

**SCFA LEAD LAB TECHNICAL ASSISTANCE AT
FERNALD ENVIRONMENTAL MANAGEMENT
PROJECT:**

**SOLUTION FOR FERNALD TREATMENT OF URANIUM
IN BRINE ION EXCHANGE REGENERATION FLUID**



**SCFA Technical Assistance Request #143
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EXECUTIVE SUMMARY

On August 6-7, 2002, a technical assistance team from the U.S. Department of Energy Subsurface Contaminant's Focus Area met with staff from the Fernald Environmental Management Project and DOE-Ohio to review the treatment of effluent from the Advanced Wastewater Treatment facility ion-exchange bed regeneration process. The site requested recommendations for cost-effective, simple approaches to reduce uranium concentrations in brine (resulting from the regeneration of resin in ion exchange vessels) from the current level of 5 parts per million (ppm) to less than 30 parts per billion (ppb).

The technical assistance team identified one critical issue, minimal impact to the current system, which must be addressed for the successful and expedient treatment of the brine eluant. The brine regeneration system is currently operating and Fernald is on an accelerated path to closure. The need for minimal impact to the current system requires that the technical solution should be easy to implement, low cost, a batch process, immediately available, able to operate 5-10 years until closure of the treatment facility, and can be implemented with few engineering changes to the current system.

A second critical issue, understanding uranium speciation, could be important if the recommended approaches to reduce the uranium oxidation state are unsuccessful. In this case, experimental and theoretical studies may provide a better understanding of the chemistry of the current precipitate, pH effects on reaction rates, process controls to eliminate oxygen for reductant methods, and the chemical form of uranium at each process step.

The technical assistance team identified 11 approaches to reduce uranium concentrations in the liquid brine phase. Chemical methods included reducing the oxidation state of the uranium from +VI to +IV and/or replacing lime with reactive magnesia in the precipitation stage. Physical methods involved evaporation and/or solidification. Biological processes to adsorb uranium were also included. Each approach was qualitatively evaluated against criteria on effectiveness, cost, ease of implementation, health and safety risks, scheduling risks, and stakeholder acceptance.

The technical team recommended a tiered approach to removing uranium from the brine solution, with each step in the tier being taken only if the previous steps are insufficient.

1. Add sodium thiosulfate to the brine solution either with or after treatment with lime. Laboratory experiments should be performed to determine the amount of sodium thiosulfate required, reaction kinetics including potential re-oxidation, the process stage for sodium thiosulfate addition, process modifications, and environmental, safety and health considerations.
2. Replace the addition of lime with addition of reactive magnesia. This will provide a lower pH process (pH 8.5 – 9) and may lower the solubility of uranium, possibly by more than an order of magnitude. The lower pH solution of magnesia addition, as compared to lime addition, may be beneficial if discharge to the Great Miami River is the selected disposition path.
3. Attempt addition of zero-valent iron or magnetite (Fe_3O_4). These solid amendments would reduce the uranium oxidation state and, consequently, the solubility of uranium.

Use of zero-valent iron could produce hydrogen gas from reduction of water, potentially requiring engineering controls; magnetite would also be an effective reductant but would not generate hydrogen. Precipitation and plugging problems are possible, but adding these solids during the lime-addition and precipitation process could add the benefit of sorption as well as co-precipitation of uranium species.

4. Evaporation could be used to increase precipitation and reduce the volume of water that needs to be treated. Complete or partial evaporation could be used, depending on the economics. The evaporate could be solidified and disposed either on-site or off-site. If total evaporation were performed, chemical treatment of the brine would be unnecessary. Potential scaling and plugging problems would require special attention. The evaporation approach would require the most additional equipment, largest changes to the process, and most difficulty to implement, and, therefore, is the last option in the tiered approach.

During the August 6-7 meeting, a recommendation was made to the Fernald team to perform bench scale testing of the uranium reduction approach. The Fernald team was able to perform the following experiments to provide some preliminary data to the Technical Assistance Team. Sodium thiosulfate, a strong reducing agent, was added to brine effluent from the regeneration process after the addition of lime. The initial uranium concentration was around 3 ppm. Several tests that added different amounts of sodium thiosulfate were performed and found formation of a white precipitate; after a few minutes, concentrations of uranium in the solution were in the 400 to 700 ppb range. After one hour, uranium concentrations were 3 to 4 ppb in unfiltered supernatant and <1.0 ppb in filtered supernatant, well below the goal of 30 ppb. The <1.0 ppb value is consistent with theoretical calculations for the solubility of uranium in the +IV state in brine solutions. This preliminary testing indicates that sodium thiosulfate addition would be a viable solution to reduce uranium concentrations in the brine.

1.0 BACKGROUND

1.1 Technical Assistance Process

Groundwater contaminated with uranium has necessitated installation of a pump-and-treat remediation system for the Great Miami Aquifer at the U.S. Department of Energy (DOE) Fernald site near Cincinnati, Ohio. Extraction wells pump about 3900 gallons per minute (gpm) from the aquifer. This water is passed through five ion-exchange treatment systems. The largest treatment system, the Advanced Waste Water Treatment (AWWT) facility system, handles up to 1800 gpm and was the focus of this technical assistance. Periodically, the resin beds require regeneration. This is accomplished using a saturated sodium chloride (NaCl) solution to remove the uranium from the resin bed. The resulting brine mixture contains uranium at concentrations of several hundred parts per million (ppm). This mixture is treated with lime to raise the pH and lower the solubility of uranium. The solution concentration subsequent to lime treatment and filtration of precipitates is 2-5 ppm, which is above the regulatory limit (30 parts per billion (ppb)) for discharge to the Great Miami River.

Dave Brettschneider, Aquifer Restoration and Wastewater Project Manager, Fluor Fernald, submitted a technical assistance request to the DOE that sought recommendations for cost-effective, easy to implement approaches for reducing uranium concentrations in the brine from the current level of 5 ppm to less than 30 ppb. On August 6-7, 2002, a technical assistance team from DOE's Subsurface Contaminant's Focus Area (SCFA) met with staff from the Fernald Environmental Management Project (FEMP) and DOE-OH (DOE-OH) to review the treatment of the effluent from the AWWT facility ion-exchange bed regeneration process.

The technical assistance team was composed of leading technical experts from Brookhaven, Oak Ridge, and Sandia National Laboratories and was assembled by SCFA's Lead Laboratory in response to the technical assistance request. A list of the technical assistance team members and names and contact information for all meeting participants is in Appendix B and information on the technical assistance team members is provided in Appendix D.

On Tuesday, August 6, the technical assistance team was given a tour of the AWWT facility by Chris Sutton, Principal Environmental Scientist, Tim Sparks, AWWT Operations Manager, and Kathy Leslie, Manager of the Analytical Chemistry Laboratory. The tour covered all aspects of the treatment facility, culminating in a discussion of the treatment train for the eluate from the regeneration process. A tour of the analytical chemistry laboratories was also provided. During the afternoon and the following morning, the technical team met to discuss potential alternatives for reducing uranium concentrations in the processed brine. A closeout briefing that provided the preliminary recommendations was presented to Fernald and DOE-OH staff on Wednesday, August 7.

Potential options for meeting the objective of reducing the uranium levels in the brine were identified and evaluated as part of the review. Each of these is discussed in the report and qualitatively evaluated against a series of criteria that relate to effectiveness, cost, ease of implementation, health and safety risks, scheduling risks, and stakeholder acceptance. A number

of these options may be successful in reducing uranium concentrations to acceptable levels. Recommendations on the best approach are provided.

