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Department of Energy

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APR 15 2003

Mr. James A. Saric, Remedial Project Manager
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Region V, SR-6J
77 West Jackson Boulevard
Chicago, Illinois 60604-3590

DOE-0333-03

Mr. Tom Schneider, Project Manager
Ohio Environmental Protection Agency
401 East 5th Street
Dayton, Ohio 45402-2911

Dear Mr. Saric and Mr. Schneider:

TRANSMITTAL OF RESPONSE TO COMMENT DOCUMENT FOR THE OHIO ENVIRONMENTAL PROTECTION AGENCY COMMENTS ON THE REVISED TEST PLAN FOR IN-SITU STABLIZATION THROUGH ENHANCED ANAEROBIC REDUCTIVE PRECIPITATION

The purpose of this letter is to transmit the subject responses for your review and approval.

If you should have any comments, please contact Robert Janke at (513) 648-3124.

Sincerely,

Johnny Reising

Johnny W. Reising
Fernald Remedial Action
Project Manager

FCP:R.J. Janke

Enclosure: As Stated

Recycled and Recyclable

cc w/enclosure:
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RESPONSES TO OHIO EPA COMMENTS ON THE REVISED TEST PLAN FOR IN SITU CHEMICAL STABILIZATION OF METALS AND RADIONUCLIDES THROUGH ENHANCED ANAEROBIC REDUCTIVE PRECIPITATION

FERNALD CLOSURE PROJECT
FERNALD, OHIO

APRIL 2003

U.S. DEPARTMENT OF ENERGY

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RESPONSES TO OHIO EPA COMMENTS ON THE REVISED TEST PLAN FOR IN SITU CHEMICAL STABILIZATION OF METALS AND RADIONUCLIDES THROUGH ENHANCED ANAEROBIC REDUCTIVE PRECIPITATION

1. Commenting Organization: Ohio EPA Commentor: OFFO
Section #: Pg #: Line #: Code: general
Original Comment #: 1
Comment: The baseline technology for the remediation of the Great Miami Aquifer (pump and treat followed by re-injection) has proven successful in reducing the greater-than 30 ppb total uranium plume. Total mass of uranium removed also indicates that the baseline technology is making good progress in achieving the remedial goals. The Ohio EPA greats this new technology with skepticism considering the success of our baseline technology and the reservations expressed below about the new technology.
Response: DOE agrees with EPAs assessment of the proven success of the pump-and-treat aquifer remediation to date. DOE also shares EPA's skepticism in the use of this new technology. DOE though has committed to assess any new or developing technology that could improve the aquifer remediation. This commitment is found in the Operable Unit 5 Record of Decision along with the commitment that any enhancement technique will only be applied to the aquifer remedy with the specific approval of the EPA and Ohio EPA.

The objective of this National Environmental Technology Laboratory (NETL) sponsored bench-scale study is to demonstrate the efficacy of ARCADIS's enhanced anaerobic reductive precipitation (EARP) technology for precipitating uranium from contaminated groundwater. DOE viewed it as a screening step to determine if there was any merit to bring the technology to EPAs attention for evaluation at the FEMP.

Although it is premature to conjecture how the technology might be used at the FEMP, DOE does not envision that it would ever be used to completely replace pump-and-treat. What is envisioned is having another tool available to address possible future recalcitrant areas that might not be responding fully to pump and treat.
Action: No action required.

2. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: NA Pg #: NA Line #: NA Code: general
Original Comment #: 2
Comment: The text states an important feature of the in-situ precipitation is its irreversibility. The reverse dissolution does occur. For example, elevated uranium concentrations occur naturally in groundwater in geologic formations containing uranium ore deposits. The key for a successful application of the technology is the understanding and characterization of dissolution kinetics for uranium or other metal precipitants. The phase diagrams illustrate the theoretical potential for the occurrence of precipitation as well as dissolution, depending on environmental conditions (e.g., Eh, pH). It is the dissolution kinetics that will dictate applicability of the EARP technology. As proposed, one of the two success criteria is that the expected dissolution time for 90 percent of the constitute of concern should be at least five times longer than the half-life of the nuclide. To assess if the IRZ/EARP technology will meet this success criterion for uranium, the relevant dissolution kinetic constants need to be established. The testing plan as currently designed will not, in our view, generate data for accurate determination of these parameters.

Response: This project is funded under a DOE/NETL demonstration contract that envisioned that bench scale demonstrations might be conducted for several DOE facilities with varying contaminants. Thus some aspects of the test plan are generic. For example the introduction (section 1) presents our mechanistic understanding of the action of the EARP technology on several metals and radionuclides including those that are not constituents of concern at Fernald. Similarly in

section 3.1 one of the "non-site specific" success criteria presented applies only to short lived radionuclides:

" (2) The expected dissolution time for 90% of the constituent of concern, ***if it is a short-lived radionuclide*** (under expected ORP + pH conditions), will be at least five times longer than the half-life of that hazardous radionuclide. This criteria should ensure that these short-lived radionuclides will have a sufficient time to decay into less hazardous forms before release."

