Response to Comments From the Colorado Department of Public Health and Environment on the New Rifle Vanadium Pilot Treatment Performance Report

From: Wendy Naugle

Comment 1.
A more detailed evaluation of the extraction system is needed. This evaluation should include: (*a*) calculation of the mass of vanadium removed versus the mass remaining at the site, and (*b*) review of vanadium concentrations in other nearby monitor wells. In addition, (*c*) the hydraulic performance of the system should also be evaluated, which would include review of drawdown data, drawing a capture zone and (*d*) comparing the results of the extraction system with the numerical model predictions.

Response (*a*): Calculations of the mass of vanadium removed versus the mass available at the site is provided on the attached worksheet (see Calculation 1). Results are summarized below:

Mass of vanadium sorbed on the aquifer matrix is estimated at 31,766 kg, based on the amount of contaminated subpile soils in the saturated zone that could be providing a continuing source of groundwater contamination. This estimate is based on the following assumptions from the *Work Plan for Vanadium Pilot Study* (DOE 2000), previously provided to your office:

- Areal dimension of the subpile soil contamination is approximately 500-ft (W) x 500-ft (L).
- Thickness of contaminated subpile soil appears to be limited to the upper third of the saturated zone. The total saturated thickness is approximately 17.25-ft based on November 2000 water level measurements. The thickness of the upper third of the saturated thickness is therefore 5.75-ft (17.25/3).
- Mean concentration sorbed on the upper third of the saturated subpile soils is 553 mg/kg.

Mass of vanadium available in the soluble plume is estimated at 271 kg. The vertical and horizontal extent of the soluble plume is based on the *Work Plan for Vanadium Pilot Study* (DOE 2000) and the mean concentration in the plume is based on the Performance Report. The following assumptions apply:

- Areal dimension of the soluble plume is approximately 500-ft (W) x 500-ft (L).
- Vanadium contamination in the soluble plume appears to extend throughout the saturated zone. The total saturated thickness is approximately 17.25-ft based on November 2000 water level measurements.
- The average vanadium concentration in the soluble plume is 8.9 mg/L. This estimate is based on the average concentration from extraction well 864 observed during the pilot test (Table 4-1, Performance Report).

Mass of vanadium removed is estimated at 99 kg, based on the following assumptions from the Performance Report:

- Average vanadium concentration extracted is 8.9 mg/L (Table 4-1).
- Volume extracted is 2,942,350 gallons (Section 4.0).

Using the above assumptions, the mass of vanadium remaining at the site is estimated at 31,938 kg. A removal rate of about 10 kg/month (99 kg/10 months) is estimated given that 99 kg was extracted during the 10 months that the pilot plant was operated. At this rate, it would require 266 years to remediate all of the vanadium remaining at the site. However, optimization modeling suggests that the maximum extraction rate that can be sustained is approximately 100 gpm. Therefore, assuming that the operating capacity of the system can be increased from the current average rate of 9.6 gpm (Table 4-1 in the performance report) to 100 gpm, it would require about 26 years to remediate all the vanadium (266 x [9.6/100]).

Response (b): A review of vanadium concentrations in nearby monitor wells is provided in Table 1. Analytical results of groundwater samples collected between December 2000 and January 2001 before the treatment system was started, during the treatment operations in June 2001, and from the most recent sampling in December 2001, approximately one month after treatment operation was discontinued, are provided in the table for comparison.

Table 1. Results of Vanadium Sampling Before, During, and After Treatment Operations were Discontinued.

| Well ID | Description of sample location | Vanadium (mg/L) | | |
|---|---|---|---|---|
| | | Before treatment operations (12/00 -1/01) | During treatment operations (6/01) | One-month after treatment operations ceased (12/01) |
| 864 | Pumping well near center of soluble plume | 8.8 | 7.9 | 8.53 |
| 855 | New monitor well adjacent to well point 658 near center of subpile soil contamination | 20.0 | 17.3 | 23.1 |
| 658 | Well point near center of subpile soil contamination | 6.9 | 15.4 | 5.7 |

Response (c): Drawdown at pumping well 864 could not be measured directly because of turbulence in the casing created from the pump and return flow to the well. The submersible pump installed in well 864 was designed to operate at or near full capacity

around 25 gpm. Feed for the treatment system was diverted from the above ground discharge line from pumping well 864 and then all excess flow returned to the well, thus creating additional turbulence in the casing.

