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STUDENT SPRING INTERNSHIP TECHNICAL REPORT

February 16, 2010 to May 14, 2010

Remedial Action Work Plan for the S-3 Ponds Site at the Y-12 National Security Complex Oak Ridge, Tennessee

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ABSTRACT

This document is an exercise for a Remedial Action Work Plan (RAWP) involving a DOE contaminated area. The purpose of this document is to help with the decision making process and is not an extended and detailed design of a remedial plan.

The RAWP addresses remediation of the S-3 Ponds site groundwater as set forth in the *Record of Decision for Phase I Activities in Bear Creek Valley (BCV) at the Oak Ridge Y-12 Plant, Oak Ridge.* The Phase I Record of Decision (ROD) includes interception and treatment of shallow groundwater contamination at the S-3 Ponds site pathway 3, including the eastern and western sides of the ponds. The S-3 Ponds site consists of four capped ponds previously used for managing liquid waste, which have been converted to a parking lot under the Resource Conservation and Recovery Act (RCRA).This remediation project is considered to be a non-time critical action under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The S-3 Ponds pathway 3 is an important contributor to uranium contamination and a main source of nitrate and cadmium contamination in Bear Creek. Groundwater remediation in pathway 3 of the S-3 Ponds will help to reduce the uranium concentration in surface water as established as a primary watershed goal of the BCV ROD phase I. This goal meets the requirements for risk-based levels for future residential land use.

This report compares different technologies or methods to reduce contaminants in the S-3 Ponds plumes. These technologies are briefly explained and some pros and cons of each one are discussed. This remedial action work plan focused on ethanol injection technology which is divided into three stages. The first stage is the removal of nitrate, calcium and aluminum using an above ground treatment. The second stage is the conversion of U (VI) to U (IV) by injecting ethanol into the groundwater and the third stage is the long-term maintenance of stable U (IV) by removing oxygen from the groundwater.

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ACRONYMS

CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DOE-EM	U.S. Department of Energy- Environmental Management
LUCAP	Land Use Control Assurance Plan
ORFRC	Oak Ridge Field Research Center
ORR	Oak Ridge Reservation
RAWP	Remedial Action Work Plan
ROD	Record of Decision
TDEC	Tennessee Department of Environmental Compliance
VOC	Volatile Organic Compound

ABBREVIATIONS

Meter	m	cubic yards	yd^3
Milligram per kilogram	mg/kg	parts per million	ppm

ACKNOWLEDGMENTS

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1. INTRODUCTION

This Remedial Action Work Plan (RAWP) presents some actions to remove contaminants in a groundwater plume originating from the former S-3 Waste Disposal Ponds at the Y-12 National Security Complex on the U.S. Department of Energy (DOE) Oak Ridge Reservation (ORR) in Oak Ridge, TN and extending down Bear Creek Valley. The former S-3 Ponds were four disposal pools used from the 1950s to the 1980s to receive toxic liquid waste that included nitrate, metals, uranium, technetium and other contaminants. These ponds were sealed by an asphalt parking lot in 1988. The contaminated waste travels by three main pathways in the subsurface and discharges into Bear Creek where it then continues down the watershed. This document analyzes the remedial plan for the eastern and western sides of the S-3 Ponds contained in pathway 3.

This document is a Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) remedial action plan, which will be conducted to support the environmental remediation efforts of the Department of Energy Environmental Management (DOE-EM) at the Y-12 National Security Complex. This plan presents and compares some remediation alternatives and briefly describes and designs one of them as an option to reduce the contamination at the site.

EXECUTIVE SUMMARY

This research has been supported by the DOE-FIU Science and Technology Workforce Development Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the spring of 2010, a DOE Fellow intern (Mr. Jose Vasquez) spent 13 weeks doing an internship at DOE Oak Ridge in the Office of Environmental Management under the supervision and guidance of Ms. Elizabeth Phillips. The DOE Fellow's project was initiated in February 16, 2010, and continued through May 14, 2010, with the objective of assisting the coordination and management of contamination research and remediation activities for DOE's Oak Ridge Reservation in Tennessee.

This Remedial Action Work Plan addresses remediation of the S-3 Ponds site groundwater as set forth in the *Record of Decision for Phase I Activities in Bear Creek Valley (BCV) at the Oak Ridge Y-12 plant, Oak Ridge.* Phase I Record of Decision (ROD) includes interception and treatment of shallow groundwater contamination at S-3 Ponds site pathway 3, including the eastern and western side of the ponds. The S-3 Ponds site consists of four capped ponds previously used for managing liquid waste, which have been converted to a parking lot under Resource Conservation and Recovery Act (RCRA).This remediation project is considered to be a non-time critical action under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Although, S-3 Ponds pathway 3 is an important contributor to uranium contamination and a main source of nitrate and cadmium contamination in Bear Creek. Groundwater remediation in pathway 3 of the S-3 ponds will help to reduce uranium concentration in surface water as established as a primary watershed goal of the BCV ROD phase I. This goal meets the requirements for risk-based levels for future residential land use.

This report compares different technologies or methods to reduce contaminants in the S-3 ponds plumes. These technologies are briefly explained and some pros and cons of each one are showed. This RAWP focused in ethanol injection technology which is divided in three stages. The first stage is removal of nitrate, calcium and aluminum. The second stage is the conversion of U (VI) to U (IV) by injecting ethanol in the groundwater and the third stage is long-term maintenance of stable U (IV) by removing Oxygen from the groundwater.

2. SITE DESCRIPTION

This section describes the S-3 Ponds site at the Y-12 National Security Complex, the potential pathways and some possible remedial actions based on plot-scale research activities which have been conducted at the site.

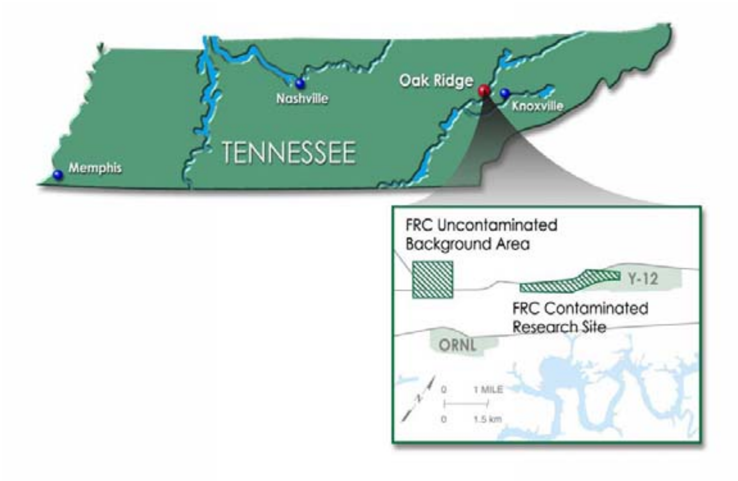


Figure 1. S-3 Ponds location.