Thus since the half-life of uranium is long (>245,000 years for all common isotopes, (Institute for Energy and Environmental Research, (IEER)) we believe it is not appropriate to apply this criteria to Uranium. We apologize if this presentation was confusing. Rather we believe that the first "non-site specific" success criteria in section 3.1 and the quantitative site-specific objective in section 3.2 would be more reasonable goals.

Since the primary theme of the reviewer's questions was reoxidation and resolubilization kinetics, we will present an extensive discussion of this matter at this point so as to avoid repetition.

Processes that effect Uranium Resolubilization and Oxidation – Introduction and Overview
We agree that process kinetics are important to this analysis but in a full scale application, the potential for uranium remobilization will be controlled by many more factors in addition to the kinetics of the uranium oxidation reaction. These are discussed more fully below but include preferential oxidation of other reduced compounds, preferential consumption of oxidants by sulfide minerals, sorption of uranium to fresh amorphous iron oxides and sorption of uranium to iron sulfide minerals.

Size, Sequence and Mineralogy of Reactive Zone Formation
If DOE and the EPAs agree to proceed to a full-scale demonstration at Fernald, ARCADIS envisions creating a reduced zone approximately 50 feet thick in the on-property portion of the Southern Plume, east of the Storm Sewer Outfall Ditch. When the EARP technology is implemented uranium is reduced around the same time the structural iron (Ferric iron in the aquifer solids) is reduced. In other words initially as the conditions become slightly reducing uranium precipitates due to reduction, and iron is initially made soluble (as dissolved ferrous iron) (Lovely, Senko). As the process proceeds and the system becomes more reducing and sulfide is formed from the molasses; the iron sulfide precipitates. This leads to a residual coating of FeS minerals, elemental S (as the sulfide reacts with the structural iron that even the bacteria don't reduce or other oxidized components, elemental S can be formed) and likely some stored organic carbon in the form of biomass. When EARP is being used for precipitation of certain metals we sometimes add supplemental iron sulfate during treatment if the soluble iron observed during treatment is relatively low, as it was in this system. Therefore for the final month of active precipitation in this bench test we fed 50 mg/l Fe as $FeSO_4$ plus molasses in site groundwater into the treated column (note that the use of ferrous iron in groundwater remediation systems is relatively common– i.e. many Fenton's reagent applications).

Thus the fully reduced zone is expected to contain a variety of reduced compounds after treatment, including:

- iron sulfides (ranging from amorphous FeS to pyrite),
- elemental sulfur,
- residual reduced organic carbon either incorporated in cellular biomass or contained in microbial storage products such as exopolysaccharides,
- reduced uranium compounds (UO_2 and potentially US_2), and
- Potentially a variety of other reduced sulfur, manganese, iron, and trace mineral compounds.

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In this zone, the reoxidation of uranium will be controlled by the interface of oxygen with uranium, and the available oxygen will be controlled by its reactions with all of the stored, reduced compounds that have been emplaced in the aquifer by the treatment process. See for example a discussion of the role of both mackinawite and biomass in redox buffering in Abdelouas 1999.

Relative Reoxidation Rates of the Various Species Present the Reactive Zone
In relative terms, expressed in molar ratios of uranium to all of the other reduced compounds stored in the aquifer, the potential oxidation of uranium will be very low compared to the potential oxidation of iron, sulfur and other reduced species. If the aquifer materials were exposed to oxygen, FeS would be expected to oxidize as rapidly, if not more rapidly, than would UO_2 and consume the oxygen prior to reaction with the uranium. Because UO_2 would be precipitated first, the FeS precipitate would be laid down over the top of the UO_2 as a FeS coating, making FeS be exposed to the oxygen in the groundwater prior to when uranium-containing precipitates would be exposed [This is true either in a source area treatment configuration or in a plume wide treatment configuration. However in a barrier configuration (such as at a fenceline) there would be a more complex layering of iron sulfides and uranium precipitates]. The relative amount of iron sulfide that needs to be deposited for this purpose after the uranium has been precipitated can be designed for the full-scale system on the basis of the calculated oxygen flux potential.

As discussed in section 1.5 of the test plan, Abdelouas's work suggests "that mackinawite ($FeS_{0.9}$) can protect uranite for hundreds of years". In other words as long as mackinawite and other sulfide minerals are present they will kinetically preferentially consume oxygen and nitrate and prevent significant Uranium resolubilization.

Thus a relevant reaction process is the ability of sulfide containing aquifers to prevent nitrate from being mobile in groundwater, a process which has been studied in some detail. Pauwels and others (1998) showed that denitrification can occur relatively rapidly - in a sulfide-containing aquifer - with half-lives of nitrate in that environment of 50 to 200 hours. Hartog and others (2001) shows that pyrite oxidation is equally important as bulk organic matter as a reductant for nitrate. They documented the formation of ferric hydroxides, which can form as a coating over the pyrite minerals and slow their oxidation. Morse (1991) showed that the formation of the ferric oxide coating over the pyrite minerals can reduce the reactivity of the sulfide, leaving a stable iron oxide-coated pyrite that resists further oxidation.