However, an estimate of drawdown in pumping well 864 can be obtained from aquifer test data collected after the well was installed (Calculation No. U0125100). Step-test results indicate that approximately 1.3-ft of drawdown can be expected in well 864 when the pump is operated at 10 gpm, the nominal operating rate during treatment. Extraction wells 862 and 863 are the nearest wells to pumping well 864, also located near the center of the soluble plume. Measured drawdown in these wells during the treatment operations are both about 5-inches. Wells 862 and 863 are located approximately 200 and 178-ft, respectively from the pumping well, a distance approximating the radius of influence.

Another first approximation of the radius of influence can be obtained by the equation:

$$r = [v/(\Pi)(b)(n)]^{0.5}$$

where;

r = radius (ft)
v = volume of water extracted (ft$^3$) during the treatment operations,
$\Pi$ = 3.14,
b = total saturated thickness (ft), and
n = porosity

Using 393,392 ft$^3$ (2,942,350 gallons) as the volume of water extracted, and assuming a saturated thickness of 17.25-ft and an effective porosity of 0.25, results in a radius of influence of 170-ft. This value is in reasonable agreement with the 200 and 178-ft radius based on the drawdown observed in wells 862 and 863, respectively. Both first approximations underestimate the actual radius of influence. The worksheet for this calculation is attached (see Calculation 2).

Response (d): The numerical model MT3DMS (McDonald and Harbaugh, 1988) was used to evaluate the amount of vanadium in the groundwater plume that could be expected to be recovered during the pilot test as a function of the linear distribution coefficient (Kd) and the volume extracted. The Kd (L/Kg) is equal to the first-order, sorption constant that describes the linear partitioning between the soil (mg/Kg) and groundwater (mg/L). A relatively high Kd value favors partitioning to the soil (i.e. immobile phase) while a relatively low Kd favors partitioning to the groundwater (i.e. mobile phase). The linear Kd retardation model assumes the system is in equilibrium between the solid and aqueous phases and does not account for the rate of mass-transfer between the soil and groundwater. Characterization results of vanadium contamination from soil and groundwater samples suggest a disequilibrium condition currently exists at the site (DOE 2000). However, for a first approximation, the bulk Kd parameter is used to describe the retardation of contaminant transport. For this modeling exercise, the actual Kd values obtained for the maximum (10.5), average (4.9), and minimum (1.2) measured

at the New Rifle site (DOE 1999) were used as input parameters. Simulations were performed at a nominal extraction rate of 10 gpm at pumping well 864. A continuing source of groundwater contamination in the subpile soil area was not modeled. Modeling results after extracting 3 million gallons of the soluble plume are shown in Figure 1. The simulations reveal that using the maximum Kd (10.5) the vanadium concentrations in the soluble plume at the pumping well can be expected to increase from the initial 8.80 mg/L to 8.82 mg/L, reflecting a rather stable concentration. Only a slight decrease to 8.61 mg/L is predicted using the average Kd (4.9). A significant decrease to 7.43 mg/L is predicted using the lowest Kd (1.2). The concentration increase observed for the lowest Kd that peaks after approximately 150,000 gallons of volume has been extracted reflects capture of the highest vanadium concentration located in the core of the soluble plume. This concentration "peak" is delayed and flatter for the higher Kds due to the greater partitioning to the solid phase. The greater partitioning to the solid phase results in relatively slower contaminant transport and explains the more stable vanadium concentrations.
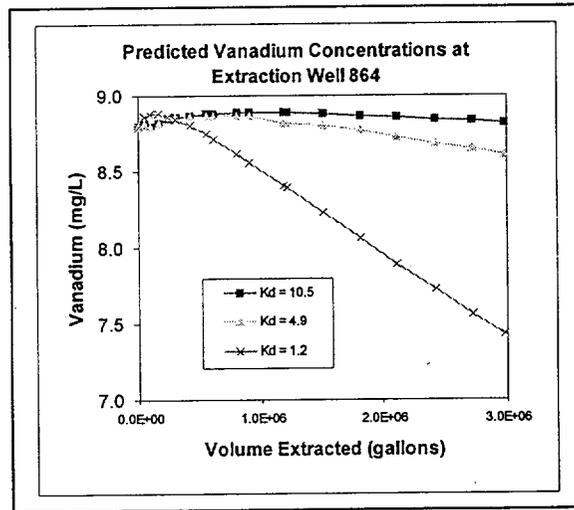