1.2 Project History and Baseline

The AWWT Facility contains three ion exchange systems. One system is primarily used to remove uranium from storm water runoff and consists of two trains containing three ion exchange vessel in each train. A second system is primarily used to treat remediation water and consists of one train with three ion exchange vessels. The third system is used solely to treat uranium contaminated ground water and consists of three trains with two ion exchange vessels in each train. Combined, the three systems typically treat from 1800 gpm to 2700 gpm, depending upon the magnitude of storm water and remediation wastewater flow. In addition to ion exchange systems, the AWWT facility consists of an aeration tank for iron oxidation, clarifier vessels to settle flocculated solids, and multimedia filtration to remove oxidized iron and other particles. Treated water is either reinjected (treated groundwater only) back into the aquifer to speed up the aquifer cleanup process or discharged to the Great Miami River. Each groundwater ion exchange vessel contains about 314 cubic feet of ion exchange resin, while the remediation wastewater and storm water vessels contain 130 cubic feet of ion exchange resin. In the interest of minimizing waste and costs, the resin is regenerated when its capacity is exhausted.

The ion exchange resin regeneration process involves flushing a uranium-saturated resin tank with 6 bed volumes of sodium chloride solution with a salt concentration near saturation (ca. 25 weight percent sodium chloride), followed by 10 bed volumes of pure water. All flush solutions are currently combined in a single tank, typically resulting in 30,000 gallons of up to 5 weight percent sodium chloride solution, containing 300-600 ppm total uranium. Several closely-monitored, full-scale regeneration tests conducted by Fernald personnel demonstrate that >98 percent of the uranium is eluted by the first 2 bed volumes of saturated sodium chloride solution, although the final 4 sodium chloride rinses and the pure water rinses may still contain uranium concentrations of several hundred ppb.

The process for precipitating uranium in the regenerant solution involves the addition of lime and flocculating agents, which results in the formation of solids that are filtered out of the solution, leaving approximately 30,000 gallons of a solution containing 2-5 ppm total uranium and 2-3 weight percent sodium chloride. The operators speculate that the precipitation process is a result of destabilization of the dissolved uranyl carbonate complexes (most likely due to precipitation of calcium carbonate associated with the lime addition), which results in supersaturation of the solution with respect to uranium (VI) oxides. There are currently no reliable data on the exact chemistry or crystalline form of the precipitate, but discussions in internal reports postulate that UO_3 and/or sodium uranate ($Na_2U_2O_7$) might be present.

The treated brine solution contains ppm levels of uranium and is reintroduced into the ion exchange system and treated again. However, elevated levels of chloride result in elution of uranium from the columns, and therefore the treated brine must be metered into the treatment flow very slowly, creating a bottleneck in the regeneration. Fernald would like to have an alternative treatment technique for the brine that would reduce uranium concentrations to less than 30 ppb and thereby remove the need to run the solution through their ion-exchange system.

2.0 ISSUES ANALYSIS

The technical assistance team identified one critical issue -- minimal impact to the current system -- that must be addressed for the successful and expedient treatment of the brine eluant. A second critical issue -- understanding uranium speciation -- that could be important if suggested technical approaches do not work, was also identified. This section presents the critical issues and a brief overview of how these issues might impact restoration activities.

2.1 Minimal Impact to Existing System

The brine regeneration system is currently operating and Fernald is on an accelerated path to closure. This causes constraints to any suggested technical solution. These constraints require that the technical solution should be:

1. Simple and easy to implement - major engineering changes in the current treatment systems would negatively impact schedule.
2. Low cost – the existing system is operational and unless a low cost system can be implemented, the current system can be tolerated.
3. Batch process - the ion exchange resins are regenerated on regular basis that requires about three days to complete. Approximately one resin bed is regenerated each month.
4. Able to be implemented immediately – the current system is causing operational and schedule difficulties and improvements are needed as soon as possible.
5. Commercially available – time constraints prevent development of a new technology.
6. Able to operate until closure of the treatment facility - operations are expected to continue for 5–10 years, depending on the success of groundwater remediation efforts.

2.2 Uranium Speciation

Based on experience at the WIPP site and knowledge of uranium chemistry, the technical team believes that reduction of uranium from the +VI to the +IV state shows great promise as a means of meeting concentration goals established by Fernald. Several inexpensive approaches to reduce the uranium oxidation state have been proposed by the technical assistance team. If these approaches are successful, a detailed understanding of the uranium chemistry during the process may not be necessary. If the approaches are unsuccessful, this would indicate that the chemistry is insufficiently understood and other factors are controlling uranium concentration. In this case, experimental and theoretical studies may be useful to provide a better understanding of the chemistry and suggest alternative approaches (e.g., different reductants, changes in operating pH, holding time, etc.). A few areas that could be explored experimentally and/or theoretically include:

1. Definition of the speciation of the current precipitate (carbonate, chloride or oxychloride)
2. Determination of pH effect on reaction rates

3. Process control to eliminate oxygen for reductant methods. Oxygen will compete with the reductant and may cause the uranium to oxidize to the more soluble +VI state.
4. Theoretical speciation calculations to determine the form of uranium at each step in the process. Key variables for modeling include total carbonate, total chloride, total uranium, major ions, and pH.
5. Control to eliminate oxygen for reductant methods. Oxygen will compete with the reductant and may cause the uranium to oxidize to the more soluble +VI state.

3.0 REMEDIAL ALTERNATIVES

The technical review team developed eleven alternative approaches that could be successful in meeting the objective of either reducing brine solution concentrations of uranium below 30 ppb or removing the need to run the brine solution back through the ion-exchange bed. Alternatives were grouped into chemical, physical, and alternative processes. Chemical approaches involve reducing the uranium from the +VI to the +IV oxidation state and include adding liquid amendments (sodium thiosulfate, stannous chloride, ferric chloride, etc.) or solid amendments (zero valent iron, magnetite). Physical processes revolve around evaporation and solidification of the resulting wastes. Independently of the uranium reduction approach, the team suggested another chemical approach involving replacement of lime with reactive magnesia during the initial treatment process. This could lower the dissolved uranium content by an order of magnitude or more, due to the lower pH established by magnesia, relative to lime treatment. Alternative approaches include biomass adsorption/reduction, installation of a secondary ion-exchange system, precipitation with phosphate coupled with reduction, and addition of hydroxyapatite. Appendix C lists the treatment alternatives for the regenerant brine at the AWWT that were discussed by the technical assistance team. Each alternative is evaluated against the following criteria:

1. Treatment strategy (reduction in solubility, ion-exchange, evaporation, solidification)
2. Effectiveness (likelihood of addressing the problem)
3. Permitting risk (likelihood of obtaining regulatory permits)
4. Schedule risk (impact on current operating procedures)
5. Health and safety risks (risks associated with installation, operation and maintenance of the remedial system)
6. Cost
7. Implementability (ease of installing, operating, and maintaining remediation system)
8. Stakeholder acceptance (public and regulatory bodies)
9. Technical maturity (young technology that is under development or mature technology that has been extensively applied in the field).

Each category is qualitatively evaluated (e.g., high, medium, or low). Detailed comments are provided for the evaluation of effectiveness, schedule risk, cost, and implementability because these are the most important categories for this problem. An overall recommendation on the use of each treatment option is presented in the table. The following sections provide the technical detail to support the findings reported in the technology matrix (Appendix C).