The significance of these studies for our purpose is that:
1) Pyrite can act as an electron donor in the reduction of nitrate and oxygen, consuming these potential oxidants and preventing uranium exposure to these oxidants.
2) In buffered groundwater the product of this oxidation is the formation of fresh amorphous ferric oxides, which will scavenge uranium.
3) The rapidity of the reaction indicates that the redox front will stay relatively sharp (a distance of a few feet parallel to the flow direction is expected in the Fernald environment), limiting the potential migration of uranium further into the reduced zone.
4) The sulfide in these studies was very old, with age correlating to sulfide's crystal size and general resistance to oxidative attack. In the remediation of Fernald groundwater the pyrite we would produce will, by reason of its young age, be more reactive with oxygen and nitrate.
5) Because the formation of pyrite will be subsequent to the precipitation of uranium under remediation conditions at Fernald, the results of Morse (1991) and Hartog and others (2001) would indicate that a substantial fraction of the uranium would not be exposed to oxidation for many years, even in portions of the aquifer where the solution redox potential has become highly oxidizing.

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6) Hartog and Morse indicate that an oxidized Fe oxide/hydroxide layer forms over the top of the FeS, making the residual oxidation of the FeS much slower. By extension, we would expect the uranium, which is even deeper in the mineral matrix, to be even less exposed.

In a field test of another reductive metals precipitation technology, the injection of dithionite at Hanford (summarized in Fruchter and others 2000), only reduced structural iron in the aquifer matrix and did not lead to the formation of iron sulfide compounds. Anoxic groundwater has been maintained for 3.5 years (DO has remained at 0.00 mg/L). Calculations and field measurements based on flux of saturated DO through the treated zone indicate a consumption rate of reduced iron compounds of approximately 4 to 6 feet per year. The approach we propose, in contrast, will deposit more than an order of magnitude greater amount of iron sulfide and other reduced compounds uniformly throughout the treatment zone. Thus a consumption rate of iron sulfide and other reduced compounds could by extension be expected to be in the range of less than 1 foot per year in the proposed treatment zone at Fernald.

To summarize there are four reasons discussed here why FeS species will be reoxidized before the Uranium species:

a) Physical position (iron sulfides tend to coat over the uranium species during precipitation)
b) Relative mass/number of moles (an excess of reduced iron species over reduced U species)
c) Kinetics (i.e., that the reaction with the iron sulfides is faster than with the U even given a hypothetically equivalent number of moles) and
d) Thermodynamics/electrochemical series (that the iron sulfide begins reoxidizing at a lower (more reduced) potential then the uranium does).

Processes that Control the Mobility of Reoxidized Uranium

Furthermore simply because uranium will eventually be slowly reoxidized does not imply that it will be mobile over distances relevant to the protection of environmental receptors. As the work plan addresses, the iron that first oxidizes (on the upgradient fringe of the reducing zone) will form amorphous, ferric oxide surfaces that will be important for controlling the concentration of dissolved uranium. At the Stråssa mine, uranium concentrations are controlled by biogenic ferric oxides. In this system, uranium strongly partitions with the iron oxide solid phase, leading to dissolved uranium concentrations between 10 and 15 μg/L, with uranium content in the solid phase in the 20 to 80 mg/kg range (Ferris and others, 2000). As Martin and Kempton (2000) point out, the ferric oxides thus formed in situ will preferentially be placed in the high conductivity zones in the aquifer. In their column experiments, the ferric oxides delayed breakthrough of metals with similar sorption behavior as uranium between 8 and 30 times. The oxidation of iron sulfides by oxygen in the aquifer will lead to secondary ferric iron phases that will sorb uranium, maintaining the low uranium concentrations in situ as this reaction front moves. Since the reduced zone will extend for perhaps a 1000' parallel to the flow direction, and contains a large mass of reduced compounds (reductive poise) for a long period of years, even centuries after active treatment ceases, the upgradient edge of the reduced zone will be gradually reoxidizing while the center and downgradient portion of the reduced zone remain reduced.

Lack and coworkers (2002) has shown that fresh amorphous Fe(III)oxide is a very strong sorbent for a variety of metals including uranium. This amorphous Fe (III) oxide is "a precursor of many natural forms of crystalline Fe (III) oxides" that adsorbs or incorporates into its structure many trace metals. They write that "selective anaerobic bio-oxidation of Fe (II)...may be an effective means of capping off and completing the attenuation of HMR (heavy metals and radionuclides) in a reducing environment, allowing the system to naturally revert to an oxic state while preventing remobilization of previously reduced and isolated HMR...by precipitating Fe (III)(hydr)oxides over immobilized HMR in situ, forming an insoluble barrier that crystallizes with time...adsorbing any leached HMR locally"

Any uranium that mobilizes past the ferric iron front located on the upgradient side of the reactive zone will be controlled by several additional factors. The remaining reduced zone of the downgradient side of the oxidation front will contain a large amount of reactive sulfides, materials that also prevent uranium mobility by providing sorption surfaces (Abdelous and others, 1998 and 2000; Shepherd Miller, 2000).

