AND RESULTS

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

As uranium mill tailings leachate from the Rifle tailings pile is acidic, pH was used as a gross indicator of geochemical conditions. Adsorption experiments were designed to simulate three geochemical environments: sub tailings (low pH), near down-gradient of tailings (intermediate pH), and far down-gradient (alkaline pH). Aquifer matrix sediment was treated with acidified Rifle groundwater under strongly acidified (pH 3) and mildly acidified (pH 6) conditions to represent near tailings and down-gradient geochemical environments. Although these sediments were treated with acidified groundwater, calcium carbonate was not completely removed from the acidified sediment batches. The background and far down-gradient geochemical environments were represented by untreated sediment and alkaline groundwater.

The metal-spiked groundwater used as stock solution in the batch tests was also acidified. Separate aliquot of Rifle background water that had been acidified to a pH of 5.8 and 2.8 with sulfuric acid were equilibrated with the mildly and more strongly acidified sediments, respectively. Owing to the residual calcite, the final equilibrium pH of the individual batch tests was variable and depended upon the soil:solution ratio of the batch tests and whether the mildly or more strongly acidified sediment was used.

Sorption Behavior of Uranium: Background pH Condition

A series of batch tests with variable soil:solution ratios were conducted using Rifle background water spiked with 10 mg/L uranium and background sediment. Uranium adsorption in the variable ratio batch tests from all three test pits was insufficient to generate a full six-point isotherm. Four variable ratio batch tests for the background system (1:1, 1:2, 1:3, and 1:4) demonstrated sufficient sorption to be precisely measured. 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 (Fig. 2). The variable slopes of these lines demonstrates that there are systematic differences in the uranium sorption characteristics between the sediment from test pits 5, 6, and 7.

Constant soil:solution ratio (1:10) 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. Only four samples from test pit 6 and three samples from test pit 5 demonstrated measurable sorption. The test pit 6 data define an isotherm that is nearly coincident with the variable ratio isotherm from test pit 7 (Fig. 2). The test pit 5 data define a constant ratio isotherm that is nearly coincident with the variable ratio isotherm from test pit 5 (Fig. 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 plotted in Fig. 2. 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 indicate that less uranium adsorption occurred during the ASTM batch tests.

Sorption Behavior of Uranium: Acidified pH Conditions

A constant ratio (1:10) isotherm (Fig. 3) was constructed for the strongly acidified system using initial solution uranium concentrations that ranged from 1.05 to 10.05 mg/L. A variable ratio (1:1 to 1:100) isotherm was constructed for the mildly acidified system (Fig. 3). These isotherms clearly demonstrate that uranium is 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. The extreme difference in uranium adsorption between the mildly and more strongly acidified systems is not, therefore, an artifact of the type of batch tests (variable versus constant ratio) that were used to construct these isotherms.

Despite the retention of carbonates in the acidified sediments, our results suggest that the neutralization of an acidic plume by a calcite-rich sediment results in an increase in the sorptive capacity of the sediment for uranium relative to background conditions.
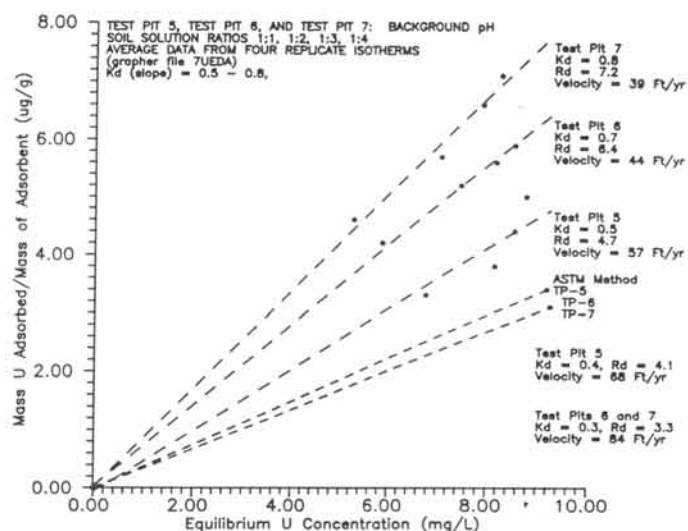
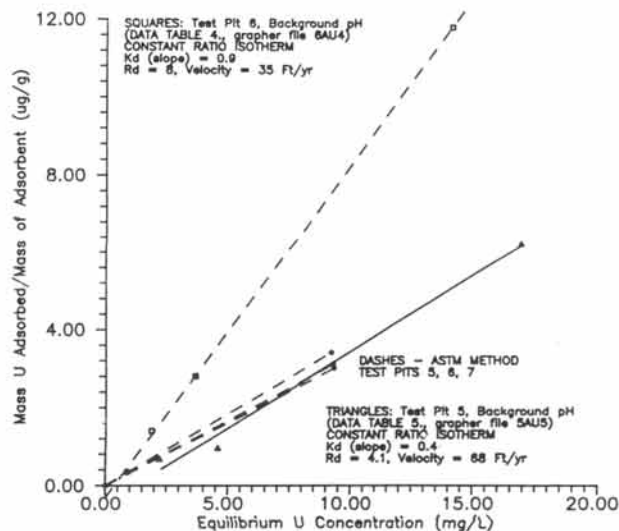URANIUM VARIABLE RATIO ISOTHERMS, BACKGROUND pH