As shown in Figure 1, the S-3 Ponds are located in the Bear Creek Valley at the western part of the Y-12 complex in Oak Ridge, TN. Figure 2 shows the S-3 Ponds site before and after being paved. The contaminated plumes are dispersed in approximately 93 hectares located in west Bear Creek Valley on DOE's ORR in eastern Tennessee. The area is mostly wooded. The facilities within the contaminated area include the S-3 Ponds (now a parking lot), the West End Treatment Facility (WETF) and Bear Creek. Also, the site has been divided into 5 different areas for experimental purposes. Each area contains a small field plot and several monitoring wells. The S-3 Ponds are located over shallow groundwater and the plumes coming from the site extend to the east and west. The direction of water flow is affected by the karst and fractured conditions of the site. The subsurface media at the site consist of fractured saprolite weathered from interbedded shale and limestone.

2.1 S-3 Ponds

The S-3 Ponds were four unlined pools located on the western edge of Y-12 plant. Each pond had a storage capacity of 2.5 million gallons. The ponds dimensions were approximately 122m x 122m. The ponds are currently covered with an asphalt parking lot built in 1984 and are under RCRA care and monitoring. Before 1984, the ponds received liquid waste containing uranium and technetium, nitrate, nitric acid and other metals. Although the ponds have been sealed with a RCRA cap, there is contamination in the groundwater plumes coming from these ponds. There is an estimated 5,740 acre-feet of polluted groundwater coming from the waste leachate produced prior to capping the ponds. This polluted groundwater is also affecting surface water, specifically Bear Creek and its tributaries. The ponds contribute approximately 26% of the risk of uranium contamination to the Bear Creek Valley Watershed. The groundwater pH is highly acidic with a pH of 3.2; the uranium contamination is approximately 60 ppm and the solid uranium contamination is 1000 ppm.

Figure 2. S-3 Ponds site before and after being paved.

2.2 Bear Creek

One of the pollution receptors is Bear Creek, located 2 miles downstream of the S-3 Ponds site (Figure 3). The upper stem of Bear Creek receives polluted shallow groundwater discharge. Also, deep groundwater contaminates Bear Creek tributaries that originate on the southern slope of Pine Ridge. The main contaminants in the creek and its tributaries are uranium, nitrate and cadmium.

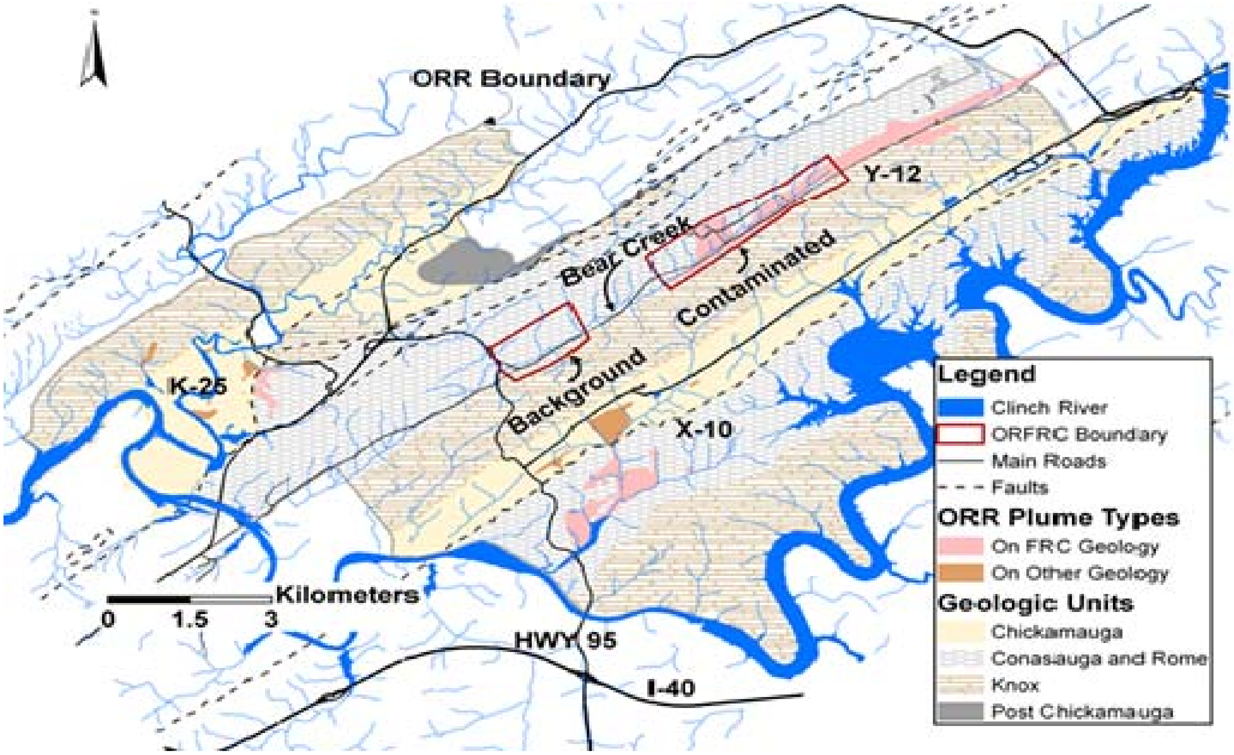


Figure 3. Bear Creek and Clinch River.

2.3 Potential Pathways

This research will analyze the eastern and western plumes. On the western side of the S-3 Ponds, three different contamination pathways have been previously identified (Figure 4). Pathways 1 and 2 are uranium contaminated flows in shallow groundwater (< 51 ft bgs) which discharge to the upper stream of Bear Creek. Pathway 3 mainly discharges nitrate and cadmium contamination to Bear Creek tributaries; it is on deep bedrock groundwater between 50 to 200 ft bgs. On the eastern side of the ponds, pathway 3 is the only one affecting groundwater. Each pathway has different hydrological, geological and biological characteristics. Rainfall patterns affect the water table and additionally the hydrogeology of the site affects the direction of the contaminant plumes. This RAWP will focus on pathway 3 (both sides), where there is a strike flow greater than 100 ft deep and a nitrate concentration greater than 10,000 mg/L.