3.1 Chemical Strategies

Proposed chemical treatments to reduce the concentration of uranium in the regeneration brine solutions are based on two methods: first, reduction of the uranium from the +VI oxidation state to the +IV oxidation state where uranium solubility is significantly lower, and second, adjustment of solution pH to a level where uranium (VI) has a lower solubility. During the site visit, the technical assistance team did preliminary calculations of predicted uranium concentrations. Assuming that the solubility of uranium in the supernatant resulting from lime addition, flocculation and filtering of the regenerant brine is controlled by the reaction $\text{UO}_{3,\text{cr}} + \text{H}_2\text{O} = \text{UO}_2(\text{OH})_{2,\text{aq}}$, the predicted concentration of total dissolved uranium would be about 1 ppm, ignoring additional uranium hydrolysis species and carbonate complexes in solution. This concentration range (2 to 5 ppm) is similar to that observed in the supernatant, suggesting that the concentration of uranium in the treated brine is solubility-controlled by a uranium (VI) oxide. Similar calculations suggest that reduction of uranium (VI) to uranium (IV) might decrease the concentration of dissolved uranium in the supernatant from the liming and filtration step, since the equivalent uranium (IV) solubility reaction, $\text{UO}_{2,\text{cr}} + 2\text{H}_2\text{O} = \text{U}(\text{OH})_{4,\text{aq}}$ gives a calculated total uranium concentration of 0.01 ppb. It is known, however, that uranium (IV) species form strong chloride, hydroxide and other aqueous complexes under the chemical conditions of the supernatant fluid, possibly raising the solubility by as much as 2 orders of magnitude, to about 1 ppb total uranium in equilibrium with uraninite ($\text{UO}_{2,\text{cr}}$). This is a factor of 30 below the target concentration for discharge into the Great Miami River, leaving a safety margin of more than an order of magnitude.

The solubility of uranium is controlled by several factors, including uranium oxidation state, pH, and presence and concentration of other ionic species. Uranium exists in primarily four oxidation states in the environment: +III, +IV, +V and +VI. By far, the +IV oxidation state exhibits the lowest aqueous solubility. Uranium is amphoteric, being more soluble in acidic or basic solutions, due to the formation of positively or negatively charged uranium ions, in addition to the neutral species. A minimum in uranium solubility in all oxidation states is observed between pH 3 to 9. Several ionic species including chloride and carbonate can strongly affect uranium solubility. Chloride and carbonate complex with uranium forming uranium (IV) and uranium (VI) chloride and carbonate species, respectively, that can substantially enhance the solubility of all uranium minerals (Grenthe, et al., 1992).

In the Fernald ion exchange water treatment system, uranium in the influent is present as uranyl carbonates. A sodium chloride brine is used to regenerate the ion exchange columns. The form of uranyl in the brine after column regeneration has not been determined. It is likely to be a mixture of uranyl carbonates, uranyl hydroxides and uranyl chlorides.

Using the Geochemist Workbench equilibrium code, Release 3.0, solubility diagrams, uranium activity versus pH, for uranium (IV) and uranium (VI) were generated and are given in Figures 1 and 2 respectively. The diagrams illustrate the significant difference in uranium solubility between uranium (IV) and uranium (VI). Although the Fernald regeneration brines contain approximately 2 to 3 molar chloride, the effect of chloride complexation on uranium (IV) and uranium (VI) solubility is minimal in the alkaline region. Hydrolysis and carbonate complexation are much more significant. Carbonate complexation can increase uranium

concentrations by many orders of magnitude for uranium (VI), but has less of an effect on uranium (IV) (Grenthe et al, 1992). Most of the carbonate in the Fernald regeneration brines is precipitated as calcium carbonate during the lime treatment step. The remaining carbonate in solution is in equilibrium with the calcium carbonate solid. For a pH of 12.6, calcium hydroxide in equilibrium with the brine, the solubility of uranium (IV) according to Figure 1 is approximately 3.2×10^{-9} M or 0.7 ppb. Regardless of the initial uranium concentration in the regeneration brine, if all of the uranium is reduced to the +IV oxidation state, uranium concentrations should fall below 1 ppb.

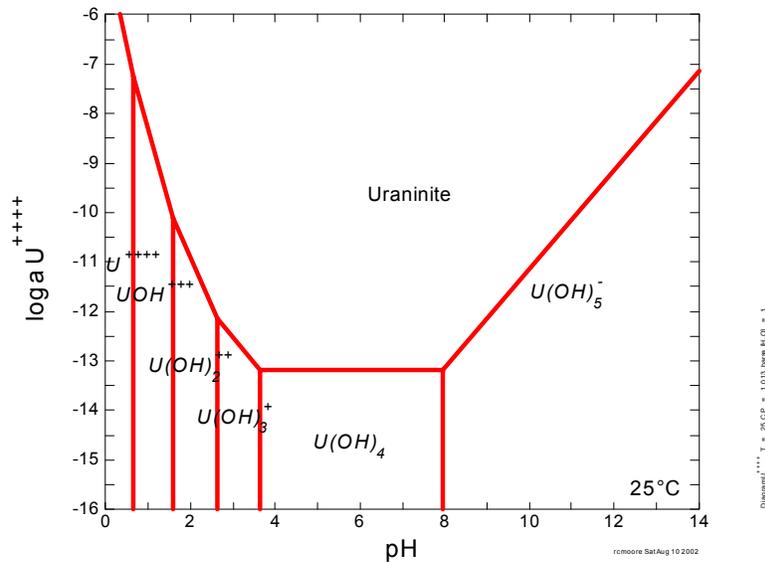


Figure 1. Solubility diagram for uranium in the IV oxidation state (Geochemist Workbench, version 3.0)

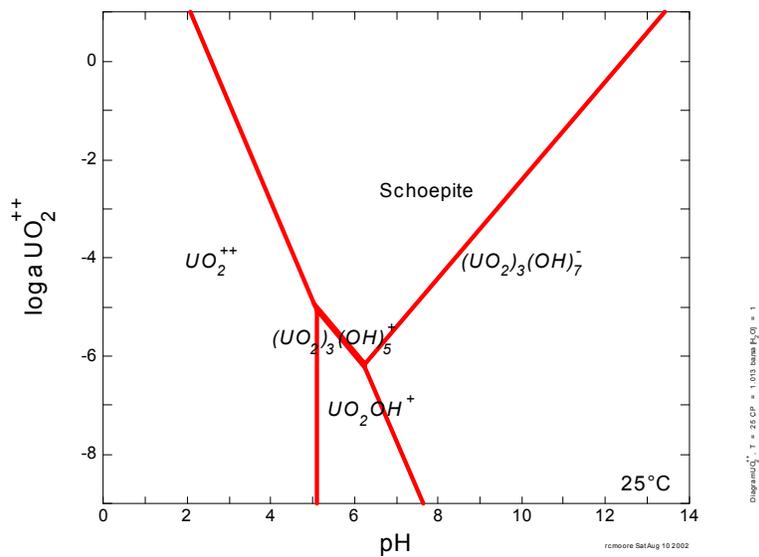


Figure 2. Solubility diagram for uranium in the VI oxidation state (Geochemists Workbench, version 3.0)

3.1.1 Sodium Thiosulfate Addition to Lime Treatment

Sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is a mild reducing agent typically used as a preservative in water analysis, photographic film development and chemical manufacture. Upon reaction with an oxidizing agent, the thiosulfate ion, $\text{S}_2\text{O}_3^{2-}$, is converted to sulfate, SO_4^{2-} (Skoog et al, 1979). Sodium thiosulfate has been studied for removing chlorine dioxide and chlorite ions in drinking water and regeneration of activated carbon used in removing methyl bromide for fumigation of agricultural produce. Sodium thiosulfate is used at the Fernald Environmental Management Project site in water analysis and groundwater treatment.