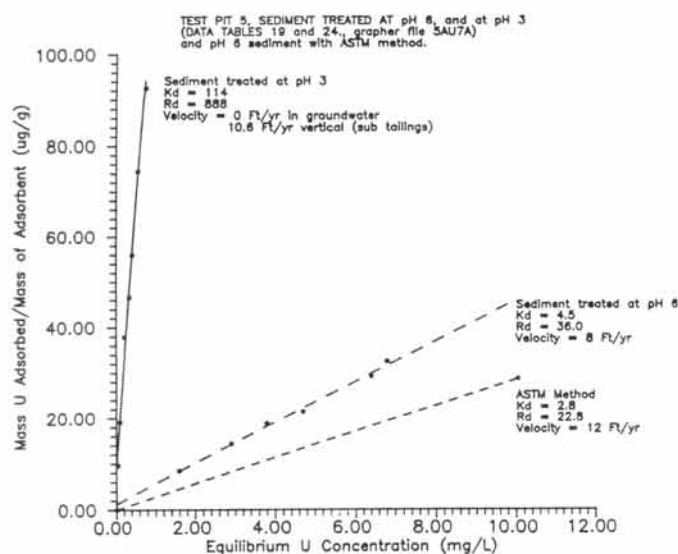Fig. 2. Uranium constant ratio isotherms, background pH.

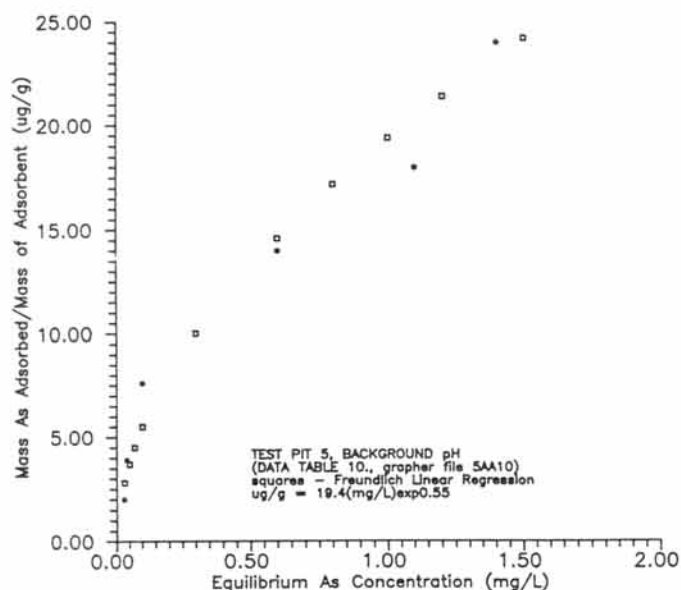Fig. 3. Uranium isotherms, acidified conditions.

Fig. 4. Arsenic variable ratio isotherm at background pH with freundlich regression curve.

Sorption Behavior of Arsenic: Background pH Condition

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. The Freundlich regression equation provided the best fit to the six-point isotherm that was generated using these batch test data (Fig. 5)

Sorption Behavior of Arsenic: Acidified pH Conditions

Variable soil:solution batch tests were also performed on arsenic in the moderately acidified system. 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 (Fig. 6).

Constant ratio batch tests were performed on arsenic in the more strongly acidified system producing a curve for which the Langmuir regression equation provided the best fit (Fig. 7). In contrast to the progressively greater sorption

observed for uranium 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 (Figs. 5 through 7).

The observed tendency of arsenic to adsorb less in the more acidified system was contrasted to the behavior of 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. 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 offset the increased sorptive capacity of the more strongly acidified sediment.

