Response to Comments from the Nez Perce Tribe
Proposed Redox Manipulation Treatability Test
J. S. Fruchter
5/09/96

General Response: The proposed 100 Area project is only a treatability test, and not a proposed remedy. Therefore, not all questions concerning the technology can be answered completely. In order to progress further, the treatability test is necessary to further evaluate its applicability to Hanford groundwater contamination.

1. Addition of more chemicals.

We share the concern about the addition of more chemicals, and are pursuing other methods of redox manipulation that result in the addition of fewer chemicals. However, these alternative methods are currently in bench-scale testing only. In the mean time, about ninety percent of the chemicals added are subsequently withdrawn from the aquifer.

2. Questions concerning longevity.

The only way to test the longevity of a redox treatment zone is through a test such as that proposed for the Hanford 100 Area. Degradation curves, derived from monitoring of groundwater and soil cores will be established. Otherwise, we must rely on modeling bench-scale experiments with sediments from the 100 Area. The circular geometry of the 100H test makes determination of the barrier reoxygenation rates difficult, because of large edge effects. The linear geometry proposed at for the Treatability Test will greatly aid in developing these data.

3. Reprecipitation of iron.

The reprecipitation of the iron is an important part of the redox concept, as it should further lower the concentration of chromium in the aquifer, as well as any low concentrations of metals (e.g. arsenic) that were mobilized during the dithionite injection. Only about 10% of the total iron in the Hanford aquifer is in the form of iron oxides/oxyhydroxides. The rest is present in the layered and other silicate minerals and is not subject to mobilization. We believe that the iron precipitation will occur slowly during reoxygenation of the plume, and thus not cause plugging problems. However, this is one of the key questions to be answered during the 100 Area Treatability Test. The 100H experiment was performed as a small proof of principle experiment. Its geometry is less well suited to answering this question.

4. Sulfate left in the aquifer.

During the 100H test, 88% of the sulfate was recovered. This could be improved somewhat by careful design, but it is probably not feasible to recover more that 95% without pumping out inordinate amounts of water. We believe this will cause less of a problem than the chromate which will be removed.

5. Increase in aquifer pH.

The pH of the aquifer is raised during the injection through the addition of potassium carbonate. This is necessary in order to keep the dithionite from decomposing to sulfate before it has a chance to react with ferrous iron in the aquifer solids. Most of the carbonate is withdrawn from the aquifer after the injection along with the sulfate. The small remaining amount is not expected to have a lasting effect. The pH in the monitoring wells within the reduced zone has returned to within 1 pH unit from pretest levels six months after the 100H field test.

The reoxidation of the structural iron in the clay minerals is the only contributor to a pH rise during the reoxidation of the reduced zone. This should be buffered principally by dissolution of matrix materials (quartz, feldspars, possibly including clay) and to a lesser extent by precipitation of Fe(OH)3 from adsorbed Fe2+ that is oxidized.

6. Anoxic water.

We agree that this is a crucial aspect of the technology as it would be applied to protection of the salmon. If we replace chromate contaminated water with anoxic water, we will clearly not have accomplished the goal. Although we will continue to monitor the 100H site, downgradient monitoring data from the 100-H Area study is not adequate to quantify reoxygenation rates due to edge effects from the limited extent of the reduced zone and the uncertainties in the gradient direction. This problem has been aggravated during the past few months during the elevated water table at the site from the flooding. Potential migration of the anoxic plume from the 100-H Area site was addressed in the test plan using a simple dispersion model which showed a 10 to 20 percent decrease in the dissolved oxygen from ambient levels by the time the 60 ft wide plume traveled the approximate 2000 ft distance to the Columbia River. One of the objectives of the proposed 100 Area Treatability Study is to collect the required data to address this issue. The length of the proposed ISRM barrier and downgradient monitoring network planned for the proposed study are adequate to reduce the influence of edge effects and uncertainty in the gradient.