For reduction of uranium, sodium thiosulfate could be added directly to the regeneration brine before, after, or concurrently with the addition of lime. Treatment with lime or another material such as low-fired magnesium oxide will still be necessary to remove carbonate species that can significantly increase uranium concentrations. The use of sodium thiosulfate has advantages over other reducing agents, including (1) no hydrogen generation (a problem with most iron-based reducing agents), (2) no generation of another solid waste stream, (3) low cost, and (4) low environmental impact.

At the suggestion of the technical assistance team during the site visit, Fernald personnel performed a proof-of-principle experiment to verify that adding a reducing agent to the regeneration brines would reduce uranium concentration. Sodium thiosulfate, available in the Fernald laboratory was used as the reducing agent for uranium. Sodium thiosulfate was added to regeneration brine that had already been treated by lime addition. The results were very promising, with uranium concentrations in the brine decreasing from 2414 ppb to approximately 3 to 4 ppb for unfiltered supernatant and to less than 1 ppb for filtered supernatant in approximately 1 hour. The results are in agreement with the value for uranium (IV) solubility given above in Figure 1, as well as with the preliminary calculations performed during the site visit.

Research and development into the use of sodium thiosulfate is recommended as a treatment method for removing uranium from the regeneration brines. Minimal impact to the current processing procedures would be realized by addition of dry sodium thiosulfate along with lime and flocculating agents during the initial brine treatment/filtration step. However, this may not leave sufficient time for the redox reaction to proceed to completion. Adding the sodium thiosulfate before lime addition might provide sufficient reaction time, depending on the details of the process stream, but much more thiosulfate would be needed, since the concentration of uranium in solution prior to lime addition is in the 300-600 ppm range. Ideally, sodium thiosulfate should be added after lime addition and initial precipitation of most of the uranium as uranium (VI) oxides, but before filtration, so that uranium (IV) oxides formed by reduction can be captured in the filter cake. Laboratory experiments should be performed to determine (1) the amount of sodium thiosulfate required for uranium reduction to acceptable levels, (2) reaction kinetics, (3) the optimal point of sodium thiosulfate introduction into the treatment process, (4) process modifications, and (5) environmental, safety and health considerations. If the results from these additional laboratory experiments are positive, then implementation as part of the regeneration brine treatment should follow.

3.1.2 Magnesium Oxide Replacement for Lime Treatment

The current treatment technology for removing uranium from regeneration brines at Fernald is to use lime to precipitate carbonate and raise brine solution pH. The technical assistance team sees no advantages of increasing the solution pH, and believes that the efficacy of lime addition is in precipitating available carbonate as calcium carbonate (calcite), thus destabilizing dissolved uranyl carbonate complexes. An alternative to the use of lime is to use magnesium oxide. Magnesium oxide is converted to magnesium hydroxide in water. It is widely used in water treatment for pH adjustment

As seen in Figures 1 and 2, the solubility of uranium in both the (IV) and (VI) oxidation states decreases with increasing pH and reaches a minimum at approximately pH 3.5 and pH 6.2 for uranium (IV) and uranium (VI) respectively. As pH further increases into the alkaline region, uranium solubility increases at a rate of approximately 1 order-of-magnitude for each pH unit above pH approximately 6.5 for uranium (VI) solids and above about pH 8 for uranium (IV) solids.

Because magnesium oxide buffers pH at approximately 10.2 and calcium oxide (lime) buffers pH at approximately 12.6, the use of magnesium oxide instead of lime would set pH at a level where uranium has a lower solubility for both the (IV) and (VI) oxidation states. The difference for both uranium (IV) and uranium (VI) is approximately 1.3 orders-of-magnitude. Because of these differences, magnesium oxide was chosen over lime for use as a backfill material in the Waste Isolation Pilot Plant Disposal Facility for transuranic waste (DOE 1996). An additional benefit for uranium precipitation may arise because magnesium carbonate is considerably less soluble than calcium carbonate. However, calcium carbonate nucleates readily and precipitates rapidly from solutions only mildly saturated with respect to this phase, whereas magnesite ($MgCO_3$) is known to be more difficult to nucleate. Bench scale experiments are recommended in order to assess the efficiency of initial uranium precipitation relative to process parameters associated with lime addition.

Magnesium oxide could be easily substituted for lime in the Fernald brine regeneration process. Because the exact composition of the regeneration brine is unknown, the substitution of magnesium oxide for lime should be experimentally tested before it is implemented in the treatment process. The substitution of magnesium oxide for lime is recommended only if reduction of uranium does not provide acceptable results.

3.1.3 Reduction with Zero Valent Iron or Magnetite

Several studies exist in the literature on the use of zero-valent iron for remediation of uranium-contaminated groundwater (Farrell et al. 1999, Abdelouas et al. 1999, Morrison et al. 2002). The mechanism of uranium removal by zero-valent iron is based on reduction of uranium from the +VI oxidation state to the +IV oxidation state and adsorption of the uranium (IV) onto the iron oxide surface. Under aerobic conditions, uranium is rapidly and strongly sorbed to the iron

oxide surface, whereas under anaerobic conditions, uranium is much more slowly reduced to uranium (IV) and sorbed (Fiedor et al, 1998).

Zero-valent iron could be added to the regeneration brine to reduce uranium to the +IV oxidation state. Because of the high chloride content of the regeneration brines, corrosion at the surface of the zero-valent iron would continuously provide a fresh surface for uranium reduction and adsorption and prevent passivation of the iron surface (Wang et al. 2001). A major drawback in using zero-valent iron is the generation of hydrogen gas from the reaction $3\text{Fe}_{\text{cr}} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_{4,\text{cr}} + 4\text{H}_{2,\text{g}}$. This hydrogen would need to be continuously removed from the reaction vessel to prevent hydrogen build up. This could be accomplished by bubbling an inert gas such as nitrogen or argon through the brine to strip off hydrogen as the zero-valent iron is oxidized and reacts with the uranium. Research and development into the use of zero-valent iron is recommended only if the use of sodium thiosulfate and magnesium oxide substitution for lime are unsuccessful.

The sorption of uranium to magnetite has been studied by Granbow et al. (1996) and Venkataramani and Gupta (1991). Magnetite is generally formed during the corrosion of mild steel and iron in oxygen deficient conditions (Wang et al. 2001). For commercial use, magnetite is primarily obtained from mining magnetite ore. Magnetite may be a cost effective alternative to zero-valent iron. Magnetite is an effective reductant for conversion of uranium (VI) to uranium (IV), and since magnetite is stable in the presence of water under mildly reducing conditions, would not cause significant hydrogen gas evolution. Furthermore, both oxidized and reduced uranium species are likely to sorb strongly on magnetite surfaces. Bench scale studies are needed to determine the effectiveness of uranium reduction and sorption by magnetite in the Fernald regeneration brines. Because the use of magnetite for uranium reduction and sorption is not a mature science and would require extensive research and development, it is not being recommended at this time.

3.1.4 Other Soluble Reductants

Other potential reducing agents for reduction of uranium in the regeneration brine were considered. These include stannous chloride, ferrous chloride, citric acid and ascorbic acid. Experimental data will be required to determine the effect of these compounds for reduction of uranium in the regeneration brines. The use of these compounds should be considered only if sodium thiosulfate is not effective.