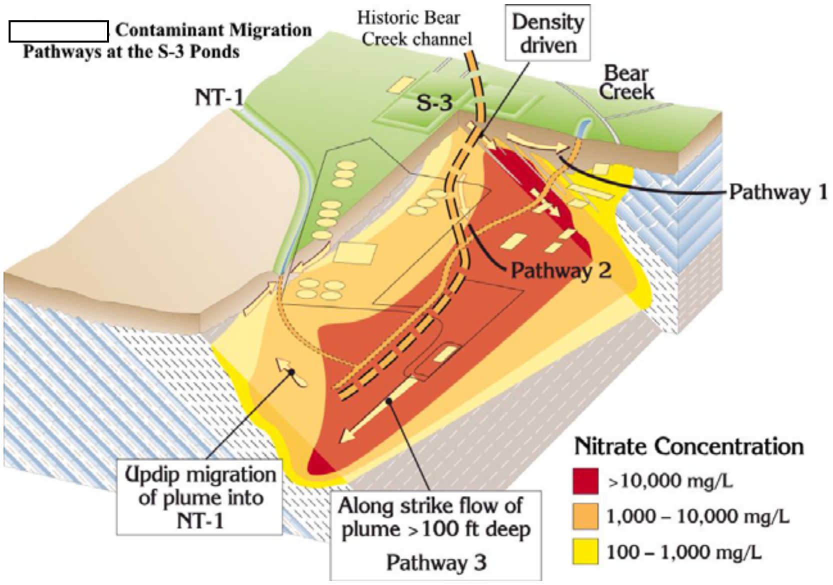


Figure 4. Three contaminant pathways from the S-3 Ponds.

3. PREVIOUS ACTIONS AND SUPPORT EXPERIMENTS

Pathways 1 and 2 of the western plume were remediated through CERCLA by a removal action in 2001. Previous actions by the Oak Ridge Field Research Center (ORFRC) have focused on working with microbial communities and bio-reduction. These microorganisms have been used to convert contaminants (U and Tc) into chemical forms which show less mobility in ground water.

- Using emulsified vegetable oil (EVO) to reduce U concentrations: ORFRC scientists accomplished a sequential decrease of sulfate, nitrate, Fe (III) and U (IV). This experiment significantly reduced U flux to Bear Creek (greater than 80% U reduction in the injection zone). Nitrate was reduced but acetate was produced.
- Two treatment systems have been tested for both pathways 1 and 2. On pathway 1, a HDPE membrane and a treatment module was installed with the objective of testing iron, peat moss and electro kinetic treatment techniques. The reduction in the concentrations of U was 80% to 99.6%, Tc-99 (51.6%), nitrate (75%) and sulfate (42%).
- On pathway 2, a permeable trench was constructed perpendicular to groundwater flow using gravel and zero-valent iron as the media. The connectivity of the iron and gravel in the trench may be decreasing over time due to cementation in the iron. U was only partially reduced and prone to reoxidation. The reductions in the concentration of contaminants were: U (90%), nitrate (83%) and sulfate (82%).
- A remedial action plan to treat pathway 3 was proposed in 2007. The plan included excavation, installation, transportation and treatment. Installation included a 450 ft long collection trench filled with a mixture of sand and apatite II (reactive media) bordering NT-1 and three collection wells to help direct flow through the media. The media proposed was 90% sand and 10% apatite. The wells were to contain some pumps, controls and a piping system to return water back to NT-1. Apatite II has been shown to be very effective at removing U where it’s converted to a stable calcium uranium phosphate precipitate (autunite).

Other experiments supporting remedial actions have been made to understand the behavior of uranium and technetium in groundwater. This research focused on chromium, uranium and other contaminants of concern in the S-3 Ponds area.

- “Push-pull” experiments: The purpose of this experiment was to define if native microorganisms capable of immobilize uranium are currently at the site. Also, this experiment researched the optimal feeding conditions of these microorganisms and how to prolong the immobilized pollutants over time.
- A tracer test and flush experiment performed using a heterogeneous porous media showed that it’s possible to create a local redox barrier after stimulating microbial activities at interfaces between zones of high and low groundwater flow rates. This barrier reduced the transfer of contaminants from the low-flow zones (long term contaminant source) to the high flow zone which transport contaminants to the receptors.
- Identification of new species of bacteria able to survive and reproduce in the heavily contaminated subsurface (nitrate and nitric acid) and low pH. These species should

stimulate uranium reduction and nitrate removal. A new uranium bacteria reducer has been investigated recently at the Kostka lab: *Geobacter daltonii*, which is able to reduce uranium and organic contaminants. Others indigenous organisms are not growing in the low pH and high acidic contamination.

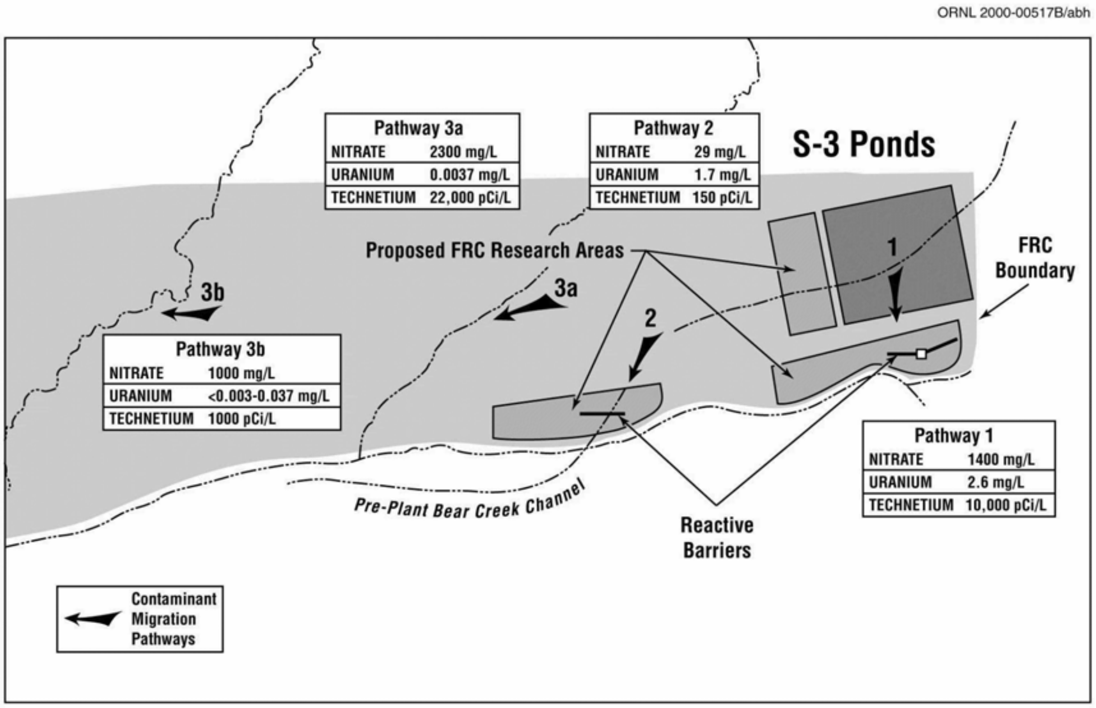
- Inhibition/ reoxidation of U and Tc: Some experiments were done with the goal of uranium reoxidation using nitrate, calcium and NOx. Humics could accelerate the uranium reduction and the uranium reoxidation rate as well.