Figure 1. Results of MT3D model predictions using the maximum, average, and minimum Kd values measured for the site.

A comparison of analytical results obtained for vanadium from grab-samples collected at extraction well 864 during operation of the treatment system (Appendix A in the Performance Report) with the numerical model predictions is shown in Figure 2. The actual vanadium concentrations measured after extracting almost 3 million gallons of groundwater are slightly higher (on average greater than 9 mg/L) than the initial 8.80 mg/L concentration. These measured results are more consistent with the predicted trend using the maximum and average Kd values than for the minimum Kd.

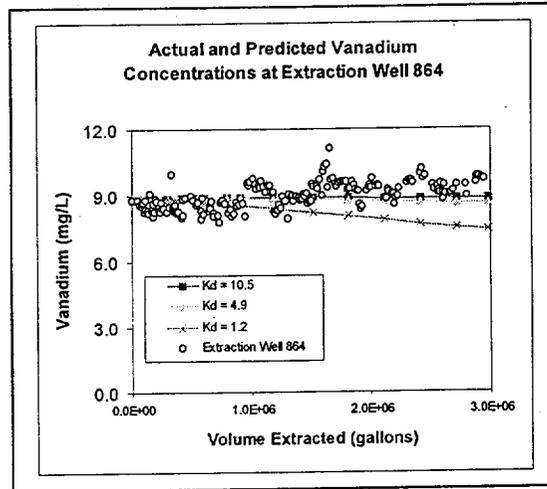**Actual and Predicted Vanadium Concentrations at Extraction Well 864**

Figure 2. Comparison of Laboratory Analytical Results for Vanadium with the MT3D model predictions using the maximum, average, and minimum Kd values measured for the site.

Comment 2.

(e) Page 5-1, section 5-1. The second sentence should use the word "influent" instead of "effluent".

Response (e): The use of the word "effluent" is correct as this sentence refers to water discharged from well 864 rather than feed to the treatment column. However, for clarification, this sentence was modified to state "groundwater collected from extraction well 864".

From: Jeff Deckler

Comment 3.

(f) What was the reason influent concentrations (9 mg/l) were well below plume concentrations (15-30 mg/l)?

   - (g) Is it because the V was being immobile? If so, would varying the pumping rates give us info to verify the hypothesis (if immobile, concentrations should decrease with increased flow rates).

   - (h) Would adding a lixivient verify the hypothesis by showing greatly increased concentrations at all pumping rates?

   - (i) What are other explanations for stable influent concentrations over 3M gallons. Is it just that this was a small fraction of the plume mass and there is still plenty there? Is the hot spot source just bleeding more off?

Response (f): The higher concentrations (15 – 30 mg/L) were measured during the vanadium characterization study from discrete 1-ft grab samples used to determine the vertical concentration profile of the plume (DOE 2000). The highest concentration of 32 mg/L was found in the middle of the saturated zone of the aquifer. Concentrations

ranged from 7 to 10 mg/L in the lower saturated zone and from 10 to 13 mg/L in the upper saturated zone. Excluding the highest concentration of 32 mg/L observed in the middle saturated zone, all the vanadium concentrations in grab samples collected from the soluble plume ranged from 6 to 13 mg/L. The average concentration (8.9 mg/L) obtained from extraction well 864 is consistent with the range in concentrations (6 to 13 mg/L) observed for most of the plume.

