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Date: Mon, Aug 15, 2005 4:23 PM
Subject: Response from "Comment on NRC Documents"

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richard j. abitz (rich.abitz@fernald.gov) on Monday, August 15, 2005 at 16:22:45

Document_Title: Consideration of Geochemical Issues in Groundwater Restoration at Uranium In Situ Leach Mining Facilities

Comments: The authors have done a good job illustrating the complexity of geochemical systems associated with in situ uranium mines. In particular, the manuscript conclusions, and the historic record of groundwater restoration at in situ uranium mines in Wyoming, Texas, and New Mexico (Mobil pilot test near Crownpoint), indicates U, As, Se and other toxic metals remain above baseline concentrations for long periods of time following restoration. This condition warrants the NRC concern on establishing appropriate bonds prior to mining to ensure ample restoration costs are set aside. Moreover, the NRC should consider the class-of-use of each aquifer as a key factor in the licensing of in situ uranium mines. Specifically, aquifers that serve as drinking water for present or future communities should never be subject to in situ uranium leaching because restoration to this class-of-use is not possible.

The manuscript can be improved by clarifying some assumptions and by providing additional summary data from historic operations. Specific examples of suggested improvements follow.

Comment 1

ABSTRACT (page iii)

In the concluding sentences of this abstract, it is noted that when the influent groundwater is oxic, concentrations of U, As and Se will remain above baseline concentrations for a long period of time. This is a very important statement because upgradient water at most in situ uranium mines is oxic, a point that is also made by the authors (page 17, first column). Therefore, the abstract can be improved by noting that this oxic condition is sufficient to restrict in situ uranium mines to those aquifers that cannot be used as a source for drinking water.

Comment 2

Section 2 (page 5)

At the bottom of the first column, it is noted that the shape of ore bodies is complex, general consisting of deposits or interconnected rolls. It would be beneficial to indicate that the complex geometry of the deposits reflects differential flow within the sandstone, with preferred flow channels pushing sections of the roll front deeper down gradient.

Comment 3

Section 3

This section is too brief and it does not illustrate the geochemical reactions that occur when lixiviant is introduced into the ore zone. At a minimum, a summary table should be added that shows the important oxidation and speciation reactions for Fe, S, U, As, Se, V and Mo. Most notably, the aqueous complexes that are considered in the non-electrostatic adsorption model discussed in Section 5.2 (page 24) are missing.

Comment 4

Section 4 (page 15)

Near the bottom of column one, it is noted that the thickness of the water contamination zone around the ore body (important for determining the pore volume) should depend on what is known about vertical mixing of the fluids during mining. As vertical migration of contaminated water within the mined aquifer is

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generally not monitored, it is better practice to set the thickness of the contaminated water based on the pre-mining class-of-use condition. Highest quality water would require the entire thickness of the aquifer or vertical monitoring to set the thickness. Lower quality aquifers would be set to the screened intervals of extraction wells. The lowest quality aquifers might be set to the ore body thickness.

Comment 5

Section 4 (page 15)

Near the bottom of column two, class-of-use conditions are brought up. The NRC should define the range in the class-of-use conditions and provide guidance on what conditions warrant the use of above-ground treatment and *in situ* reduction after mining. For example, drinking water aquifers would be exempt from *in situ* uranium mines, while aquifers suitable for livestock and agriculture would require above-ground treatment and *in situ* reduction after mining.

Comment 6

Section 4 (page 16)

In the second column, it is noted that heterogeneity in aquifer sediments results in variable porosity and permeability in the aquifer, and contamination can bleed from these immobile zones long after mining is complete. This observation supports the suggestion to the NRC to establish restoration practices and costs that are tied to pre-mining class-of-use conditions for the aquifers, and to limit *in situ* uranium mines to those aquifers that cannot be used as a source of drinking water.

Comment 7

Section 4 (page 17)

A general discussion on the water quality information available for other sites (bottom of column one) should be expanded to include a table that summarizes the pre-mining baseline, restoration condition, and post-restoration monitoring for the sites. This information is critical to compare with the simulation of the Ruth ISL facility. Moreover, information on post-restoration water quality sheds light on the time needed to return the disturbed mining zone to baseline conditions (see discussion in the middle of column one on page 17). In particular, post-restoration water quality in wells tied to early operations in the 1970's would illuminate the thirty-year picture of returning an aquifer to a reducing condition.