Additional information about these different technologies and experiments can be found at the NABIR website at http://public.ornl.gov/orifc/orfrc4_pastresearch.cfm.

4. PROJECT DESCRIPTION

This remedial action plan presents the best alternative for remediation of the contaminated groundwater plumes coming from the S-3 Ponds at the ORR in East Tennessee. Some remediation alternatives address the hydrogeology, modeling, and microbiology aspects of the problem. This RAWP will focus on targeted manipulations to convert radionuclides and metals to stable forms. The former S-3 Ponds received approximately 3.2×10^8 liters of acid, uranium and nitrate bearing-waste from the 1950s to the 1980s. These ponds were denitrified and sealed by an asphalt parking lot in 1984. However, leaching of primary and secondary groundwater zones of contamination has created polluted groundwater plumes, which ultimately contaminate surface water and create a human health hazard. These groundwater contaminated plumes extend 4 kilometers through Bear Creek Valley. The main direction of contaminant transport is predictable because it is parallel to the valley’s axis and the strike of bedding planes and is guarded between stratigraphic layers.

Today, the residual sludge in the ponds contains an average uranium concentration of 1023 mg/L and a technetium concentration of 479 mg/L. Most of the contaminants have moved from the ponds to the groundwater plumes; near the source, there is a uranium contamination greater than 60 ppm (60 mg/L), technetium greater than 40 pCi/L and nitrate between 1000 and 10,000 ppm (10,000 mg/L). Also, the uranium solid phase is around 1000 ppm. Thorium and VOC’s are other contaminants in the groundwater and fixed gases include CO_2, CO, N_2O, H_2, N_2 and CH_4. The pH near the ponds is 3.2 and goes up to greater than 7 in more distant wells. The uranium concentration has an inverse relationship with pH; where the pH is higher, the uranium concentration is lower and less mobile. Figure 5 shows the contaminant concentrations around the S-3 Ponds.



Pathway 3a	
NITRATE	2300 mg/L
URANIUM	0.0037 mg/L
TECHNETIUM	22,000 pCi/L

Pathway 2	
NITRATE	29 mg/L
URANIUM	1.7 mg/L
TECHNETIUM	150 pCi/L

Pathway 3b	
NITRATE	1000 mg/L
URANIUM	<0.003-0.037 mg/L
TECHNETIUM	1000 pCi/L

Pathway 1	
NITRATE	1400 mg/L
URANIUM	2.6 mg/L
TECHNETIUM	10,000 pCi/L

Figure 5. Contaminant concentrations around S-3 Ponds.

The main objective of this study is to restore the uranium and nitrate contamination to levels below EPA limits. These maximum contaminants levels (MCL) are 30 ug/L for U and 10 mg/L for nitrate. The technetium MCL is 900 picocuries/L. To attain these goals, a treatment system will be designed for pathway 3 on the western and eastern sides of the plume. A system of injection wells will be installed on the perimeter around the parking lot containing the S-3 Ponds.

The following sections give a general idea of project flexibility (section 4.1), a synopsis of an engineering study (section 4.2) and a contaminant reduction goal for the S-3 Ponds boundary (section 4.3).

4.1 Project Flexibility

Flexibility is necessary in the execution of this remedial plan in response to variations in data, observations and/or the development of new technologies that may occur during the development of the remedial execution. The DOE-EM team has the authority and responsibility to change the design of this remedial plan in order to adapt it to relevant new data and observations. The DOE technical team may recognize a need for a change in the remedial design and they should submit to the core team a complete description of the changes with supporting diagrams and data. The core team will approve these changes before any variation in the implementation to the remedial action plan occurs.

4.2 S-3 Ponds Engineering Study

Since 2001, scientists have conducted many field-scale research studies to achieve accelerated bio-reduction and to slow down the mobilization of contaminants in the subsurface. Over 60 publications have been written about the contamination at the S-3 Ponds site and some conceptual and numerical models have created a base to support this remedial plan. Thousands of samples have been collected, including groundwater, surface water and sediments to determine the concentration of contaminants at hundreds of points. The site has been divided into 5 sections and each section has wells, multi-ports, boreholes and geophysics wells required by the different studies. The site also contains a trench and a trailer to support the operations. Besides the 5 study sections, there is a clean background area with similar hydro-biogeochemical conditions. Rainfall (daily and hourly) and elevation data have been collected as well. All the data is contained in an ORNL website for public research.

4.3 A Contaminant Reduction Goal for the S-3 Ponds Boundary

The goal of this remedial action plan is to reduce the contaminants to levels required by EPA under CERCLA or to alternate risk-based standards. Site characterization has been made in previous studies by the FRC. Prior to starting the remedial action, the initial concentrations at the contaminated site should be compare with the baseline. This comparison should determine how effective the actions of the remedial plan were. The main contaminants to be treated with this remedial plan are uranium (VI), Tc (VII), nitrate, calcium and aluminum. The last three contaminants will be treated first to allow better uranium removal efficiency.

The long term stability of biologically reduced uranium depends on the complex interplay of microorganism activity, aqueous geochemistry, soil and sediment mineralogy and potential U oxidants. The impact of all these factors on uranium cycling is still unknown and for this reason it is recommended to complement long term measurements of uranium reduction at contaminated sites with laboratory experiments.

5. EVALUATION OF REMEDIAL ACTION METHODS

The following items should be evaluated in the decision making process of selecting an appropriate technology: depth of contamination, nature of contamination, hydro-geological characteristics, cleanup goals and timeframe. Defining the objectives of the remedial action plan will help in the decision making process as well.

5.1 Objectives

1. Reduce the concentrations of uranium and nitrate in NT-1 and Bear Creek such that the concentrations of these chemicals in surface water and groundwater are reduced to acceptable levels.
2. Reduce the overall concentration of total dissolved solids and the concentrations of nitrate and metals.
3. Hydraulically restrain the plume of polluted groundwater that is moving in bedrock in the Nolichucky Shale and reduce the contaminant concentration for the long term.

Some field research projects were executed at the ORFRC with the goal of understanding the contaminant behavior in the subsurface. Still, there are many uncertainties and questions to be answered in this complex system. The remedial action method will reduce uranium and other contaminants in the area by growing indigenous bacteria. Big barriers for growing these microorganisms are low pH and the high acidity of the area. Because of regulatory concerns, it is not recommended to alter the local environment with non-native microorganisms. Some of the alternatives to be evaluated in this project are discussed in the following sections.

5.2 The No-Action Alternative

The contamination would be left in groundwater and soil and no remedial efforts would be conducted. This alternative is rejected because of the resultant escalated contamination to surface and groundwater and the effects to the environment and human health. There is a massive spatial distribution of contaminants and leaving them in place will allow the continued interacting with the geo-sphere. There is no state and community acceptance to this alternative.