Current concentrations from well 864 cannot be directly compared with the 1-ft grab samples. This is because the grab samples were collected from temporary boreholes in slightly different locations than well 864 and water collected from well 864 represents more of an integrated sample over the screen interval rather than a discrete sample, explaining the difference in concentrations noted by the reviewer.

Response (g): The reviewer suggests that if vanadium is immobile then reduced concentrations should be correlated with increased flow rates and varying the pumping rates can test the hypothesis. Even though the pump rates were not varied during the pilot test to specifically address this hypothesis, examining the pump rates plotted in Figure 4-7 of the Performance Report can provide some insight. It is apparent from Figure 4-7 that the pump rates varied considerably during the pilot test. Considering one example, the pump rates were maintained constant at approximately 8 gpm from April 25 through May 14. The pump rates then increased to approximately 12 gpm and were maintained constant at this rate from May 21 through May 29. Vanadium concentrations versus the two different pumping rates are shown in Figure 3. No correlation between vanadium concentration and pump rate is apparent. In addition, the vanadium concentration during the 8 gpm period (April 25 through May 14) averaged 8.4 mg/L and during the 12 gpm period (May 21 through May 29) the concentrations also averaged 8.4 mg/L, indicating no significant difference in concentrations due to varying the pumping rates.
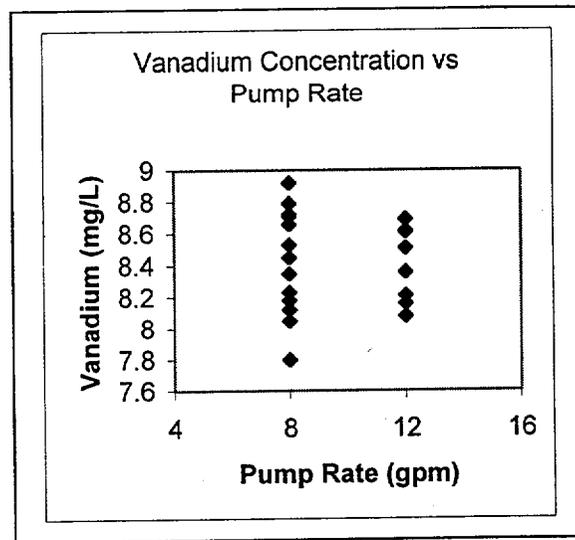


Figure 3. Vanadium Concentrations Versus Two Different Pump Rates.

Response (h):  The reviewer suggests that adding a lixiviant should result in greatly increased concentrations thereby verifying the hypothesis that vanadium is immobile. This hypothesis was tested at the DOE ESL by a column experiment using contaminated subpile soil collected from 8 to 10 ft below ground surface adjacent to monitor well 658. The vanadium concentration measured in the subpile soil sample was 857 mg/Kg (DOE 2000). Background groundwater collected from up gradient monitor well 215 was used as influent to the column filled with subpile soil. Three column tests were conducted; no lixiviant, 0.5M citric acid, and 0.5M Na citrate. Results of the column experiment are presented in Figure 4.
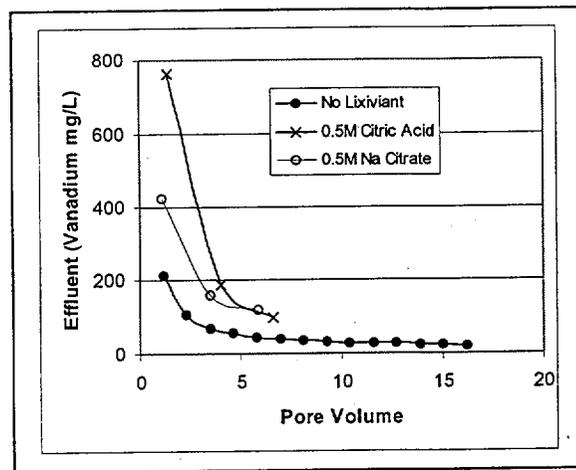


Figure 4. Vanadium Concentrations in Effluent from Column Experiment.