Some additional simulations were conducted accounting for diffusion and dispersion within the aquifer in order to estimate a conservative limit to the magnitude of the anoxic plume. Taking into account additional processes (e.g., trapped air bubbles, water table fluctuations) would act to increase the reoxygenation rates. The geometry and hydraulic properties used in these simulations were taken from the 100-H Area ISRM Site. The unconfined aquifer (Hanford Formation gravels) is approximately 3 m thick with a clay unit forming the base (Ringold Formation mud). The domain was 100 m long with a porewater velocity in the unconfined aquifer of 1 ft/day. Simulations were conducted in which anoxic water entered the system in the lower 1.5 m of the aquifer and other simulations were conducted with the anoxic water entering the upper 1.5 m of the aquifer. The diffusion coefficient (in free solution) for dissolved oxygen in the model was 2.29×10^{-5} cm^2/s and the dispersivities used in the model were 0.1 m for longitudinal and 0.01 m for transverse (these are conservative for gravels and cobbles).

For the case where the anoxic plume is in the lower 1.5 m of the aquifer (similar to the 100-H Test), the anoxic plume is reoxygenated to more than 10% of the ambient value starting at about

25 m downgradient. The plume has reoxygenated to 33% of the ambient value at a 100 m distance downgradient. In the simulation where the anoxic plume is in the upper 1.5 m of the aquifer, the plume has reoxygenated to 10% of the ambient value at about 7.5 m distance downgradient, 30% at a 20 m distance, and 75% at an 85 m distance. The upper zone case reoxygenates faster and in a shorter distance than the lower zone anoxic case due to the proximity of the upper zone to the vadose zone (results of this simulation are more sensitive to assumptions of flux through the vadose zone). The reoxygenation of the lower anoxic plume is limited by the aqueous diffusion and transverse dispersion rates.

Additional studies to quantify reoxygenation rates are ongoing and similar modeling is planned for the proposed 100 Area Site once the pre-design characterization is completed at the site and the depth interval that will be targeted for reduction is determined.

7. Other reduced metals.

The only other metal present in the Hanford groundwater expected to be retained is uranium. If significant quantities of uranium are present in the groundwater at the 100 Area Treatability Test Site, it could be immobilized in the reduced zone, and later remobilized during oxidation, since uranium is not as resistant to reoxidation as chromium. There is at present no reason to believe that it would be released at any higher concentration than that present in the ground water at this time. When reoxygenation data become available from the 100 Area test, this factor will be reevaluated.

8. Groundwater monitoring.

We agree that monitoring is necessary.

9. Redox costs.

One of the important goals of the proposed 100 Area treatability test is to develop a realistic cost model for the entire life cycle of the technology, so that it can be compared with other candidate technologies. Both well emplacement costs and well abandonment costs will be considered. Monitoring costs will also be considered. Although many constituents will have to be monitored, because redox manipulation is a passive system, it will only have to be monitored infrequently (probably quarterly), which will help keep the monitoring costs down.

Response to Comments from Larry Gadbois, EPA
Proposed Redox Manipulation Treatability Test
J. S. Fruchter
5/09/96

Comment #1:

Chromium-III is less toxic and less mobile than chromium-VI, however it still has toxic properties and has some mobility. Will the end state of chromium (following in-situ treatment) be adequately protective? For example:

> "sensitive species of freshwater aquatic organisms showed reduced growth, inhibited reproduction, and increased bioaccumulation at 10 ug/l of Cr+6, and other adverse effects at 30.0 ug/l of Cr+3".
>
> Eisler, Ronald 1986. "Chromium Hazards to Fish, Wildlife, and Invertebrates: a Synoptic Review". U.S. Fish and Wildlife Service, Biological Report 85(1.6). Page 44.

Eisler, 1986 provides reference to a number of "maximum acceptable toxicant concentration" values, including the following for Cr+3:

"Daphnia magna" 47-93 ppb.
Rainbow trout 30-157 ppb.

Does the Cr+6 to Cr+3 coming out of solution tend to bind to colloids with which they have been traveling (and thus still be mobile) or does it tend to attach to the aquifer matrix (the desired reduced mobility)? The data presented at the April 3 meeting indicated that sampling was done for Cr+6, not for total (or +3) chromium. Thus we don't know the extent to which chromium was de-mobilized. Also if samples were filtered prior to analysis, we have lost relevant information.