5.3 Sand and Apatite II Collection Trench

Another alternative to treat contamination at the site would be the installation of a trench with a media of sand and apatite. In 2007, a remedial plan proposed to install a 450 ft long collection trench which would be filled with 90% sand and 10% apatite as a reactive media. The plan included excavation, installation, transportation and treatment. The trench would border NT-1 and three collection wells would be installed to help direct flow through the media. The wells would contain pumps, controls and a piping system to return water back to NT-1.

In laboratory experiments, using apatite as a media removed U in both low and high ionic strength influents. U removal in high ionic strength is lower than in low ionic strength. More than 99% of U and Cd could be removed from contaminated groundwater using this system.

5.4 Two-Phases U Immobilization in Groundwater Using Ethanol Injection

ORFRC scientists used ethanol injection to lower U concentration in groundwater from 60 mg/L to less than 0.030 mg/L. These lower concentrations could be preserved over time with a reduced ethanol injection. According to Istok et al (2006), adding ethanol could be effective for removing uranium and technetium from groundwater; however, more studies are needed for long term applications where the effectiveness could be constrained by a depletion of bio-available Fe (III) or by hydraulic conductivity reductions. This technique converts highly mobile uranium VI into insoluble and non-mobile uranium IV.

Stanford and ORNL scientists have combined above-ground treatments with subsurface treatments. Above-ground actions remove contaminants which impede uranium transformation by microbes. Contaminants like nitrate, aluminum and calcium can restrain the chemical transformation, making uranium more mobile. These above-ground actions include pH adjustment and a fluidized bed reactor to allow better experimental control of the bioremediation.

In an experiment by ORNL and Stanford university scientists, more than 50 tests using ethanol injection (1.0 - 1.5 mM) provided similar U reduction (Figure 6). This experiment was performed in a low nitrate and neutral pH remediation zone, where dissolved uranium concentrations in the inner treatment zone decreased rapidly from 2 µM to <1 µM.

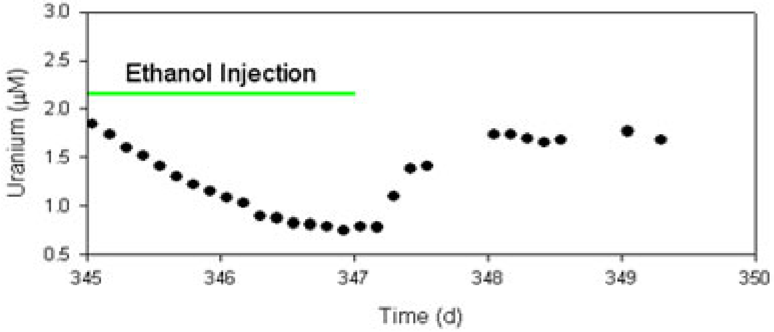


Figure 6. Dissolved U(VI) concentration in a sampling well during and after ethanol injection.

Continued U bio-treatment in this experiment resulted in U concentrations levels below the EPA drinking standards (0.126 uM). Subsurface treatments follow the above-ground actions, stimulating microorganisms which transform contaminants from one form to another. A series of injection-extraction wells simulate a bioreactor containing the organisms. Scientists have confirmed that these methods work in reducing uranium on a small scale, but still it is not comprehensive enough to apply it on a larger scale. Future studies are necessary to access the longer term stability of immobilized uranium.

5.5 Using Emulsified Vegetable Oil (EVO)

Another treatment to reduce U concentration in the subsurface uses vegetable oil. Scientists at ORFRC accomplished sequential decrease of U (IV), nitrate, sulfate and Fe(III), where U flux to Bear Creek was reduced by 80% in the injection area. Nitrate was reduced as well but acetate production was increased.

5.6 Inhibition and Re-Oxidation of U and Tc

Long-term field experiments were conducted researching redox conditions. Oxygen, nitrate or ethanol was introduced to determine if there was a re-oxidation or remobilization of U (IV). Statistical analysis and other techniques were used to characterize the microorganisms and to determine the variation in the microbial population. Results of these experiments showed that both ethanol and nitrate dominates DO in the microbial community.

5.7 Uranium Removal by Synthetic Resins

These studies show that strong base anion-exchange resins (ex: Dowex 21k, Dowex 1X-8 and purolite A-520E) are effective in removing uranium from neutral-high pH low nitrate groundwater while metal-chelating resins (ex: Diphonix and exchange100) perform better in neutral-high pH high nitrate containing groundwater.

Table 1. Comparison of Alternatives for Contaminants Treatment at the S-3 Ponds Area

METHOD	DEFINITION	MATERIAL	ADVANTAGE	DISADVANTAGE	CONTAMINANTS	NOTES
Sand and apatite collection trench	450 ft long collection trench filled with sand/apatite	Sand & apatite media; Pump, controls, piping	-Low energy requirement >99% U and Cd removal	-High construction costs -Limited to depths(<50 ft) -Labor intensive	U, Cd	
Two Phases Ethanol injection	P1-Above ground treatment to remove Ca, Al, nitrate. P2-Suburface treatments injecting ethanol in wells	Ethanol	99.5% U reduction Tc reduction	-Long term effects limited by depletion of bio-available Fe (III) or by hydraulic conductivity. -Unknown larger scale and long term effects.	U, Tc, Ca, Al Nitrate	
Emulsified vegetable oil	Injecting oil in wells.	Vegetable Oil	80% U reduction Nitrate reduction	Production of acetate	U, Nitrate, sulfate, Fe (III)	
Inhibition & reoxidation of U and Tc	Determines variation in microbial community	Ethanol, oxygen and nitrate	Humics could reduce U.	Humics could accelerate U reoxidation process	U and Tc	Ethanol and nitrate dominate DO in microbial community
No Action	No remedial action performed.	N/A	No short term cost.	-Contamination may still be present and dispersing. -Long term cost could be very expensive.	NONE	Leaving contamination could cause greater contamination in Bear Creek Valley
Uranium removal by synthetic resins	- Anion-exchange resin (Dowex™ 21K) remove U from neutral-high-pH-low nitrate groundwater. - In an acidic-pH -high-nitrate- groundwater, metal-chelating resins (Diphonix and Chelex-100) removed more uranium than anion-exchange resins.	-Strong-base anion exchange resins -Metal chelating resins	-Loading capacity for Dowex 21k (43mg/g) is higher than other resins & > than 90% U removal. -Resins have high capacities, fast reaction rates & a greater selectivity. -Diphonix and chelex 100 remove >80% U.	-Synthetic resins can be an expensive option (ex: Dowex 21k ~$4.16/lb) comparing with other resins.	-U and Tc	-In highly acidic and high nitrate zones is recommended metal-chelating resins than anion-exchange resins. -In the long term Diphonix is more U removal efficient than Chelex 100.