Processes that effect Uranium Resolubilization and Oxidation – Conclusion
Thus it not necessary to prevent all oxidation of uranium to prevent its mobilization because of the potential for both iron oxide and hydroxide (in aerobic environments) and iron sulfide and organic matter (in reduced environments) to remove uranium from solution. The concentration of uranium measured at some downgradient point will be a factor of the overall rate of uranium dissolution and re-precipitation through the treatment zone. Post precipitation concentrations of uranium in the presence of iron oxide and hydroxide, and iron sulfides have been shown in the works cited to be substantially lower than the regulatory standard of 30 μg/L. By ensuring that there is sufficient iron and sulfide placed in the system during remediation, reoxidation of uranium can be prevented for centuries. When it does occur, it will occur in very localized portions of the reactive zone and the uranium will largely be reabsorbed. Thus mobilization will occur at a slow enough rate (flux) that the groundwater concentrations downgradient will remain below regulatory standards.

Action: As stated in response.

3. Commenting Organization: Ohio EPA Commentor: OFFO
Section #: NA Pg #: NA Line #: NA Code: general
Original Comment #: 3
Comment: Increases in redox potential have been observed in areas that are under the influence of surface water, namely in the area of surface water drainages along Willey Road. We note that the restoration of the south field will allow Paddy's Run Creek to overflow to the north of its low-flow banks and that some existing low areas are designed to function as infiltration galleries to increase the hydraulic gradient. In the longer term, it is possible that Paddy's Run will leave its current channel and develop a new course through the South Field and thereby increase the redox potential in the South Field.
Response: DOE agrees that this scenario is possible. Consideration to this scenario must be factored into any future decision by DOE and EPA to further evaluate use of this technology at the FEMP.
Action: As stated in response.

4. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 1.2 Pg #: 4 Line #: 18 Code: C
Original Comment #: 4
Comment: The text states that the conditions created by EARP are sufficient to reduce ferric iron, which is usually present in most aerobic geochemical systems, to ferrous. If the condition is such that ferric iron (Fe3+) is readily reduced to ferrous (Fe2+), then it is not kinetically supportive of the proposed chromium reduction from Cr(VI) to Cr(III). This is because the proposed chemical reaction requires the ferrous iron to be oxidized to ferric. This would not happen under the reductive environment created by the EARP technology.
Response: As discussed earlier, portions of this document were intended to be applicable across multiple sites. While Section 1.2 of the test plan is generally useful for understanding EARP technology, it is of limited interest at Fernald, since chromium VI is not present at Fernald. Furthermore ferrous iron has been shown in numerous studies to be the direct reductant of Cr (VI) (for example Patterson and others, 1997; Buerge and Hug, 1998; and Wielinga and others, 2001).
Action: No action required.

5. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 1.2 Pg #: 4 Line #: 18 Code: C
Original Comment #: 5

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Comment: In the strong reductive environment created by the use of EARP, chromium can be reduced and immobilized in the soil matrix. At same time, however, other hazardous heavy metals such as arsenic can become soluble and mobile in groundwater. (See William J. Deutsch, Groundwater Geochemistry, Lewis Publishers, page 175) Reductive arsenic, for example, can enter groundwater from waste materials or natural formation materials when present in high levels. Therefore, it is recommended that the evaluation include consideration of potential effects on other metals in the groundwater geochemical system. Caution needs to be exercised to avoid the inadvertent creation of unwanted secondary contamination as the by-product of the EARP application.

Response: We agree that it is possible for secondary water quality impacts such as arsenic mobilization to result from the production of reducing conditions in-situ, although our experience at over 100 sites suggests that this is rarely a significant problem. Although most metals are less soluble (and precipitate as hydroxides or sulfides) under the reduced conditions formed during EARP among the metals of regulatory significance the potential for mobilization of natural geologic arsenic, antimony and selenium should be considered on a site specific basis. However even in solubilized form under anaerobic conditions metals such as arsenic are substantially retarded by adsorption to the aquifer matrix (Smedley and Kinniburgh 2002) and coprecipitation with iron sulfides (Harvey 2002). Both As(III) and As(V) have relatively high Kd's for adsorption onto a variety of iron, aluminum and manganese oxides and hydrousoxides (Smedley and Kinniburgh 2002). Furthermore, the mobilized arsenic will be reprecipitated/immobilized downgradient of the reactive zone when the conditions return to their preexisting state (which, for the purposes of this discussion, is assumed to be aerobic1)). Similarly, reprecipitation/immobilization will occur within the reactive zone sometime after system shutdown.

To screen for the significance of this concern we plan to analyze three samples of the initial pretreatment soil homogenate for arsenic, antimony and selenium and one sample for a longer list of metals typically regulated (antimony, arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, vanadium, zinc). We have compared concentrations in the untreated column effluent water to concentrations in the treated column effluent during reducing treatment conditions for arsenic, antimony and selenium. As can be seen from the table below no excedences of MCLs were noted during the treatment period.