An ASTM batch test was conducted on the mildly acidified sediment. The sorption of arsenic demonstrated by the ASTM batch test (1:4 ratio) was comparable to that observed
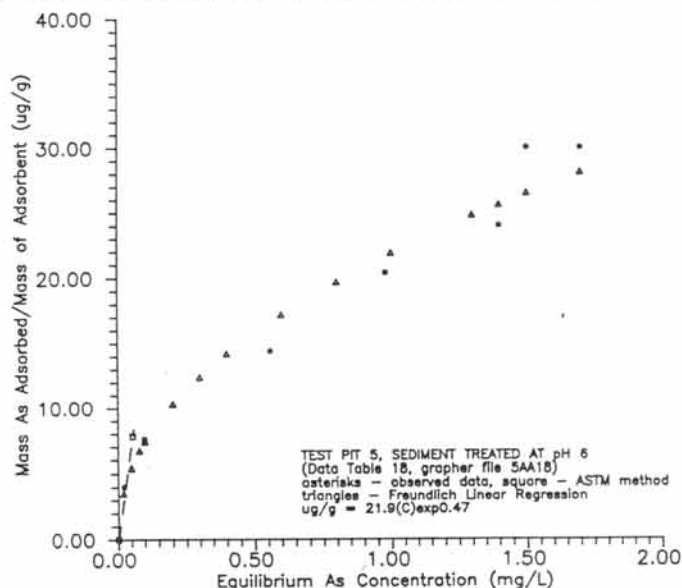

Fig. 5. Arsenic variable ratio isotherm, acidified sediment with freundlich regression curve.
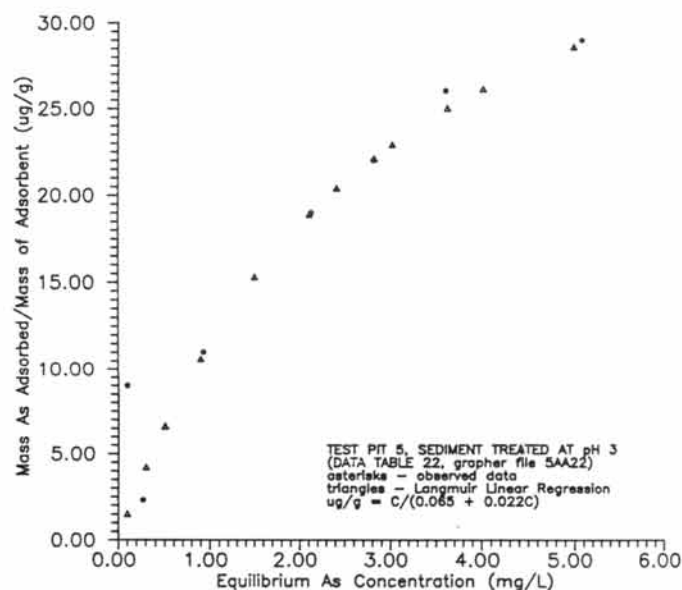

Fig. 6. Arsenic constant ratio isotherm, acidified sediment, with langmuir regression curve.