Comment 8

Section 5.1 (page 19)

Near the bottom of the first column, the discussion correctly notes subsurface heterogeneity in porosity and permeability leads to excursion of lixiviant along paleoflow channels within the aquifer and the storage of mobile U, As, and Se species in clay-rich silt and sand deposits adjacent to the paleochannels. The continual bleed of contaminants into well connected flow channels is a serious problem if the aquifer class-of-use is drinking water, and this slow bleed over long periods of time is the basis for NRC to restrict *in situ* leach mining to those aquifers that cannot serve as a source of drinking water. This guidance should appear in the document because the elimination of *in situ* leach mining in aquifers that possess drinking-water quality is a direct conclusion from the consideration of geochemical issues in groundwater restoration at existing *in situ* leach mining facilities.

Comment 9

Section 5.1 (page 19)

Prior to Section 5.2, the values of the dimensionless mass transfer coefficients are given as 10 and 0.0001. What do these values imply about the mixing proportions between the immobile and mobile cells? Does 10 mean 10% immobile component and 90% mobile? Additionally, a brief discussion on the geochemical basis for selecting this range of values would be helpful. For example, 10 may account for the rapid desorption of contaminants and 0.0001 for the oxidation and dissolution of uraninite as redox values slowly increase in the low-permeability zones.

Comment 10

Section 5.2 (page 20)

In the first column, it is noted that only thermodynamic simulations were considered in this report. Realistically, this is the only approach possible. Although PHREEQC, EQ3/6 and other geochemical

codes have the option to do kinetic modeling, the cost and time needed to produce a data set to model the important kinetic reactions (e.g., each step in a dissolution reaction, competition of ions for each different adsorption site, etc) is prohibitive. As such, the limited data sets produced from the study of kinetic reactions are generally not sufficient to describe the dynamic sediment-water system, which leaves us with our thermodynamic models.

Comment 11

Section 5.2 (page 20)

In the second column, the authors correctly state that uranium recovery is always less than 100 percent, which implies uranium minerals are left in the ore zones. Based on this factual statement, it is puzzling to the reader to see model scenarios that have no uranium minerals present (Scenarios 1, 2, 3 & 4). Clearly, there are secondary U(VI) phases that can form as alteration rinds around uraninite (e.g., shoebite) and these could be modeled as the stable U phases using the initial oxic conditions found in the aquifer prior to the onset of restoration.

Comment 12

Section 5.2 (page 20)

The authors correctly note, near the bottom of the second column, that mining companies cannot minimize restoration costs by assuming that reducing conditions will return to the mined zone by natural processes. This ties back to NRC establishing restoration guidance based on the class-of-use concept. On one end of this guidance, if water quality meets drinking water criteria, then in situ mining would be prohibited in the aquifer. The anchor point on the other end of this scale would be no restoration, if the pre-mining water quality showed the water to be too brackish for any domestic use.

Comment 13

Section 5.2 (page 23)

The first paragraph states that the presence of reduced minerals has the greatest influence on the post-restoration contaminant concentration levels. This is not necessarily true if the influent water is reducing, as demonstrated by some of the modeling runs. The most important parameter is the redox state of the influent groundwater.

Comment 14

Section 5.2 (page 24)

In the upper part of column one, the authors note that stability constants for the adsorption reactions were estimated using selected experimental data found in Dzombak and Morel and Waite et al. It would be beneficial to the reader to have a summary table that indicates the experimental data used from the cited studies and the process of their estimation.

Comment 15

Section 5.2 (page 24)

At the bottom of column one, and continuing to the top of column two, the statement is made that sulfate adsorption is assumed to be negligible for the chemical conditions modeled. This assumption is not justified, as sulfate becomes the second most abundant anion present in the groundwater when pyrite is oxidized by the injection of lixiviant into the ore zones. As uranium will form anionic uranyl carbonate complexes, sulfate will compete for available sites. Notably, sulfate is 20 times more abundant, relative to U, based on groundwater sweep charts on Figure 11.