Analysis of other metals in effluent (mg/L)

	Sample Date	As (MCL: 0.010)	Sb (MCL: 0.006)	Se (MCL: 0.05)
Treated	8/16/2002	0.004	< 0.001	< 0.002
	10/21/2002	0.006	< 0.001	0.008
	12/15/2002	0.005	< 0.001	0.004
Untreated	8/16/2002	0.006	< 0.001	< 0.002
	10/21/2002	0.004	< 0.001	0.003
	12/15/2002	0.003	< 0.001	< 0.002

Action: As stated in response.

1 Although some localized anaerobic zones exist downgradient at Fernald and indeed may be controlling the migration of uranium, our antidotal information suggests that the bulk of the Great Miami aquifer regionally is aerobic (moderate to high redox) especially in areas of rapid withdrawal. Thus it is reasonable to consider that the groundwater will likely enter an aerobic zone before reaching a receptor.

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6. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 1.2 Pg #: 5 Line #: 11 Code: C
Original Comment #: 6
Comment: The cited principle is based on the kinetic argument that in the EARP-induced reductive environment, MnO_2 is in solid phase and has low concentration in groundwater. As such, the MnO_2-induced chromium dissolution reaction is unfavorable kinetically in post-remediation period. After remediation, when molasses introduction to groundwater is ceased and groundwater has recovered to its pre-treatment more oxidative state, MnO_2 mobility will be increased. MnO_2 chemical mobility under the new environment should be investigated. Chromium solubility under these conditions may actually be increased.
Response: We are having difficulty understanding this question, our understanding is that while manganese will be mobilized under reducing conditions, that will be as Mn(II) which is not an oxidant of concern in this context. MnO_2 available in the solid phase will be consumed during the onset of uranium and sulfate-reducing concentrations in groundwater. Due to the amount and duration of sulfide we will produce during the remediation phase, we would expect little to no residual MnO_2 after treatment (Gounot, 1994). Thus we would not expect to have MnO_2 available to act as an oxidant after treatment has been completed.
Finally we note that the portion of text commented upon here is of limited relevance to the specific situation at Fernald, since it deals with chromium resolubilization and several years of monitoring indicate No action required.es chromium is not a constituent of concern in groundwater at Fernald.
Action: No action required.

7. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 1.4 Pg #: 6 Line #: 30 Code: C
Original Comment #: 7
Comment: The text proposes that uranium precipitates from groundwater in the form of UO_2 and is present as impurities and inclusions of co-precipitated FeS. It is then stated that this will reduce the potential of UO_2 dissolution back into groundwater in the post-remediation period. It is recommended that further studies of this mechanism be undertaken through SEM and DRF studies of precipitants. The proposed study does not appear to adequately investigate this mechanism or to evaluate the potential of uranium re-dissolution into the groundwater.
Response: We have addressed the form of precipitated uranium at length in our response to Comment #2. The form of uranium is also discussed in sections 1.4 and 1.5 of the plan. While it is possible that some of the uranium will be co-precipitated with FeS, it is more likely that the uranium will precipitate first and then be coated with the FeS precipitates [This is true either in a source area treatment configuration or in a plume wide treatment configuration. However in a barrier configuration (such as at a fenceline) there would be a more complex layering of iron sulfides and uranium precipitates]. Dissolution questions are being addressed in at least three ways:
A. The response to Comment #2 above and section 1.5 present arguments based on the published literature regarding dissolution
B. Speciation approaches to be used are detailed in appendix A of the test plan. Given the relatively low concentration of the uranium precipitates in the solid phase it appears to us that multiple extraction approaches will most likely be needed to study the uranium forms. However instrumental approaches such as SEM may provide interesting information about iron speciation in the postprecipitation soils.
C. As discussed in the test plan and elsewhere in these comments a redissolution test is planned as part of the column experiment. However as discussed elsewhere in these comments and responses, the time scale for this is limited by practical considerations.
Action: As stated in response.

8. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 1.5 Pg #: 10 Line #: 23 Code: C
Original Comment #: 8
Comment: The statement regarding the uranium concentration in that the earth's crust is irrelevant and misleading. Granites and uranium ores do release uranium into environments during the weathering process. This observation is well documented in geological literature and is the principle upon which several methods in geochemical mineral exploration are based.
Response: The comment has been noted. While the reviewer correctly notes that naturally occurring uranium minerals do weather at some measurable rate, we do not believe that this makes the comment irrelevant. Rather as noted below in our response to Comment 11 the increased uranium concentration precipitated in the subsurface by this process will likely be low – for example 2.6 ppm in the bench scale example. Thus if these precipitates are geologically stable, typical concentrations in naturally occurring surface and subsurface materials are a reasonable point of reference for evaluating the relative risk of leaving precipitated uranium materials in-situ. This point of reference is appropriate since in our experience such typical background solid phase uranium concentrations do not normally release concentrations sufficient to contaminate ground or surface water supplies above safe limits.