3.2 Physical Strategies

The physical strategies identified by the technical team revolve around evaporation of the brine in combination with solidification of the remaining salt cake. There are several possible scenarios that are useful to consider, including (1) evaporation to dryness, (2) partial evaporation to allow solidification, and (3) partial evaporation to saturate the solution with brine, thereby reducing uranium concentrations. This report assumes that commercial evaporators, using heat from natural gas flame or on-site process steam, can be obtained and installed. The evaporator is further assumed to be of the continuous-feed type with provision for removal of precipitates, since large quantities of sodium chloride and minor amounts of other solids, including uranium

precipitates, would be generated as a result of water extraction and concentration of the dissolved components. The economics of this operation would need to be evaluated by Fernald. However, generally, evaporation systems are inexpensive to operate.

Scenario 1 involves evaporation to dryness of the regenerant brine. Since there are no significant volatile components other than water in the brine, all dissolved constituents, including sodium chloride, uranium compounds, sodium carbonate, etc., would be captured. It is anticipated that since sodium chloride is highly hygroscopic, a small amount of Portland cement or other water-absorbing agent will need to be added to the salt cake in order to maintain dry conditions. The salt cake for each regeneration cycle, estimated to consist of approximately 5 to 15 metric tons of sodium chloride depending upon the volume of the ion exchange resin bed being regenerated, 100-120 pounds of uranium salts, and minor amounts of other constituents, principally sodium carbonate, would then be packaged for shipment to an offsite storage facility.

Scenario 2 involves partial evaporation to reduce the volume of brine plus salt precipitate to a level that would permit practical conversion of the brine plus sludge to dry concrete, involving the addition of Portland cement and other agents, such as blast furnace slag, that facilitate incorporation of large amounts of salt into the dry concrete (DOE 1999). If the volume of brine plus sludge could be reduced by a factor of 5-10, this process might prove practical, since the remaining material could probably be converted to approximately 10-20 tons of concrete for shipment to an offsite storage facility. Depending on economic and regulatory considerations, it might prove more economical to balance the degree of evaporation and the amount of concrete produced in order to permit disposal in the Fernald On-Site Disposal Facility.

Scenario 3 involves only sufficient evaporation to bring the regenerant brine sodium chloride concentration up to near saturation (volume reduction by a factor of 5-10). If the solid phase precipitated during subsequent lime addition is a sodium uranate, then an increase in the sodium concentration by a factor of 5-10 might result in precipitation of more of the dissolved uranium. However, the increase in ionic strength and chloride content of the brine might be an opposing factor in the solubility of the precipitate, and the precipitate may not in fact be a sodium-bearing compound. Furthermore, it has not been established whether the solid phase formed is indeed a sodium-bearing compound. Nevertheless, the total uranium in solution would also be concentrated during the evaporation process, and this may enhance the efficiency of the uranium removal during lime addition due to the commonly-observed phenomenon of adsorption and co-precipitation when a large amount of precipitate forms in a previously-homogeneous solution. Whether or not partial evaporation would result in precipitation of a greater amount of the total uranium loading in the regenerant brine can only be adequately answered by large-scale bench tests, since there are many kinetic and equilibrium processes operating simultaneously, rendering the chemical reaction process extremely difficult to model.

Scenarios 1 and 2 completely eliminate the need for any chemical treatment of the regenerant brine, because all contained uranium and all dissolved components would be converted to dry concrete. Scenario 3 could be used in combination with any of the chemical treatment processes described in this report, and might have a beneficial effect on the efficiency of several of the proposed alternative treatments, such as addition of reductants or addition of magnesia in place of lime in subsequent processing.

Careful consideration would have to be given to corrosion of the evaporator and downstream components, since concentrated sodium chloride brines are rather aggressive, particularly in contact with mild steel. However, there is on-site experience with concentrated brines in the regeneration process, and evaporation will not result in significantly higher levels of dissolved sodium chloride than is currently contained in the initial regenerant solutions. Fernald can draw upon industrial experience in the production of salt sludges from undersaturated brine solutions for guidance in optimizing the design and maintenance of the facilities.

Scaling and plugging problems that might interfere with operations commonly plague evaporation systems. First of all, as the solution is dried, the dissolved sodium chloride will concentrate. The solubility of sodium chloride is prograde, so a heated brine can become more concentrated before reaching saturation. At 100°C the sodium chloride saturation state is at 28 weight percent, whereas at 25°C, the saturation limit is 26 percent. So, a saturated solution at 100°C, if cooled to room temperature, will spontaneously precipitate 2 percent of its total weight as sodium chloride crystals. The feed solutions introduced into the ion exchange columns are known to contain iron, aluminum, silicon, and sulfate (some added in the pretreatment stages), though it is not expected that any significant amount of solids will be eluted with the uranium during regeneration. Nevertheless, there will be finite levels of all of these in the regenerant brine, as well as calcium, hydroxide and carbonate if the brine is first treated with lime prior to evaporation, and uranium in either case. The various dissolved cation species present could form scales on the evaporator walls, most likely in the form of calcium and/or sodium carbonate, iron-aluminum-calcium silicates, and uranium oxyhydroxides. Unlike sodium chloride, these minerals all exhibit retrograde solubility, meaning they become less soluble with increasing temperature, and it is common for these minerals to form scales on hot metal surfaces in contact with cooler water containing iron-aluminum-silicon-calcium, as is observed at the Savannah River evaporator, at Oak Ridge's Melton Valley evaporator, and in geothermal production wells. It is difficult to predict whether or not scaling will represent a significant operational problem, or whether plugging of pipes, valves, etc., by these minerals and/or sodium chloride will be problematic. Therefore, a small-scale testing program would be required to address these issues prior to implementation of an evaporation system at the plant.

Partial evaporation appears to be a more promising treatment than total evaporation based on operational considerations. Solids containing iron-aluminum-silicon may not form at all during partial evaporation, unless the solubility limit of some amorphous or crystalline solid is reached. This would be an additional argument in favor of only partial evaporation to reduce the total volume of solution for subsequent treatment or incorporation into concrete.

3.3 Alternate Strategies

Alternate strategies that were considered but not recommended include biomass adsorption or reduction, ion exchange specific to uranium in brine, precipitation with phosphate and reduction, and hydroxyapatite. These technologies are described and discussed below.

3.3.1 Biomass Adsorption or Reduction

Biomass adsorption or reduction is a method that has been successfully used to remove uranium from wastewater streams under a wide range of conditions. A number of *in situ* barriers and bioremediation approaches also exist for removal of metals and other contaminants from groundwater (Liu 1993, Derome 1991, Premuzic 1991). Some of these may be appropriate for removal of uranium from aqueous streams, but most are not viable for high salt/ionic strength systems such as the high sodium chloride regeneration stream. These methods may remove up to 95-99 percent of the uranium present in the solutions, which would result in uranium removal from a nominal 5 ppm to 50 ppb under the best conditions. Other uses for biosystems include the solubilization of the uranium during mining and recovery operations. Biosystems also require a carbon source if the method uses a living organism, and require an immobilization method for non-living biological materials. Although organisms have been found that can operate in a highly saline environment (Francis 2000), growth and uranium uptake is generally much slower than required in the removal of the uranium in the regeneration brine. Because of the need for uranium removal to less than 30 ppb in a relatively short time, these methods do not offer an efficient solution. In addition, bench and pilot testing of any system chosen would be required to determine operating conditions. Because of these and other effectiveness and schedule risks, and the requirements for additional infrastructure for implementation, biosystem methods are not recommended for this application.