5.8 General Recommendations

Recommendations are based on the research provided by the ORFRC team and may be used as a guiding principle for the remediation of the S-3 Ponds area. These guidelines could be changed or modified if new and better alternatives are developed or if new data or institutional knowledge indicates that a different approach should be used to get better results.

Given the options presented in Section 4 and the project description facts introduced in Section 3, it is recommended that a combination of ethanol injection and above ground actions to reduce nitrate and calcium should be implemented. Injecting ethanol in wells around the area is recommended because it is expected to feed the indigenous microorganisms responsible for chemical transformation from uranium (VI) to uranium (IV) which is less mobile. At the same time, treating nitrate and calcium will reduce U re-oxidation. The option using emulsified vegetable oil is not recommended because it is less aggressive in reducing uranium and will produce acetate. The HDPE membrane and the permeable trench methods tested also did not give good results.

Another recommendation is to treat the area as close as possible to the S-3 parking lot, which is the main source of the plume contamination. The remediation will be located in the boundary of the S-3 parking lot.

Also, supporting technologies like modeling and/or geophysical methods have been used by researchers to examine groundwater flow and subsurface behavior using tracers, radar, seismic waves and electrical currents. Transport and three-dimensional modeling have been implemented on the site to get an estimate of the contamination dispersion and concentration to optimize the remediation effort. These tools can be used to provide a multi-scale predictive modeling and characterization of the site. Combining hydrological with geophysical data can allow a better estimate of the pollution dispersion and a better evaluation of the long-term natural attenuation and efficacy.

6. REMEDIAL DESIGN REPORT

The remedial action work plan contained in this remedial design report will be in accordance with CERCLA, be protective of human health and the environment, and will include remediation efforts like excavation, installation, transportation and treatment.

6.1 Remedial Actions

The remedial action will be divided into three stages. The first stage is removal of nitrate, calcium and aluminum. The second stage is the conversion of U (VI) to U (IV) and the third stage is the long-term maintenance of stable U (IV). Injection wells will be installed in the western and eastern boundaries of the S-3 parking lot. The distance between each well and the parking lot is calculated according to the cone of depression of each well. The rate of ethanol feeding for each well will be calculated after some preliminary tests with an initial number of wells. After the results given by these preliminary tests, the exact number of wells and the correct feeding rate will be determined. After the water is treated above ground, additional water quality standards may have to be met before injecting the water back into the plume, in order to minimize potential aquifer impacts.

Table 2. Three-Step Remediation Process Description

STAGE/ METHOD	BRIEF DESCRIPTION	CONTAMINANTS
1) Treating metals above ground	Treating metals above ground will reduce U re-oxidation (increasing pH, removal of clogging inhibitors)	Nitrate, calcium, aluminum
2) Ethanol injection	Injecting ethanol into the groundwater using a system of wells located around the S-3 Ponds for the purpose of stimulating microbial growth and reducing U (VI)	Uranium(VI), Tc-99
3) Maintaining stable U	Oxygen will be removed in this stage for the purpose of maintaining a low uranium mobility	Uranium (IV)

6.1.1 First Stage: Removal of Nitrate, Calcium and Aluminum

Contaminants like nitrate, calcium and aluminum will be treated above ground to optimize the uranium transformation by microbes in the subsurface (second stage). These contaminants make uranium more mobile. Other contaminants affecting microorganisms such as Ni and other metals, still need to be identified. The actions for the first stage include pH adjustment and a fluidized bed reactor to allow better experimental control of the bioremediation. The pH will be increased to 6 and nitrate concentrations will fall below 1 mM, which are adequate conditions for bio-stimulation.

a) Nested recirculation loops
b) Conditioning the subsurface:
   - pH increase: the groundwater will be flushed with a higher pH (4.5 to 6.3), increasing U sorption.
   - Acidified clean water study and flush.
   - Above-ground removal of clogging inhibitors.

Cones of depression for the extraction wells

The extraction wells will be distributed every 27 meters, calculated using the equation of the effects of the cone of depression created by each well, and will use some of the existing wells. The cone of depression creates a change of direction of the natural groundwater flow (Figure 7). The pumping well creates an artificial discharge area (cone of depression) by lowering the water table around the well. One theory about the cone of depression is that most groundwater contaminants could be captured in this cone and could be treated or removed or on the surface.

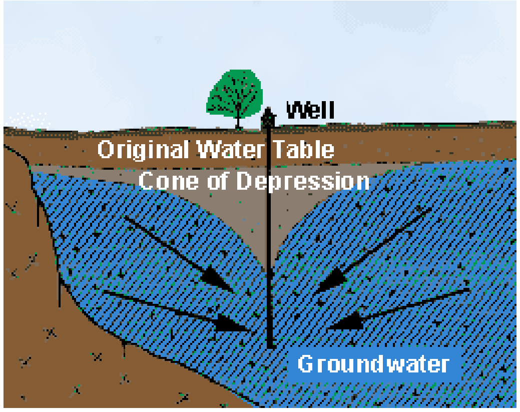


Figure 7. Cone of depression around the extraction wells.

The shape and size of the cone of depression depends on factors like the type of aquifer material (mainly limestone/shale and clay surrounding pathway 3), the pumping rate of the wells, the thickness of the aquifer and the amount of water in storage. The cone of depression reaches equilibrium when the amount of water released from storage equals the rate of pumping. The cone of depression will decline to greater depths if it contacts a barrier like a clay body or the edge of the aquifer.

When there are multiple wells, there is a combined effect on drawdown because the different cones of depression and will result in water levels lower than a single cone of depression would produce.

Drawdown

Previous pumping tests in the area suggest that most of the contamination is located in the bedrock and not in the regolith, reason to have a pumping rate of 8.18 m^3/day.

The calculation of the drawdown and the distance between wells were based on a simple analytical approach, and an anisotropic confined aquifer was used to develop an estimate of the likely zone of capture for a single well pumping at 8.18 m^3/day. The hydraulic parameters used for this calculation are presented in Table 3 from historical data.

Table 3. Hydraulic Parameters to Calculate Distance Between Wells

Parameter	**Value**	**Unit**
Pumping rate, Q	8.18	m^3/day
Hydraulic conductivity, K	0.275	m/day
Aquifer thickness, b	52	m
Transmissitivity, t= k*b	1.43	m^2/ day
Storage coefficient, S	0.0004	n/a
Pumping time, t	30	days
Radius of the well, r	0.10	m
Drawdown, s	5.89	m
Distance between wells, R	27	m

Equation 1 was used to calculate the distance R between wells:

$$Q= 2.73\ Kb(s)/ (\log R/r)$$

Or: $$\log R= (2.73Kb\ (s)/Q) + \log r \qquad \text{(Equation 1)}$$

Where,

b= thickness of aquifer, m
K= hydraulic conductivity, m/day
s= drawdown, m
R= distance between wells, m

Substituting the data from Table 3: Or: log R= (2.73Kb (s)/Q) + log r (Equation 1, the distance between wells is 27 meters.