Evident from the data presented in Figure 4 are greatly increased vanadium concentrations at the beginning of the experiment using the two test lixiviants, as the reviewer suggested. Vanadium concentrations decreased by a factor of 4 using 0.5M Na citrate and by a factor of 8 using 0.5M citric acid after approximately 6 to 7 pore volumes, respectively. Concentrations decreased by approximately a factor of 5 using no lixiviant after a similar pore volume exchange.

It is also of interest to note that the rate of decrease in vanadium concentration observed using no lixiviant was greatly reduced after 5 to 6 pore volumes (Figure 4). This "tailing effect" suggests the partitioning between the solid and aqueous phase is not at equilibrium and that the linear Kd sorption model may not apply. The decrease in the rate of mass-transfer between the soil and groundwater phase observed in the column experiment may help explain the relatively stable concentrations (i.e. "tailing effect") observed at extraction well 864.

Clement (RT3D manual, PNNL-11720, 1998, see attachment) describes that in a rate-limited sorption reaction. . . "the exchange of contaminants between the soil and groundwater is dictated by the value of the mass-transfer coefficient. When the mass-transfer rate is high (relative to the overall transport), the rate-limited model relaxes to the

retardation model (i.e. Kd). On the contrary, very low mass-transfer coefficients would mimic fully sequestered conditions where the contaminants in the soil phase are assumed to be irreversibly adsorbed and trapped into the soil pores. Under this extreme condition, it might be possible to simply clean the groundwater plume and leave the sequestered soil contaminants in the aquifer because the sorbed contaminants may not pose any potential risk to the environment. In either of the extreme conditions, pump-and-treat is the best option to remediate the groundwater plume. Unfortunately, in most instances, the mass-transfer coefficient is expected to lie in an intermediate range, causing the well-known limitations to the pump-and-treat system".

This is the geochemical condition that exists for vanadium at the New Rifle site. Evidence that the soluble plume has migrated very slowly (approximately 400-ft in 40 years, DOE 2000) in a cobble-gravel alluvial aquifer with high hydraulic conductivity and recharge from the Colorado River suggests a low mass-transfer coefficient relative to the more mobile constituents (i.e. uranium) that have migrated much further (DOE 1999). Site-specific distribution coefficients (Kds) are also consistent with a relatively low geochemical mobility for vanadium (DOE 1999). The presence of a continuing source of relatively immobile vanadium on the aquifer matrix is suggested by the "tailing effect" observed from the column experiment (Figure 4) and evidenced by the stable vanadium concentrations during the removal of a mass representing 37 percent of the soluble plume. It is apparent that the low geochemical mobility for vanadium is limiting the restoration potential of the aquifer.

Response (i): The reviewer suggests that the 3 million gallons of ground water extracted from the plume may be a small fraction of the plume mass and there is still plenty there and alternatively suggests the presence of a hot spot source that is just bleeding more off. In actuality, a relatively large fraction of the soluble plume was removed during the pilot test. The assumptions to support this response are provided in the response to comment 1 above. The mass of vanadium available in the soluble plume is estimated at 271 kg. The mass extracted is estimated at 99 kg. This represents 37 percent of the soluble plume. However, because removal of this mass did not result in a decrease in plume concentrations, a relatively immobile form of vanadium is present in the aquifer matrix that is providing a continuing source that is "bleeding off".

Comment 4: (j) Should they look at reintroducing the water upgradient rather than downgradient in the full scale system (we are not there yet).

Response (j): Optimization modeling using a flow and particle-tracking algorithm was performed to evaluate the location of the pumping wells, the number of pumping wells, and the pumping rates to best design the extraction field. The modeling also considered reintroducing the treated water both up gradient and down gradient of the extraction field. Because the quality of the treated effluent required the water to be returned to the aquifer at a location within the plume boundary, the up gradient location for an infiltration gallery was relatively close to the extraction field. Modeling results indicated that several more extraction wells and 25 percent higher flow rates would be required to capture the plume by reintroducing the treated effluent to the aquifer at a nearby up gradient location

rather than at a down gradient location. In addition, locating the infiltration galley in the down gradient McCauley pit area provided a source of higher water quality to the mitigation wetland, which will help dilute ammonia and nitrate concentrations and accelerate plume migration through the wetland.