3.3.2 Ion Exchange Specific to Uranium in Brine

Since ion exchange is the method used to remove the uranium from the water currently being treated in the AWWT, using ion exchange to remove the uranium from the regeneration brine was discussed. One ion exchange method using a system from 3M™ called Empore™ is currently being bench-tested at Fernald (Miura 2000, Beals 1998). Others using inorganic ion exchangers have also been proposed (Song 1997). Other macroporous and organic exchangers such as Reillex(TM) HPQ, Dowex 1-X8, and Reillex(TM) HP have also shown promise for removing uranium from salt solutions (Chanda 1992a). Microporous resins like microporous polybenzimidazole have also been tested (Chanda 1992b). Each of these resins and ion exchange materials would require bench- and possible pilot-scale testing before engineering and design and implementation could be started. The cost to implement would be higher than other methods because of the need for equipment, piping, and instrumentation. For these reasons, use of an ion exchange method is not recommended.

3.3.3 Precipitation with Phosphate, Coupled with Reductant

Phosphate has been used as a precipitation and immobilization agent for uranium, actinides, and transuranic waste materials (Read 2001). However, it requires a reductant to reduce the uranium VI to uranium IV to reduce the solubility. When uranium phosphate minerals are contacted by leach water, substantial amounts of uranium may be released. Since some of any phosphate added may proceed to the outfall, permitting risks may occur. The method would also require bench scale testing to determine the methods for introduction, the procedures for use, and the requirements for additional equipment. Although it has been used in the uranium mining industry, its applicability in this case is questionable due to the uncertainties. Because of the

additional research and development required for possible use and the uncertainties in permitting and stakeholder acceptability, this method is not recommended.

3.3.4 Hydroxyapatite

Hydroxyapatite is a family of compounds with the general chemical structure $\text{Ca}_{10-n}\text{X}_n(\text{PO}_4)_{6-m}\text{Y}_m\text{Z}_2$, where X and Y are cations and anions, respectively, that substitute for Ca^{2+} and PO_4^{3-} groups in the hydroxyapatite structure. Typical cation substitutes include Sr^{2+} , Na^+ , Pb^{2+} and Cd^{2+} while anion substitutes include HPO_4^{2-} , and CO_3^{2-} . Z is usually OH^- , F^- , Cl^- , or Br^- (Elliott, 1994). Hydroxyapatite is an ideal material for long-term containment of contaminants because of its low water solubility ($K_{sp} < 10^{-40}$), high stability under reducing and oxidizing conditions and over a wide temperature range, availability, and low cost (Christoffersen and Christoffersen 1981, Saalfeld et al. 1994). It is well documented that hydroxyapatite strongly sorbs uranium (Arey et al. 1999, Bostick et al. 1999, Jeanjean et al. 1995, OrdonezRegil et al. 1999) and many other radionuclides and heavy metals.

For removing uranium from brine regeneration solutions at Fernald, apatite could be added to the brine before filtration or used in a column arrangement. It is unknown what effect the high chloride concentrations in the regeneration brines would have on sorption of uranium by hydroxyapatite. Therefore, experiments would need to be performed to determine the effectiveness and optimum conditions for using hydroxyapatite to treat regeneration brine. A drawback of using hydroxyapatite is the creation of another solid radioactive waste. The use of hydroxyapatite would require extensive research and development and other treatment technologies given in this manuscript are viewed as more promising, either from the scientific or economical aspect. Therefore, hydroxyapatite is not being recommended at this time.

4.0 CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

The technical assistance team commends the staff at Fernald on their resourcefulness, ingenuity, and dedication to solving this problem under less than ideal conditions. They were extremely helpful during the review process and open to the recommendations made during the review. They quickly tested the technical assistance team's suggestion to add sodium thiosulfate to the brine eluant and had bench scale confirmation that the process could work by the second day.

The AWWT currently typically treats from 1800 to 2700 gpm of uranium-contaminated groundwater, storm water runoff, and remediation wastewater using an ion exchange process. Regeneration of the ion-exchange resins produces a brine that contains 2-5 ppm uranium after precipitation by lime addition. The review team was asked to identify and recommend approaches that would provide for cost-effective, easy to implement processes for reducing uranium concentrations in the brine from the current level of 5 ppm to less than 30 ppb.

The technical team developed eleven alternatives and grouped them into chemical, physical, and alternative processes. Chemical approaches involve reducing the uranium from the +VI to the

+IV oxidation state, and/or substitution of reactive magnesia for lime in the precipitation process. Uranium solubility should be less than the operational goal of 30 ppb in the reduced state; simply replacing lime with magnesia in the current process might only result in a supernatant containing several hundred ppb total uranium. These approaches appear to be the most promising. Physical processes revolve around evaporation and solidification of the wastes. These approaches appear to be technically feasible but would be difficult to implement and operate and may be cost prohibitive. Alternative approaches included biomass adsorption/reduction, a secondary ion-exchange system, precipitation with phosphate coupled with reduction, and addition of hydroxyapatite. Each of these were either technically infeasible (e.g., biomass adsorption/reduction is unlikely to reduce concentrations below 30 ppb), or were technically immature and would require an extensive testing program to verify and optimize performance and were therefore, not recommended for further consideration.

4.2 Recommendations

The technical team developed the following tiered approach to removing uranium from the brine solution. Steps in the tier should be taken only if the previous steps are insufficient.

1. Add sodium thiosulfate to the solution in conjunction with or after treatment with lime. Preliminary testing indicates that this would be a viable solution to reducing uranium concentrations in the brine. Laboratory experiments should be performed to determine (1) the amount of sodium thiosulfate required for uranium reduction to acceptable levels, (2) reaction kinetics including oxidation to the +VI state if oxygen is present (the process may be open to air), (3) the point of sodium thiosulfate introduction into the treatment process, (4) process modifications, and (5) environmental, safety and health considerations. If the results from these additional laboratory experiments are positive, then implementation as part of the regeneration brine treatment should follow.
2. Replace the addition of lime in the treatment process with reactive magnesia. This will provide a lower pH process (pH 8.5 – 9) and may lower the solubility of uranium slightly. Keeping the pH of the water at a lower level may be advantageous if discharge to the river is the selected disposition option.
3. If sodium thiosulfate does not provide acceptable performance, attempt addition of zero-valent iron or magnetite. These solid amendments would also reduce the oxidation state of uranium and therefore, its solubility. Addition of the amendments could occur during or after the liming process. Use of zero-valent iron could produce hydrogen gas and therefore, engineering controls may need to be added to the system. Use of solid amendments is more likely to have precipitation and plugging problems as compared to liquid amendments.
4. If chemical controls prove inadequate, evaporation may be used to increase precipitation and reduce the volume of water that needs to be treated. Complete or partial evaporation may be used depending on the economics. The evaporate could be solidified and disposed either on-site or off-site, depending on uranium concentrations in the resulting solid waste form. If total evaporation is performed, there is no need for chemical treatment of the brine. If evaporation is chosen, scaling and plugging problems will require special attention. Evaporation is the approach that requires the most additional equipment (evaporator, solidification), largest changes to the process, and most difficulty to implement, and, therefore, is the last option in the tiered approach.