Comment 16

Section 5.2 (page 24)

In column two, the authors enter into a general discussion on the evaluation of the concentration term for surface sites. It would be helpful to provide some basis for their surface-area value of 0.13 m²/g. It is also recommended that the authors strengthen the conclusion on adsorption constants for real sediments being less than those in their study. For example, they state "...may be several orders of magnitude smaller..." There is little doubt that the adsorption constants will be much lower, and an expanded discussion as to why they will be lower seems warranted. This discussion would note the sulfate issue in Comment 15, some estimate on the mass of hydrous ferric oxide produced by oxidation of pyrite, the fact

that arsenic, selenium and vanadium tend to form oxyanions under the strong oxidizing conditions imposed by the lixiviant, and the elevated pH associated with the sodium-bicarbonate lixiviant is likely to be near or in excess of the pH of zero point charge for hydrous ferric oxide, hence little to no adsorption of anions.

Comment 17

Section 5.2 (page 26)

The second column notes that influent water was switched to a mix of 25% effluent and 75% pure water after removing the initial pore volume. Based on the mass transfer of material from the immobile to the mobile cells, there is a third component to the mixture.

Comment 18

Section 5.2.1 (page 27)

In the second paragraph of the second column, the discussion on the field observations for the Ruth ISL, the authors note that small secondary peaks occur for chloride, bicarbonate and sulfate after the first pore volume is removed. Based on Fig 11, the behavior is more complex for sulfate, as it remains elevated throughout restoration. This elevation is no doubt tied to the oxidation of sulfide during the H₂S treatment and, possibly, an adsorption-desorption mechanism for sulfate. The adsorption-desorption mechanism may account for the disagreement between the observed and modeled results for sulfate (see Comment 15).

Comment 19

Section 5.2.1 (page 34)

The first column notes that Simulations 5 & 6 are not consistent with the field observations that show higher U values during restoration. This is probably another kinetic issue with mildly oxidizing water existing with uraninite in the immobile zones. A more realistic result may be obtained if the immobile water is modeled as mildly oxidizing and schoepite is considered as the U phase surrounding remnant uraninite.

Comment 20

Section 5.3 (page 38)

The authors correctly note that hydraulic conductivity and hydraulic gradient vary substantially at ISL sites, which results in differential groundwater velocity within and proximal to the ore zones. The variation in groundwater velocity means that when 100 pore volumes are pumped from the aquifer, most of that water comes from the zones with the highest groundwater velocity, and it should be made clear that the low-velocity zones will not have exchanged 100 pore volumes when the total volume of water removed equates to 100 pore volumes. This is the difficult nature of cleaning up contaminated aquifers; it is hard to exchange the water in low-flow zones in a timely fashion. Therefore, the simulations will underestimate the long-term concentration of the contaminants.

Comment 21

Section 5.3.1 (page 55)

Two important points are raised in the second column: 1) the number of adsorption sites and 2) adsorption sites occupied by those ions with the highest affinity for the site. This particular example used V(V) as the ion with the highest affinity for the sorption site, but it may well be sulfate if sulfate were considered in the model. It would not hurt to restate that the anionic U, As, Se, and V specie concentrations predicted by the model are underestimated because anions with the highest concentrations (bicarbonate, chloride and sulfate) are not considered in the adsorption model.

Comment 22

Section 6 (page 66)

The overall conclusion is that oxic groundwater flowing into a mined zone will remobilize constituents, and this is the normal case for ISL sites. Therefore, it is very important for NRC to define the aquifer class-of-use and provide guidance on the issuance of an ISL license and the remediation effort necessary to restore a mined zone. For an aquifer class-of-use that meets drinking-water criteria, a license to mine should not be issued, as the groundwater cannot be restored to drinking-water standards. When an

aquifer is suitable for domestic livestock or irrigation, a license would be issued under the conditions that above-ground treatment and injection of a reducing agent are part of the restoration plan. When an aquifer is too brackish for any domestic use, restoration would not be required.

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