Calculation 1. Mass removed versus mass remaining.

mass removed:

8.9 $\frac{mg}{L}$ x 2,942,350 gl x 3.78 $\frac{L}{gl}$ = 98,986,539 mg x 0.001 $\frac{g}{mg}$ x 0.001 $\frac{kg}{g}$ = **99** **kg** removed

mass available in saturated soils:

500 ft x 500 ft x 5.75 ft = 1,437,500 $ft^3$ x 0.037 $\frac{yd^3}{ft^3}$ x 2,400 $\frac{lb}{yd^3}$ x 0.45 $\frac{kg}{lb}$ = 5.7E+07 kg sat. subpile soil

553 $\frac{mg}{kg}$ x 5.74E+07 kg x 0.001 $\frac{g}{mg}$ x 0.001 $\frac{kg}{g}$ = **31,766** **kg** available in saturated soils

Mass available in soluble plume:

500 ft x 500 ft x 17.25 ft = 4.31E+06 $ft^3$ x 7.48 $\frac{gl}{ft^3}$ = 3.E+07 gl x 0.25 porosity = 8.1E+06 gl total vol of plume

8.9 $\frac{mg}{L}$ x 8.06E+06 gl x 3.78 $\frac{L}{gl}$ = 2.71E+08 mg x 0.001 $\frac{g}{mg}$ x 0.001 $\frac{kg}{g}$ = **271** **kg** available in soluble plume

Mass remaining at site:

| | | |
|---|---|---|
| mass available in saturated soils | | 31,766 |
| mass available in soluble plume | + | 271 |
| total mass available | | 32,037 |
| less mass removed | - | 99 |
| mass remaining | | **31,938 kg** |

Calculation 2. First approximation of radius of influence from pumping well 864.

| Volume of water (gls) extracted | | ft3/gl | | vol (ft3) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,942,350 | x | 0.1337 | = | 393,392 | | | | | | | | |

| vol (ft3) water | | pi | | sat. thick (ft) | | porosity | | r² | | exponent | | radius (ft) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 393,392 | / | 3.14 | / | 17.25 | / | 0.25 | = | 29,051 | ^ | 0.5 | = | 170 |

Volume of water based on actual volume treated at end of operations (2,942,350 gls).
Saturated thickness based on water levels measured November 2000.

# *Rate-Limited Sorption Reaction*

This tutorial illustrates the steps involved in using *GMS* and *RT3D* to model sorption reactions under mass-transfer limited conditions. The flow model used in this simulation is different from the one used in other example problems. Hence, the steps involved in creating input data for both the flow and the reactive transport models will be described in this tutorial exercise.

## 6.1    Description of the Reaction Model

The fate and transport of an organic pollutant in subsurface environments is often highly dependent on its sorption characteristics. Under most natural groundwater flow conditions, the partitioning of contaminants between the solid and aqueous phases can be assumed to be at a local equilibrium. Thus, the more widely used retardation approach for modeling sorption may provide an adequate description for the overall transport. However, when external pumping and injection stresses are imposed on an aquifer (e.g. using a pump-treat-system), the equilibrium assumption may fail. This would lead to some well-known conditions such as the plume tailing effect (i.e. low contaminant levels always observed at the extraction well) and/or the rebounding effect (i.e. aquifer seems to be clean but the aqueous concentrations start to increase immediately after stopping the treatment system). These conditions cannot be simulated using the standard linear retardation approach since they require a mass-transfer description for the sorption reactions.

In the mass-transfer limited sorption model, the exchange of contaminants between the soil and groundwater is assumed to be rate limited. The rate of exchange is dictated by the value of the mass-transfer coefficient. When the

mass-transfer rate is high (relative to the overall transport), the rate-limited model relaxes to the retardation model. On the contrary, very low mass-transfer coefficient would mimic fully sequestered conditions where the contaminants in the soil phase are assumed to be irreversibly adsorbed and trapped into the soil pores. Under this extreme condition, it might be possible to simply clean the groundwater plume and leave the sequestered soil contaminant in the aquifer because the sorbed contaminants may not pose any potential risk to the environment. In either of the extreme conditions, pump-and-treat is the best option to remediate the groundwater plume. Unfortunately, in most instances, the mass-transfer coefficient is expected to lie in an intermediate range, causing the well-known limitations to the pump-and-treat system.