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APPENDIX A TECHNICAL ASSISTANCE REQUEST

Request for an OST Technical Solution

Project Title: **Solution for Fernald Treatment of Uranium in Brine Ion Exchange Regeneration Fluid and in the Leachate from the On-Site Disposal Facility**

Section 1 – Required Signatures

Site Contact or Operable Unit Manager

OST/HQ Program Manager

Site Manager

OST/HQ Office Director

Section 2 – Point of Contact Information (Contractor Program Manager)

Name of Requestor: **Dave Brettschneider**

Site/Operable Unit: **ARWWP Project**

Address: **Fluor Fernald, Inc., P.O. Box 538704, Cincinnati, Ohio 45253-8704**

Telephone Number: **513-648-5814**

Email Address: david.brettschneider@fernald.gov

Section 3 – Project Information

Project Title and Location: **Fernald Advanced Waste Water Treatment Project and On-Site Disposal Facility**

Description of Requested Technical Solution: **Convene a Technical Assistance Team of experts to review technologies for the removal of uranium in both brine ion exchange regeneration solution from the Advanced Wastewater Treatment Facility (AWWT) and in the leachate from the Fernald On Site Disposal Facility (OSDF). The team will identify one or more technologies for bench-scale testing as a cost effective alternative to remove uranium so that the brine regeneration solution from the AWWT and the leachate from the OSDF can be discharged without further treatment. The team will prepare a recommended development and demonstration plan for the alternative technologies. Finally, the team will make recommendations for the optimum Technical Solution for Fernald's problem of field implementation.**

Qualification and Expertise of Person(s) needed to provide the Technical Solution: **The person or persons should have a background in aqueous uranium chemistry, uranium treatment technology, and must understand treatment field operations and closure site schedule needs.**

Type of Deliverable Requested: **Technical Solution Recommendation Report and supporting documentation.**

Benefits and/or Objectives of Technical Solution: **Schedule acceleration, cost reduction, and long-term stewardship implementation.**

TA Uranium removal comparisons

APPENDIX B PARTICIPANTS AND CONTACT INFORMATION

**SCFA Technical Assistance: Fernald Uranium in Brine Treatment
Fernald Environmental Management Project, Fernald, Ohio
August 6-7, 2002**

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APPENDIX C TECHNOLOGY MATRIX

Fernald Treatment of Uranium in Brine Ion Exchange Regeneration Fluid

Note: Recommended technologies are listed in priority order.

Technology	Strategy	Effectiveness	Permitting Risk	Schedule risk	Health and Safety Risk	Cost	Implementability	Stakeholder Acceptability	Technical Maturity	Overall Recommendations
Add sodium thiosulfate in addition to lime	Reduction of U solubility	High - May require blending to achieve final increment to 30 ppb	Low - Less of a problem than alternate reductants; environmentally friendly	Low	Low	Low	High - May require additional vessel for staged processing with lime first and then reductant; may need to treat only first 4-6 bed volumes	High - If blending required, would have to discuss with stakeholders	High - Proven by lab test; mature water treatment method	Highly recommended as addition to lime treatment
Reactive magnesium oxide instead of lime	Minimize U solubility	Medium - Accomplishes same thing as lime at lower pH; uncertain if will reduce to 30 ppb, requiring additional step to precipitate U; will reduce carbonate concentration also	Low - Same toxicity as lime; would be at lower pH	Low - No net change	Low - Same as current method	Low - Slightly greater than lime	High - Straightforward; switch out lime bag with magnesium bag	High - Should not be an issue	High - Mature	Recommended if sodium thiosulfate is not enough
Zero valent iron or magnetite	Reduction of U solubility	Medium - Needs testing to determine how well it will work with brine and if it will achieve 30 ppb; works well with groundwater; gets rid of liquid without putting it back through system; calculated 3 orders of magnitude reduction to 3 ppb; might need to add something to reduce carbonate concentration; magnetite would allow magnetic separation of solid but also is dense, allowing filtering	Low to Medium - Possibility of hydrogen generation; would be smaller concern if doing only first few bed volumes; magnetite would mitigate hydrogen concern	Low - Can be done in less than a month	Low to Medium - Hydrogen generation for iron; reduces risk from U because in less reactive form; iron filings could lead to fire (low probability) so storage facility needs to take this into account	Low - Less than current operation; need 500 # iron/month (less than \$1000/yr); magnetite is very inexpensive	Medium to High - Straightforward except for hydrogen problem; hydrogen monitoring would be needed; technically comparable to current baseline; options include direct addition or cartridge (cartridge flow-through system has risk of bio-fouling); may only need to treat first 4-6 bed volumes; iron could present problem with adherence to sides of tanks	Medium to High - U will re-oxidize once discharge to River but meets regulatory limit	High - Mature technology for groundwater although may not be for brine; mature for wastewater treatment	Strong; need to do scale-up testing; bench-scale testing should provide good indication of whether this will work

Technology	Strategy	Effectiveness	Permitting Risk	Schedule risk	Health and Safety Risk	Cost	Implementability	Stakeholder Acceptability	Technical Maturity	Overall Recommendations
Alternate Soluble reductants (ferrous chloride, stannous chloride, hydrazine, citric acid, ascorbic acid)	Reduction of U solubility	Medium to High - Would need flocculating agent to gather U colloids; have to keep solution non-oxidizing; could combine with other methods to increase their effectiveness (e.g., magnesia)	Low to Medium - Higher for hydrazine; Vitamin C not a problem; stannous chloride could be greater challenge	Low	Low to Medium (depends on reductant)	Low	Medium to High - Might have to change operating methods to keep solution from becoming oxidizing while do filtration, etc.; may only need to treat first 4-6 bed volumes	Medium to High - Depends on which additive is used	Low to Medium - Could work but not mature	Potential backup solutions; need to do literature search
Partial evaporation to 98% (first 6 bed volumes) to increase Na content and decrease U solubility	Physical evaporation	Medium - Would remove most of U to solid; last 10 bed volumes might still be too high in Cl to send back through system; does not create any salt cake; could be pretreatment before reductant or post-treatment drying or grouting	Low - No VOCs or tritium	Medium - Adding new equipment; commercial equipment is available (needs to be self-fired)	Low - No concern with U dust	Medium - Relatively inexpensive (cost of tank and natural gas); need corrosion protection; \$20/ft ³ or \$1000-1500/month for disposal; requires extra storage tank (site has)	Medium to High - Reacting 3000 gallons lot easier than 30,000 gallons; if low enough, could discharge without treating; would need big holding tank; could add concrete or lime to remaining volume	High - Easier than full evaporation because does not go to dryness	High	Would recommend if reductant alone is not enough
Full Evaporation	Physical evaporation	High - Get 100% of U in solid; no solution remaining to treat	Low - No air pollutants; no permits required to ship solid offsite	Medium - Time to build evaporation tank; commercial units available (need to be self-fired)	Medium - U dust if let go dry	Medium - Relatively inexpensive (cost of tank and natural gas); need corrosion protection; \$20/ft ³ or \$3000/mon for disposal; requires extra storage tank (site has)	Medium to High - Unsure if commercial systems available for brine; eliminates number of steps; have to package so does not pick up moisture from air	High - Straightforward and familiar technology; could increase transportation concerns but already running rail cars now; eliminates discharge to River	High - Very mature	Could also combine with other methods; would knock U concentration down
Mix with grout for disposal onsite or offsite	Solidification	Medium - No discharge to River; large volume of grout (140 yd ³ /mon)	Medium - Need approval; show meets WAC (may require leach testing)	Medium - Grout-making equipment; may need bench-scale testing	Low - Risk from silicates (worker safety issue)	High compared to other options due to concrete	High - Could contract out work, making it easy to implement;(longer to do in-house)	Medium	High - Need to test formulation for high Cl	Consider if other alternatives do not work