Because the dimensions of the S-3 Ponds site is 122m X 122m, then 5 wells will be needed to border each of the west, east and south sides of the parking lot. In total, 15 multi-use wells will be needed, including some already installed in past experiments.

The calculation was based on the following assumptions:

- The aquifer is confined, homogenous and anisotropic.
- The aquifer has uniform thickness over the treated area.
- The aquifer will be pumped at a constant rate.
- The well penetrates the entire thickness of the plume.

6.1.2 Second Stage: Ethanol Injection (Bio-Stimulation)

Ethanol will be injected into the subsurface using a series of multipurpose wells located in the S-3 Ponds area with the goal of stimulating microbial growth, causing U (VI) reduction. This procedure controls groundwater flow and consists of a recirculation system with a protective outer zone which separates the inner remediation zone from geochemical conditions. U (VI) concentration will be monitored in the inner zone extraction and injection wells, as well in the center of the bioremediation area (Figure 8).

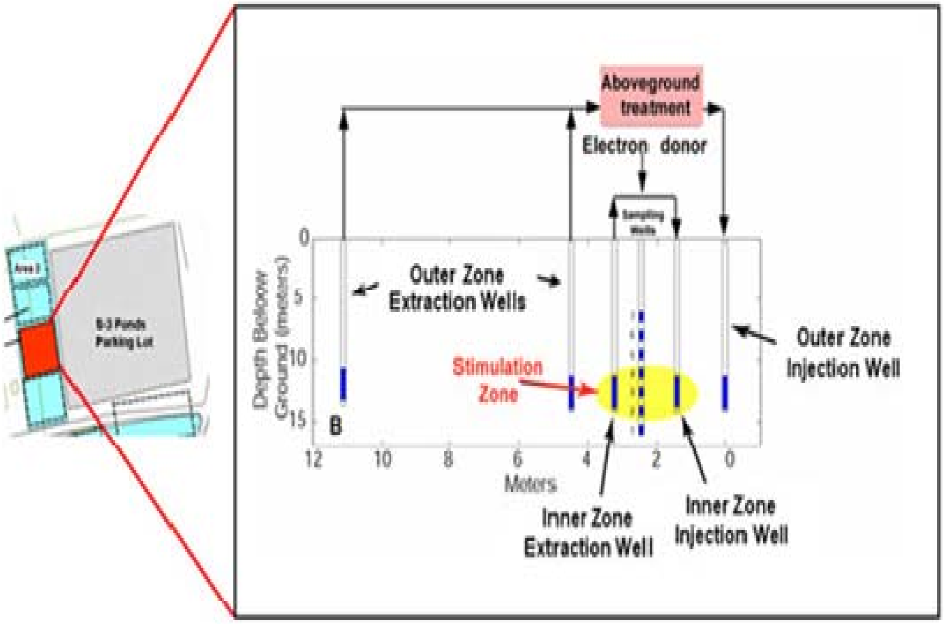


Figure 8. Ethanol injection wells and aboveground treatment

Figure 9 shows the proposed injection well locations which were calculated base on the cone of depression and existing wells

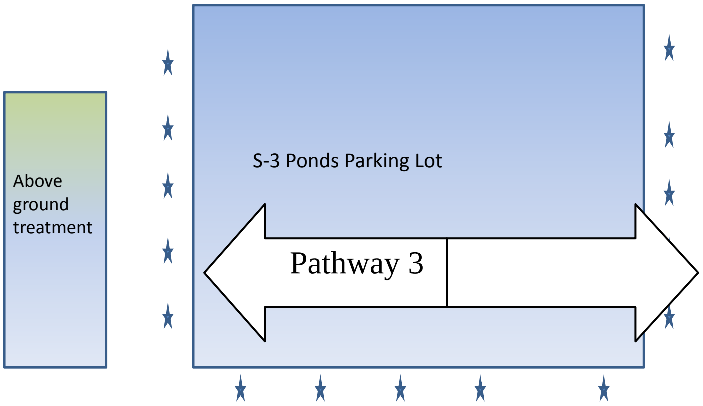


Figure 9. Wells locations around S-3 Ponds area.

6.1.3 Third Stage: Maintenance of Stable U (IV)

Oxygen will be removed in this stage for the purpose of maintaining low uranium mobility. Some studies show the effects of molecular oxygen on the long-term stability of biologically reduced uranium.

6.2 General Design Parameters

- Low pH (~3.5) is bad for robust microbial activity.
- High nitrate (130-480 mM) and high Ca (~20mM) inhibits U (VI) reduction.
- The depth of contamination is greater than 50 ft.
- U reduction will be evaluated by measuring U oxidation in sediment samples from the inner treatment area wells using X-ray absorption. The results will be analyzed with the XANES spectrum method.

6.3 Some Implementation Considerations

The following considerations and recommendations are based on past experiences from treatments in pathways 1 and 2:

Piping and valves: Leaking pipes and valves could cause operational and maintenance problems, which could be prevented by accommodating a separation of components used for troubleshooting and maintenance. Also, easy access to valves must be considered to facilitate maintenance and operation.

Utilities: It is recommended to use electronic equipment to locate old utilities above ground which may not be present on maps of the area or historical site drawings.

7. COSTS

The costs for installation, startup and initial operations are determined in this section. However, there could be a large variation in the cost calculation when long-term operation and maintenance is considered. The purpose of Table 4 is to identify major cost items and is not intended to be a detailed cost breakdown for the remediation strategy.

The costs are based on the waste management issues and the conceptual design shown in Section 8. There is a high degree of uncertainty associated with major cost items because the final system design has not been completed. The costs presented in this section provide a rough estimate for the remediation.

The cost estimate is presented in Table 4. Installation cost summary assumptions used to develop this estimate and a description of each cost element is presented below.

- Waste treatments costs are not included in this estimate.
- Already established observations wells and background wells will be monitored for the duration of the test.
- The water pumped from the well will be classified as a RCRA hazardous waste.
- Labor is assumed to cost $80/h.
- The treatment unit has the ability to remove radionuclides, suspended solids and metals.
- Water samples to analyze nitrate and calcium will be collected every two hours for the first day of pumping, every 6 hours for the next 3 days and once a day after the 4th day. The price will be approximately $400 per sample.
- An initial ethanol feeding rate will be assumed in the second stage and corrected after some preliminary tests.
- Future site characterization with more advanced technologies and monitoring tools could reduce the contaminant distribution uncertainty and as a result could change the feeding rate and other parameters.
- Injection wells will be installed along the west and east border of the S-3 Ponds area (covering approximately 244 m in total length).