When sorption is assumed to be rate-limited, it is necessary to track contaminant concentrations in both mobile (groundwater) and immobile (soil) phases. Following Haggerty and Gorelick's (Water Resource research, 30(2), 435-446, 1994) approach, the fate and transport of a sorbing solute at aqueous and soil phases can be predicted using the following transport equations:

$$\frac{\partial C}{\partial t} + \frac{\rho}{\phi}\frac{\partial \tilde{C}}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s}{\phi}C_s \quad\text{.............................} (6.1)$$

$$\frac{\rho}{\phi}\frac{\partial \tilde{C}}{\partial t} = \xi\left(C - \frac{\tilde{C}}{\lambda}\right) \quad\text{.............................} (6.2)$$

where C is the concentration of the contaminant in the mobile-phase [ML$^{-3}$], $\tilde{C}$ is the concentration of the contaminant in the immobile phase (mass of the contaminants per unit mass of porous media, [MM$^{-1}$]), $\rho$ is the bulk density of the soil matrix, $\phi$ is the soil porosity, $\xi$ is the first-order, mass-transfer rate parameter [T$^{-1}$], and $\lambda$ is the linear partitioning coefficient (which is equal to the linear, first-order sorption constant $K_d$) [L$^3$M$^{-1}$]. It can be mathematically shown that the above model formulation relaxes to the retardation model when the value of $\xi$ becomes high (see Clement et al. 1998 paper in the spring issue of Groundwater Monitoring and Remediation journal).

The mass-transfer model discussed above has been implemented as an RT3D reaction package (one mobile species and one immobile species). After employing reaction-operator splitting, the reaction package for the problem reduces to:

$$\frac{dC}{dt} = -\xi\left(C - \frac{\tilde{C}}{\lambda}\right) \quad\text{.............................} (6.3)$$

$$\frac{d\widetilde{C}}{dt} = \frac{\phi\xi}{\rho}\left(C - \frac{\widetilde{C}}{\lambda}\right) \quad\text{..........................................................................(6.4)}$$

These two differential equations are coded into the model #4 designated as the rate-limited sorption reaction module.

## 6.2   Description of Problem

The example problem we will be solving in this tutorial is shown in Figure 6.1. The site is a 1000 ft x 500 ft section of an unconfined aquifer with flow gradient from left to right. A spill at the center of the site has created a contaminant plume as shown in the figure. A pump-and-treat system, using three injection and extraction well at the constant rate of 4000 ft³/day, will be used to clean the contaminant plume. Aqueous concentration of contaminant level throughout the plume is assumed to be at 300 mg/L. The linear partitioning coefficient ($K_d$ or $\lambda$) for the contaminant is assumed to be $1.0 \times 10^{-7}$ (L/mg), soil dry bulk density, $\rho$, is assumed to be $1.5 \times 10^{6}$ (mg/L), and porosity is assumed to be 0.3. Note these parameters yield an effective retardation coefficient value of 1.5 ($R = 1 + \rho\lambda/\phi$). Assuming equilibrium conditions exist before starting the pump-treat-treatment system, the initial soil-phase contaminant concentration levels, $\widetilde{C} = \lambda C$, can be estimated to be at $3 \times 10^{-5}$ (mg of contaminant/ mg of soil). The objective of the treatment system is to clean both dissolved and soil-phase contamination. The model will simulate the effectiveness of the system under different mass transfer conditions. A 3000 day simulation will be performed. The mass-transfer coefficient values will be varied to simulate retardation conditions (using $\xi = 0.1$ day⁻¹), intermediate conditions (using $\xi = 0.002$ day⁻¹) and sequestered conditions (using 0.0001 day⁻¹). Time series plots and contour plots will be used to visualize the treatment scenarios under different field conditions.