Technology	Strategy	Effectiveness	Permitting Risk	Schedule risk	Health and Safety Risk	Cost	Implementability	Stakeholder Acceptability	Technical Maturity	Overall Recommendations
Hydroxyapatite	Adsorption and co-precipitation of U	Unknown; U very attracted to apatite; NaCl should increase formation but other components' effects unknown	Low	High - May require lot of testing; difficulty in obtaining materials	Low	Low - Slowly introduce reagents (CaCl and NaPO ₄)	Low - Difficulty in obtaining sufficient quantities of materials; solid is not readily available but may be able to make it in-situ	High - No concern	Low - Not mature	Alternative if other options fail
Phosphate coupled with reduction	Precipitation	Medium – Will not lower solubility enough without reductant	High - Phosphates are often not acceptable for discharge to river	Low	Low	Low	Medium - Would have to figure out how to introduce with lime	Low – Discharge of phosphates to River	High - Well-known in U mining	Probably not recommended because of discharge to River issues
Ion exchange specific to U in brine (includes 3M work)	Ion exchange	Unknown - Testing being done now	Low if it works	Medium to high because of testing (bench-scale and full-scale) and engineering design needs	Low	High	Low - Requires engineering design and impacts on closure schedules	High - No concerns anticipated	Low – Not mature (being developed)	Not recommended
Biomass adsorption or reduction	Adsorption or reduction	Unknown - Will remove U from certain solutions under certain conditions but unsure how well would work under these conditions	Medium - May be some questions; is used for other similar situations	High - May require lot of testing	Low unless use organism that presents risk	Low to medium – operating costs low; medium overall	Low to Medium - Questionable because effectiveness is unknown; subject to weather and temperature	Medium	Low for this application	Not recommended

Cost: Low = Less than \$20,000 /yr; Medium= \$20,000-\$200,000 /yr; High= Greater than 200,000 /yr
Stakeholders: includes site owners and the public

APPENDIX D TECHNICAL ASSISTANCE TEAM

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B.S. in Nuclear Engineering, University of Virginia

Areas of Expertise:

Dr. Sullivan is a member of the Environmental Research Division staff at Brookhaven National Laboratory. His PhD dissertation was on mechanistic modeling of the leaching behavior of nuclear waste glass. Dr. Sullivan joined the staff of BNL in 1983 and has worked extensively on the application and development of models for radioactive and hazardous waste performance assessment. For the Nuclear Regulatory Commission, he has developed six different computer models to perform source term analysis and predict subsurface fate and transport from shallow land disposal facilities. These codes have gained international acceptance and use. Dr. Sullivan has provided four International Atomic Energy Agency (IAEA) courses on low-level waste source term analysis and has been a technical expert for the IAEA on five missions. He is also a member of the National Council on Radiation Protection subcommittee on low-level waste disposal performance assessment. Dr. Sullivan has also been heavily involved in source term analysis and modeling of the tritium plume from the High Flux Beam Reactor at BNL, tritium soil contamination underneath the Brookhaven Linear Isotope Production facility and the g-2 beam stop area. Dr. Sullivan's other research interests are in the use of gas tracers for detecting flaws in subsurface barriers, underground ducts, and waste covers. He is also involved in the application and critical review of decision support software to assist in making environmental remediation decisions and human health risk assessments.

DOUGLAS D. LEE

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Education:

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Areas of Expertise:

Dr. Lee has worked since 1976 as a staff member in the Chemical Technology Division (now the Nuclear Science and Technology Division), where he is currently working in radioactive waste treatment technology development. Current activities include the development and operation of the cesium removal experiments in support of and in cooperation with Savannah River for the Alternative Salt Disposition Program. These are using the continuous-flow stirred-tank reactor system he designed and installed in two hot cells to study the small tank tetraphenylborate precipitation process to decontaminate liquid waste in the underground storage tanks at Savannah River. He has also supported the CSSX cesium removal process development in the same program. Previous activities included the development and operation of radioactive cesium removal equipment using various proposed new ion-exchangers and sorbents in a hot cell on actual tank waste. This was performed to support decontamination of the liquid waste in the underground storage tanks in the DOE complex and the ORNL TRIAD liquid radioactive waste treatment program. Previous research has included development and design work on the NAC active metal nitrate reduction process for treatment of high-nitrate level radioactive liquid waste at various DOE facilities in the USTID program. He has developed separation methods for the removal of the radioactive portion of mixed low level/hazardous supernate solutions and liquids wastes. Dr. Lee has conducted development work on AVLIS technology for conversion of uranium oxide to uranium chloride, biotechnology methods for volume reduction of organic radioactive waste, and biodegradation methods for toxic and carcinogenic contaminants in coal conversion wastewater streams. Dr. Lee has also developed bioreactor systems for denitrification of high nitrate-containing radioactive waste streams.

ROBERT C. MOORE

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Education:

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B.S. in Chemical Engineering, University of Tennessee

Areas of Expertise:

Dr. Moore is a Principle Member of the technical staff at Sandia National Laboratories. He has 7 years experience measuring and modeling thermodynamic properties of actinides in brine systems from the Waste Isolation Pilot Plant Project. He has another 3 years experience measuring and modeling the thermodynamic properties of inorganic and organic compounds in water at elevated temperatures. In the last 3 years, his work has focused on development of sorbents for treatment of the residuals from Hanford tanks and containment of uranium and technetium in the vadose and saturated zones. Currently, his work involves development of *in situ* formed permeable barriers of calcium hydroxyapatite in soil and groundwater for

containment of radionuclides, treatment of groundwater for removal of arsenic, and decontamination of radionuclide contaminated surfaces using a new decontamination foam based on isaccharanic acid.

DAVID J. WESOLOWSKI

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Education:

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B.S. in Geology, University of Pittsburgh

Areas of Expertise:

Dr. Wesolowski received a Eugene P. Wigner Fellowship at Oak Ridge National Laboratory (1983-85) and has remained at ORNL throughout his career. From 1989 through 1996 he was Leader of the Geochemistry Group, and he is currently a Distinguished R&D staff member of the Aqueous Chemistry and Geochemistry Group, Chemical Sciences Division. From 1995 through 2001, he served as Secretary of the Geochemical Society, and has served as an Associate Editor of this international society's flagship journal *Geochimica et Cosmochimica Acta* from 1992 to present. He is also a member of the Editorial Board of *Chemical Geology* and he has chaired numerous symposia at international chemical and geochemical conferences. His research interests include metal speciation and mineral solubilities in hydrothermal solutions, the surface chemistry and sorptive properties of minerals in contact with aqueous solutions from ambient to high temperatures, and the partitioning of the stable isotopes of the light elements in geological environments. He has published over 60 articles in the chemical, geochemical and environmental literature.

CAROL EDDY-DILEK

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Education:

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Areas of Expertise:

Ms. Eddy-Dilek is a research scientist in the Environmental Restoration Technology Section at the Savannah River Technology Center, the research and development laboratory supporting SRS. Her responsibilities have included many aspects of applied research related to characterization of hazardous waste sites and monitoring and performance assessment of remedial technologies. This work has a strong geotechnical, geological, and geohydrologic basis. For the last four years, she has been the lead investigator for the DOE's cone penetrometer sensor testing and evaluation program and has been actively involved in the development, evaluation, and application of new sensors and approaches for site characterization and monitoring. During 1998-1999, she led the site characterization efforts for the Interagency DNAPL Consortium Program at the Cape Canaveral Air Station, Florida, a joint EPA-NASA-DoD-DOE program for evaluation of innovative technologies for DNAPL remediation.