The referenced statement in the Work Plan could have perhaps been better phrased "A) the concentrations of Uranium in the aquifer matrix after this precipitation process will not add markedly to the naturally occurring concentration of 2.4-3.0 mg/kg (USGS 1987) up to 15 ppm in granites (Merian)".
Action: No action required.

9. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 1.5 Pg #: 10 Line #: 23 Code: C
Original Comment #: 9
Comment: It is not clear that the proposed experimental design will provide information sufficient for determining the dissolution kinetic constant needed for determination of the indicated success criteria (e.g., future environmental concentrations will be 30 percent of the proposed regulatory limit and 10 percent of the pretreatment value and the time required for 90 percent of the dissolution is at least 5 times the nuclide half-life). For example, the experimental duration may not be long enough for meaningful scientific determination when the South Field groundwater without any compositional modification is used as the source water for testing.
Response: As noted in the response to Comment #2 it is not appropriate to apply the short lived radionuclide success criteria to uranium. However, the comments raise a reasonable question about whether the experimental design provides a sufficiently long redissolution period.

The plan calls for column operation for two months after the influent is switched to aerobic uncontaminated water and one month after the degradable carbon has been consumed/flushed out. It is obviously difficult to predict a priori how long the reoxidation process will take at bench scale; since the amount of reductive poise built up in the system as well as the reprocessing of organic carbon in the form of microbial biomass is difficult to simply model. As discussed above the reoxidation will take a long period of years in the field (where the reduced zone is longer in the direction of groundwater flow).

The bench scale column test accelerates the reoxidation testing somewhat because the zone is not as long in the direction parallel to groundwater flow as it is in the field. It is however still difficult to study the kinetics of a process expected to take years to centuries at field scale in a reasonable time frame. This difficulty is not unique to EARP – indeed it applies to all waste management options for radionuclides. We could attempt to accelerate the kinetics using a larger than realistic column flow rate, elevated temperature etc. but these measures would likely perturb this complex biogeochemical system in such a way as to make the results unrepresentative.

We have certain practical constraints on our ability to carry out the bench scale testing long term:

- Results need to be available in time for Fernald and the applicable regulatory bodies to make necessary site management decisions.
- The funding and period of performance on our current contract are both limited.

While we believe we should be able to extend the column-testing period somewhat, uranium effluent concentration results from even 6 months of reoxidation testing may not fully address all possible questions. We therefore plan to use several other lines of evidence to predict the long-term fate of uranium in this system:

- Measurements of dissolved oxygen, nitrate, iron and sulfate/sulfide in the treated column effluent during reoxidation can be used to predict the rate at which the protective effects of iron sulfate coatings are being exhausted. As discussed above in the response to Comment 2 these coatings, which are formed in plume wide treatment and source area treatment applications, are the first but not only "line of defense" against uranium mobilization.
- Speciation of the uranium present in the solid phase soils after testing can be combined with the body of geochemical information from the literature presented above (in the answer to question #2 and in section 1.5 of the test plan) to predict the long-term fate of the uranium. Of particular importance for this purpose are studies of uranium deposits that are known to be stable over geologic time. See for example the discussions of the Gross and Abdelousas (1999) papers presented in test plan section 1.5 and the discussion in the response to Comment 2 of the work by Ferris (2000).
- As discussed in section 2.3 of the test plan evidence from the field at the Fernald site suggests that uranium mobility is already being naturally limited by a redox decrease front. Such a natural attenuation process would only be enhanced by the implementation of an EARP system. The existence of such a front before in-situ treatment strongly suggests that such a front will continue to exist and limit uranium mobility after treatment.
- It may be appropriate at a later time for Fernald to request permission to conduct a field pilot test of this process that could be used to address the long-term performance of such a system.

Action: As stated in response.

10. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 4.1 Pg #: 17 Line #: 17 Code: C
Original Comment #: 10
Comment: Would repacking the columns result in an artificially high porosity? It would seem advantageous to the study to keep the core in tact, given that the rotosonic drilling procedure produces very accurate core samples in large volume.
Response: There are indeed tradeoffs between using intact cores and repacked columns in this type of study. Rotosonic drilling methods can provide relatively undisturbed core samples in homogeneous, cohesive, fine-grained materials (e.g., clay, silt, and fine sand). However, less cohesive coarse materials (e.g., coarse sand and gravel) tend to fall from the sampling device, making it difficult to collect an intact core. The collected interval did include fine gravels and coarse sands. Devices can be used to retain the materials in the sampler, but they tend to alter the sample from its natural, intact state. One of the most important considerations in this case was a desire to ensure that the treated and control columns were as similar as possible. This could best be achieved through homogenization, which of course precludes the use of intact cores.