Response:

Cr(III) is present in the reduced zone in concentrations of 5 - 11 ppb. This is due to equilibrium with $Cr(OH)_3$. At the pH of the unconfined aquifer (i.e., between 7 and 10) the amount of Cr(III) in solution would be on the order of 5-10 ppb (i.e., $\sim 10^{-7}$ M; Rai et al., 1987). This 5-10 ppb Cr(III) should only be present within the reduced zone. Sass and Rai, 1987, showed that precipitation of ferric hydroxide lowers the Cr(III) solubility by at least a factor of 100 due to the formation of iron-chromium solid solutions. It is expected that when the Cr(III) reenters the oxidized aquifer outside the reduced zone, that the total chromium concentration will drop well below analytical detection limits. In addition, Cr(III) is known to be specifically adsorbed by iron oxyhydroxides and, once out of the reduced zone, would be rapidly incorporated into these phases. We will continue to analyze the monitoring well samples for both hexavalent and total chromium, both at 100H, and at the proposed 100 Area Treatability Test Site.

Concerning the possibility of colloidal transport, it is doubtful that significant colloidal transport would occur because the relatively high ionic strength (ca. 10 mM) and the ionic composition (i.e., high Ca) of the groundwater causes a high rate of colloid flocculation.

Comment #2:

The data presented on April 3 regarding remobilization of other metals contradicts the conclusion provided on April 3. Arsenic, selenium, antimony, lead nickel, and copper all increased in concentration. Cadmium was the only metal analyte that did not measurably increase in concentration. The following data was provided:

Metal	Pre-Treatment (ppb)	6-months Post-Treatment (ppb)
Arsenic	<1	7
Selenium	<1	6
Cadmium	<1	<1
Antimony	<1	3
Lead	<1	2
Nickel	3	16
Copper	4	9

This data was summarized as "no significant metals mobilization". Statistically, these numeric changes are clearly significant. Post-treatment selenium exceeds the freshwater chronic ambient water quality criteria for protection of aquatic life. Also with the very low criteria for arsenic for the protection of human health via the aquatic pathway for arsenic as a carcinogen, any increase in arsenic concentrations is adverse.

Response:

It is true that the concentrations of several metals were slightly higher in the reduced zone than beforehand. This increase would be expected (in the absence of sulfides), especially for arsenic due to mobilization of the iron oxides in the aquifer. Arsenic is strongly adsorbed by iron oxide surfaces and thus very low arsenic concentrations would be expected once the reduced arsenic ions in the reduced zone migrate into the oxidized sediment, where the iron oxides should reprecipitate. Likewise, selenium concentrations would tend to decrease upon reaching an oxidized zone containing iron oxides and oxyhydroxides. This question will continue to be addressed in the proposed 100 Area Treatability Test. The geometry of this test will permit verification that concentrations of these metals will decrease upon reoxidation.

Comment #3:

Nearly anoxic conditions and most aquatic life is a deadly mixture. Data provided on April 3 shows the in-situ redox technique is obviously very good at driving the treated aquifer towards anoxia. As this reduced plume moves downstream of the treatment area, what is the re-oxygenation rate? When the Columbia river starts dropping and the current plume

migrates to the river, will its oxygen content be monitored? If oxygen levels are not rebounding in time to protect the river substrate community, what is DOE's contingency plan to protect the river? What about future larger-scale testing or use of this technique? I can imagine the tremendous uncertainty associated with:

(a) estimated gaseous transport through the vadose zone (oxygen getting down to the water table),

(b) diffusion into and through the relatively stagnant capillary fringe (note that oxygen transport via diffusion in water is 10,000 times slower than in air), so this may be the controlling factor,

(c) calculating the oxygen debt associated with colloids moving with the water (i.e. more than just the mass of water that needs to be re-oxidized)...

Thus, I'd trust real data, but I'd be leery of modeled estimates.

Response:

We agree that many of the factors that could attenuate the anoxic plume are complex, poorly understood, and some important parameters are not well characterized. Although we will continue to monitor the 100H site, downgradient monitoring data from the 100-H Area study is not adequate to quantify reoxygenation rates due to edge effects from the limited extent of the reduced zone and the uncertainties in the gradient direction. This problem has been aggravated during the past few months during the elevated water table at the site from the this spring's unusually high river stages. Potential migration of the anoxic plume from the 100-H Area site was addressed in the Hanford 100-HR-3 Operable Unit In Situ Redox Manipulation Treatability Test Plan using a simple dispersion model which showed a 10 to 20 percent decrease in the dissolved oxygen from ambient levels by the time the 60 ft wide plume traveled the approximate 2000 ft distance to the Columbia River. One of the objectives of the proposed 100 Area Treatability Study is to collect the required data to address this issue. The length of the proposed ISRM barrier and downgradient monitoring network planned for the proposed study are adequate to reduce the influence of edge effects and uncertainty in the gradient.