ARSENIC VELOCITY IN GROUNDWATR VERSUS
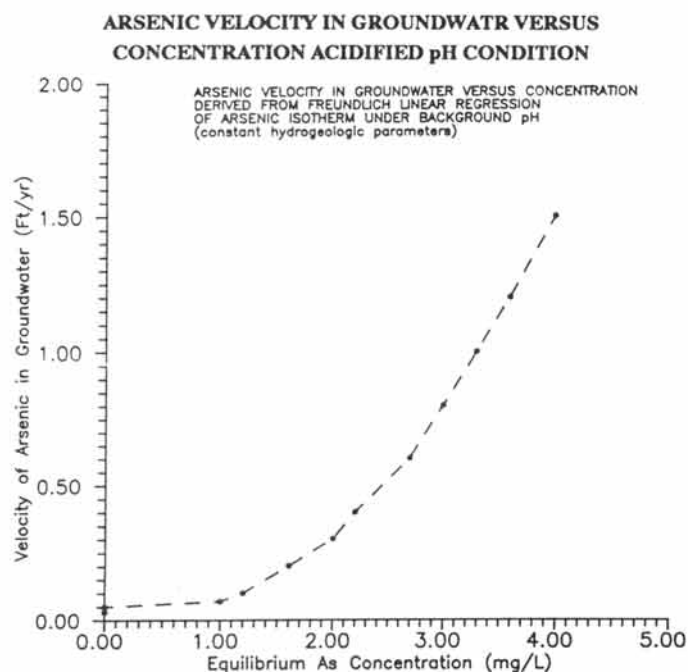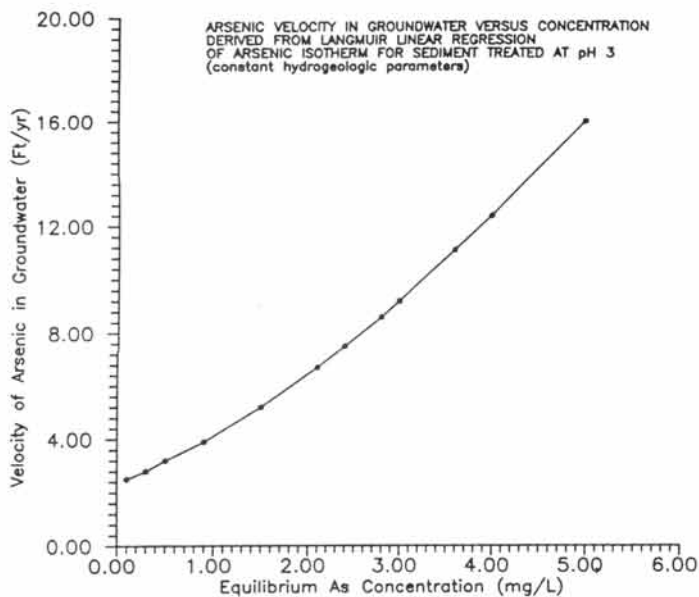CONCENTRATION ACIDIFIED pH CONDITION

Fig. 7. Arsenic velocity in groundwater versus concentration
alkaline pH condition.

observed for the 1:4 ratio batch tests of arsenic in the background and mildly acidified systems (Fig. 7).

Comparison of Different Methodologies

Uranium and arsenic 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 significantly lower than the K_ds generated by the variable ratio isotherms (Fig. 2). The EPA method constant ratio isotherms for uranium produced K_ds that were either higher than or very similar to the ASTM values (Fig. 2). Furthermore, the ASTM-derived K_ds for uranium showed very little variability for sediments of different test pits compared to the EPA methodology. Values ranged from 0.3 to 0.4 resulting in migration velocities differing by 24 percent (Fig. 2). 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 (Figs. 2 and 3) 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 sorbet 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 (Fig. 6).

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 be used.

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. 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.

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 0.33 percent, 0.50 percent, and 0.62 percent, respectively. This is consistent with increasing K_ds observed from test pit 5 to 7 (Fig. 2). 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.

APPLICATIONS OF ISOTHERMS TO CONTAMINANT TRANSPORT PREDICTION

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 the different types of adsorption isotherms determined in this study.

Uranium Migration Velocity

In alkaline pH conditions representative of groundwater unaffected by uranium mill tailings leachate, uranium migration velocity estimates range from 39 ft/year (ft/yr) [12 meter/year (m/yr)] to 84 ft/yr (26 m/yr) (Fig. 2) in comparison to the advective groundwater velocity estimate of 280 ft/year. The ASTM method yielded the most conservative (faster) migration velocities. There was significant migration velocity variation between sediments from different test pits, probably reflecting variations in organic carbon content or clay quantity or type in the area represented by each test pit.

As pH decreased, the estimated migration velocity decreased remarkably (Fig. 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 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 10.5 ft/yr (3.2 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 down-gradient 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.

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 (Figs. 4, 5, and 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. 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 (Fig. 7) under constant hydrogeologic parameters. These curves show the variation in arsenic migration velocity with respect to arsenic concentration in groundwater. They also illustrate the immobility of arsenic at low concentrations in alkaline conditions. Comparison of the two velocity curves for arsenic in alkaline groundwater and in acidic groundwater shows the extreme variation of arsenic mobility with respect to pH conditions.

CONCLUSIONS

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. However, our study shows that one adsorption parameter for the modeled area cannot represent the lithologic and geochemical spatial variability expected in an aquifer. 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 53 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. In the prediction of arrival times at down-gradient receptors for a risk assessment study, this would lead to differences on the order of tens of years. 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 (for example, extraction and land application).

In the case of uranium, this study has shown that migration velocities will increase as the Ph increases. At a site in which the tailings have been removed, neutral precipitation migrates downward and higher pH 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 to increase with time after tailings removal. Likewise, in the case of arsenic, this study has shown that migration velocities decrease as the pH increases. The pH change could cause arsenic migration velocities to decrease after tailings removal. These processes should be anticipated and addressed in groundwater restoration planning.

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

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.