Repacking coarse materials into the treatability columns probably does alter the porosity somewhat. However, given the coarse nature of the material, the effect on permeability should be relatively small. We calculated a bulk density of 2.1 g/ml for the repacked columns versus and estimated field bulk density of 1.6 g/ml. Minimal vibration and tampering was used to pack the columns, and thus it would have been difficult to achieve a lower density using this particular soil homogenate. Any moderate changes in the porosity and permeability between the field and lab

systems would only effect the bulk flow (engineering) properties of the system. The column test was not designed primarily to address bulk flow issues (such as the distribution of reagent throughout the matrix). These engineering issues are better addressed in a potential later field pilot testing stage or from a review of site geological conditions as compared to operational experiences at other similar sites. Rather the intent of the bench scale study was to evaluate the effectiveness and durability of the precipitation process, which depends on biogeochemical characteristics but not strongly on porosity.

Action: As stated in response.

11. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 4.2.5 Pg #: 21 Line #: 2 Code: C
Original Comment #: 11

Comment: The purpose of soil testing is apparently to examine the changes, if any, of uranium concentrations in the column as the result of chemical fixation induced by the technology. However, it is likely that the amount of uranium transferred from the water to the column will be minimal. A 90 percent reduction of uranium concentration in groundwater after numerous pore flushings would result in the precipitation of 7.3E-5 kg uranium in the 12.2 kg of soil in the column. This result is based on the maximum South Plume uranium concentration (600 ug/L). Even if the column is 100 percent efficient, the uranium concentration change in the soil is less than 6 ppm. Please check the detection limit, accuracy, and precision of uranium analysis for the proposed 6020 ICPMS method. These should be compared to the predicted concentration changes to ensure adequate analytical sensitivity and accuracy of experimental data used to determine the degree of chemical fixation achieved.

Response: The baseline U measured in the homogenized soil was 1.79 mg/kg. During the contaminated water phase of column operation we have pumped 91.5 L of water through the column. The average concentration of the U in the contaminated groundwater influent was measured to be 0.48 mg/L. The average dissolved U analyzed in the effluent of the treated column is 0.02 mg/L which is 4% of the influent concentration. Thus, assuming 96% treatment or immobilization of the U in the soil, which would yield approximately 42 mg of U deposited in the soil. The mass of soil in the column is approximately 16 kg, which yields an additional uranium concentration in the soil of 2.6 mg/kg assuming it was distributed uniformly. Thus the predicted post test concentration of 4.4 mg/kg is well above detection limit for the method as well as the quantitation limit (The MDL for the initial soil analysis was reported by the testing laboratory at 0.005 mg/kg).

Additionally, we do not expect the deposited U to be uniformly distributed throughout the column. The majority of the U should be in the first half of the column. The study design does allow for investigation of this hypothesis through post testing column sacrifice and subsampling. Thus it is likely that the U in the initial portions of the column will be higher than 4.4 mg/kg and the upper portions of the column should be between 1.8 and 4.4 mg/kg. Therefore the U in both sections should be easily detectable.

Action: As stated in response.

12. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 4.2.3 Pg #: 19 Line #: 12 Code: C
Original Comment #: 12

Comment: The experimental design is not an analog of the natural groundwater system at the site. For example, the groundwater samples were not obtained in-situ with the aquifer material. No attempt is made to reproduce the natural equilibrium/disequilibrium condition of the system in the field. As a result, flow entering the columns may have a different composition from the exiting flows. The proposed experimental design, however, assumes column inflow and outflow are chemically identical when groundwater is recycled through the columns.

Response: Although the recycling of effluent water was left as an option in the test plan, it has not, and is not, expected to be implemented for the subject study. Although the reviewer correctly notes that

pore water from the collected soil samples was not extracted to use as influent to the columns, we believe that the use of water from a nearby monitoring well is appropriate given the general homogeneity and interconectedness of the Great Miami Aquifer.

Action: No action required.

13. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 4.2.3 Pg #: 19 Line #: 35 Code: C
Original Comment #: 13

Comment: The proposal does not address the control of experimental conditions such as DO and ORP of the test groundwater samples. The DO level and other conditions of the groundwater collected from the site should remain unchanged during month-long testing period. Similarly, no change should occur in the process of water recirculation. Please clarify how these parameters will be maintained in the experiment.

Response: Although the option for recirculation was provided for in the test plan as a contingency, the system was not set up in a recirculation mode and has not been operated in such a mode to date. All column effluent water was collected in glass bottles and either submitted as samples or kept on hold at about 10°C.

Contaminated water was drawn from Well 62433. Although we don't have specific field ORP and DO data for that well, there is data for other wells in the area. These wells have DO measurements 6-10 mg/L and oxidation reduction potentials measuring from 120-390 mV. Our initial analysis of this groundwater as received indicated a DO of 9-10 mg/L and an ORP of 149-203 mV. The influent was sampled periodically during the experiment as it flowed into the column. The influent DO has averaged 7.83 mg/L over the first six months of the study. The redox has averaged 164.8 mV during the first month to 180 mV over the last 5 months. The variance if any in these readings between field conditions and the condition of the water as used in the column experiments is small (given especially the known variability in ORP measurements and that several analysts/instruments were involved). This indicates that there has been little change in the overall aerobic condition of the contaminated groundwater.