In addition to the factors listed in the comment that influence the reoxygenation rates, other mechanisms that complicate the analysis include the composition of the air within the vadose zone, concentration and variation of dissolved oxygen within the aquifer, and water table fluctuations. Recent field and laboratory studies by Dr. J. D. Istok at Oregon State University have discovered the importance of trapped air bubbles below the water table in controlling dissolved gas concentrations and transport due to the partitioning of the gases between these trapped air bubbles and the aqueous phase. Depletion of the dissolved gas will drive the gas from the air bubbles into the aqueous phase, thus increasing the dissolved gas content. The volume of trapped air bubbles and magnitude of this effect in the upper unconfined aquifer at the Hanford Site is unknown, but can be determined through multiple gas tracer injection tests.

Although the comment mentioned being leery of modeled results, we conducted some

ditional simulations taking into account diffusion and dispersion within the aquifer in order estimate a conservative limit to the magnitude of the anoxic plume. Taking into account additional processes (e.g., trapped air bubbles, water table fluctuations) would act to increase the reoxygenation rates. The geometry and hydraulic properties used in these simulations were taken from the 100-H Area ISRM Site. The unconfined aquifer (Hanford Formation gravels) is approximately 3 m thick with a clay unit forming the base (Ringold Formation mud). The domain was 100 m long with a porewater velocity in the unconfined aquifer of 1 ft/day. Simulations were conducted in which anoxic water entered the system in the lower 1.5 m of the aquifer and other simulations were conducted with the anoxic water entering the upper 1.5 m of the aquifer. The diffusion coefficient (in free solution) for dissolved oxygen in the model was 2.29×10^{-5} cm^2/s and the dispersivities used in the model were 0.1 m for longitudinal and 0.01 m for transverse (these are conservative for gravels and cobbles).

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Additional studies to quantify reoxygenation rates are ongoing and similar modeling is planned for the proposed 100 Area Site once the pre-design characterization is completed at the site and the depth interval that will be targeted for reduction is determined. Measurements will also continue at 100H this year and next.

As mentioned in the comment, the aqueous diffusion rate of dissolved oxygen is a limiting factor compared to the much greater gaseous diffusion rates in the vadose zone. Fluctuations in the water table elevation would help to increase the flux of dissolved oxygen into the aquifer. The magnitude of the reoxygenation in the simulations with the anoxic plume in the lower 1.5 m of the aquifer is not very sensitive to the flux of oxygen through the vadose zone, although it does influence the dissolved oxygen depletion of the upper portion of the aquifer. Two phase (air and water) transport simulations of the saturated and unsaturated zone are underway to bracket the boundary conditions used in the 1.5 m upper zone anoxic plume simulation.

c) The number of colloids moving in Hanford groundwater is negligible in comparison to other sites in the eastern part of the US, where ionic strengths are as much as an order of magnitude lower and the cation suite contains fewer multivalent cations.

Comment #4:

What happens to the chemistry of other chemicals in the aquifer matrix and groundwater -- beyond the handful of metals that have been monitored? What are their toxicological side-effects.

Response:

During the Redox Field Test at 100H, the metals analyzed were selected for the following reasons:

A. Those which are regulated.
B. Those which may be toxic.

We felt that this covered most of the trace metals of concern in the Hanford system. Some major constituents in Hanford groundwater, such as silica, alumina, barium and calcium, are controlled by mineral solubility, and should not be affected by redox manipulation. Monovalent and divalent cations, such as sodium, potassium and magnesium are in fact monitored in some, but not all samples to conserve funds. They were not reported in our viewgraphs because they did not meet criteria A or B. If they are of interest, they will be reported in the future.

References

Rai, D., B. M. Sass, and D. A. Moore. 1987. "Chromium III Hydrolysis Constants and Solubility of Chromium III Hydroxide". Inorg. Chem., 26, 345-349.

Sass, B. M., and D. Rai. 1987. "Solubility of Amorphous Chromium(III) - Iron(III) Hydroxide". Inorg. Chem., 26, 2228-2232.