Uncontaminated water was drawn from the Well 2096. Although we don't have specific field ORP and DO data for that well, there is data for other wells in the area. These wells have DO measurements 1- 10 mg/L and oxidation reduction potentials measuring from 197-329 mV. The water from this well upon receipt had a DO of 9 mg/l and ORP of 216 mV. Although we do not yet have data collected on the redox condition of this water, as it is introduced into the column, we note that it is broadly similar in redox, DO and pH to the contaminated water. The uncontaminated water is somewhat lower in dissolved organic carbon, somewhat higher in sulfate and total iron and somewhat lower in total manganese. Therefore we have no reason to suspect that it will not be as stable in storage as the contaminated water was.

Action: No action required.

14. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 4.2.5 Pg #: 21 Line #: 2 Code: C
Original Comment #: 14

Comment: The text indicates that soil samples will be taken at the end of testing for analysis of COC concentrations. These concentrations will be compared with the concentrations before testing. However, any concentration changes may reflect the combined results of both chemical fixation and post-remediation dissolution processes. How will the contributions from each process be determined?

Response: It is the technical intent of the column study test to not expose the columns to air and therefore, a mid-test soil sampling event was not scoped. In addition, any intermediate COC mineral form that rapidly redissolves in the post-EARP test phase is not a suitable mineral form for long term precipitation. Thus identification/speciation of that hypothetical intermediate mineral form is unnecessary.

However, pre-and post-testing soil samples, combined with effluent aqueous samples collected during the EARP and dissolution testing, including biogeochemistry and solid phase speciation, will provide data needed to determine the following:

1) The final and/or dominant COC precipitation mineral resulting from enhanced anaerobic and reducing conditions,
2) The overall stability of the COC minerals against dissolution when the geochemistry returns to site background conditions, and
3) The masses of uranium fixed and re-dissolved.

Action: As noted in response.

15. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 4.2.4 Pg #: 20 Line #: 27 Code: C
Original Comment #: 15

Comment: One of the objectives stated in Section 3.0 is to evaluate the potential for colloidal transport. Will colloid concentrations and characteristics be determined in any of the 19 liquid samples that are planned?

Response: Total and dissolved U will be analyzed in the influent and effluent in accordance with Table 2 of the Test Plan. These analyses will be compared to baseline data to determine the mass of dissolved U, colloidal/particulate U, precipitated versus total U and the mass of total U fixed to the soil matrix. Current data indicate parallel trends for total and dissolved U, and similar values for total and dissolved U, suggesting no or minimal colloidal generation and/or transport.

Action: As stated in response.

16. Commenting Organization: Ohio EPA Commentor: GeoTrans, Inc.
Section #: 4.2.6 Pg #: 21 Line #: 7 Code: C
Original Comment #: 16

Comment: It is unclear how the data obtained from the experiment and the data analysis approach discussed will provide an estimate of the dissolution kinetics constant needed for evaluating the technology against the success criteria.

Response: As discussed in the response to Comment 2 we don't believe that the relevant processes that control uranium mobility in this system can be summarized with any single dissolution constant (as might be obtainable from a long term sequence of batch experiments). As we discuss in the response to Comment 9 there are real experimental problems in predicting the long-term fate of a radionuclide directly from short-term column tests. But we outline in the response to Comment 9 a number of lines of evidence that we believe will be able to provide assurance that the mobility of uranium in this system can be limited to below regulatory standards over the long-term.

Action: As noted in response.

17. Commenting Organization: Ohio EPA Commentor: OFFO
Section #: 4.2.6 Pg #: 21 Line #: Code: C
Original Comment #: 17

Comment: The data analysis should include a discussion and comparison of the redox potential as measured in the apparatus and as calculated using the Nernst equation for the nitrate/ammonia couple and the sulfate/sulfide couple. These species may prove useful in assessing the redox potential of the aquifer.

Response: We agree that there are limitations to using electrode redox potential measurements for making any quantitative conclusions regarding geochemical status of a system. These measurements have proven useful only in comparative evaluations of oxidation-reduction status due to the lack of reactivity of many intermediates (nitrous oxides) in the reduction of nitrate to ammonia, for instance and to the fact that many systems are not truly at equilibrium. In a practical application, measurement of redox in a system with higher concentrations of sulfide can also be problematic due to the highly corrosive nature of dissolved sulfide, and the short lifespan of electrodes in such solutions. Because uranium, nitrate, ammonia, sulfate, and sulfide (and for that matter, ferrous

and ferric iron) can be accurately preserved and then measured in laboratory settings with highly accurate analytical equipment it would be possible to use these results as you suggest to calculate a potential. However the redox potentials derived are of limited utility in making conclusions relative to environmental risk –for the same reason – lack of equilibrium in the system. Thus while we do plan to semi-quantitatively check the overall data set for consistency between the measured redox potential and the relevant couples, a more quantitative analysis is not necessary as long as the redox potential is treated as an approximate, relative measurement (USGS 1989).

Action: As stated in response.

<u>References Specific to Comment Responses</u> (additions to those in the revised test plan)

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