Table 4. Installation Cost Summary

Action	Labor costs($)	Direct cost ($)	Subcontractor ($)	Subtotal ($)
Planning	15,000			15,000
Implementation				
Install pumps	6,000	40,000		46,000
Install electric outlets	60,000			60,000
Data management	20,000			20,000
Test equipment	4,000			4,000
Pump well	58,000			58,000
Sampling	24,000	2,500	100,000	126,500
Waste Management				
Waste Managem. pretesting	20,000			20,000
Ethanol purchase	2,000	30,000		32,000
Preatreatment	20,000			20,000
Waste sludge disposal	2,000	50,000		52,000
Transportation to waste site	1,000			1,000
Reporting				
Evaluate data	60,000			60,000
Produce report	40,000			40,000
Total	332,000	122,500	100,000	554,500

8. DOCUMENTATION AND COMMUNICATION

8.1 Project Documentation

The following are descriptions of project documents supporting the S-3 Ponds remedial actions:

8.1.1 Plans to Support Identified Remedial Actions

Planning documents will be prepared with the goal of supporting the remedial action. The plans include: Construction Specifications; Transportation Plan; Environmental, Safety and Health Plan; Radiological Protection Plan; Quality Assurance Plan; and Project Design Drawings.

8.1.2 Phased Construction Completion Report

After the RAWP is completed, including any modifications implemented during field work, a Phased Construction Completion Report (PCCR) will be prepared to support this RAWP. This document will be submitted to the regulators for approval. The PCCR will provide information necessary for the FFA parties to evaluate the S-3 Ponds remediation project against the stated goals. The PCCR will contain data collected and the results of the field surveys and remediation efforts. Also, it will contain the names of the facilities receiving project wastes.

8.2 Communication

The ORFRC conducts research on processes that influence the transport of subsurface metal and radionuclide contaminants and improves remediation strategies. The DOE Office of Science, Environmental Remediation Sciences Division, sponsored the Integrated Field-Scale Challenge (IFC) project through a peer review solicitation process. ORFRC procedures are used on the project for data management, sample labeling and tracking and quality assurance. The existing ORFRC database stores new IFC data and there is a public website and list-server which shares information with interested people. The IFC review teams which consist of people from different organizations meet regularly to ensure all issues and actions are known, understood, and approved by all the team members.

Communication with external stakeholders will make sure project decisions are supported by the community and stakeholders. It is important to communicate with stakeholders frequently to present accomplishments, issues and new activities.

8.3 S-3 Ponds Related Land Use Controls

The Land Use Control Assurance Plan (LUCAP) requires that DOE, EPA and TDEC prepare an implementation and annual monitoring plan for each selected land used control (LUC) as long as is required to protect health and the environment. This site is designated as a controlled industrial area which requires controls for excavations deeper than one foot below ground surface.

9. APPLICABLE OR RELEVANT AND APPROPRIATE REQUIREMENTS

9.1 Chemical-Specific ARARS

Appendix A, Table A.1, lists the chemical specific ARARs associated with this project, which provides protection and restoration of groundwater. These ARARs provide contaminant concentration and discharge limits to soil, groundwater and surface water.

9.2 Location Specific ARARS

Location specific ARARs provide the requirements and restrictions related to specific areas like floodplains, wetlands, threatened species habitats and others.

9.3 Action-Specific ARARS

The action specific ARARs for the S-3 Ponds remediation project are listed in Appendix A, Table A.2, and are presented in the below:

- **Waste generation, characterization, segregation, treatment, disposal and storage.**
- **Institutional Controls:** Some administrative and engineering controls are necessary to prevent unauthorized contact with hazardous substances. In addition, re- injecting treated groundwater may require an underground injection permit from the State of Tennessee
- **Site preparation and excavation activities:** These activities could create storm runoff so it is important to control erosion.

10. WASTE MANAGEMENT PLAN

10.1 Waste Management Issues

Contaminants (see subsections below) at different concentrations, both below and above regulatory limits, may be present during the treatment. Removal of contaminated media and the management of the liquid and solid phase wastes resulting from the treatment process will be implemented by the contractor in compliance with the ARAR's defined in Appendix A. On-site project activities will also be subject to DOE specific orders and Y-12 specific procedures for training, safety, security and environmental protection.

10.1.1 Groundwater Contaminants

Contaminants identified in the 1990's at the S-3 Ponds groundwater monitoring well (GW-243) include metals, VOC's, radionuclide and ions. Metals include aluminum, barium, beryllium, cadmium, boron, cobalt, copper, iron, lead, mercury, nickel, silicon, silver and zinc. The VOC contaminants include acetone, chloroform, tetrachoroethene, trichloroethene, toluene, methylene chloride, toluene and dichloreothene. Radionuclides include uranium, technetium and thorium. Nitrate also occurs in elevated concentrations.

10.1.2 Pretreatment

Pretreatment concerns for the S-3 site groundwater are suspended solids, radionuclides, calcium and nitrate. A pH adjustment followed by ion exchange is the pre-treatment recommended to reduce contaminants. To reduce organics and metals, granular activated carbon could be used. Also, nitrate can be treated using acetic acid.

10.1.3 Treatment/Disposal

Accumulated waste will be protected from precipitation using roofs and walls or the use of best management practices allowed by Y-12 procedures. The storage area should be maintained and organized to avoid spills or leaks. The containers used for the waste accumulation will be labeled or marked according to Y-12 procedures and project ARARs.

Waste generated from the treatment will include a liquid-phase rinsate and a solid phase waste, requiring characterization and appropriate treatment or disposal. Liquid phase waste will be treated with an appropriate treatment. Solid phase wastes will be transferred to an appropriate disposal facility depending of the characterization results.

10.2 Waste Minimization

Whenever is practical to reduce the volume of waste that must be treated or transported, waste minimization techniques and volume reduction should be employed. Uncontaminated waste should be separate from contaminated waste.

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APPENDIX A

Table A.1 Chemical-Specific ARARs Guidance for the Selected Remedy, S-3 Ponds

Action/Medium	Requirements	Citation(s)
Release of radionuclides into the environment	Exposure to individual members of the public shall not exceed a total EDE of 0.1 rem/year, exclusive of the dose contributions from background radiation, any medical administration the individual has received, or voluntary participation in medical programs-**applicable**	10 CFR 20.1301(a)(1)
	Shall use, to the extent practicable, procedures and engineering controls based on sound radiation protection principles to achieve doses to members of the public that are ALARA- **applicable**	10 CFR 20.1101(b)
Restoration of surface water classified for fish and aquatic life	Water shall not contain toxic substances or a combination of substances including disease causing agents that, by way of either direct or indirect exposure through food chains, may cause death, disease, cancer, genetic mutations, physiological malfunctions, physical deformations, or restrict growth in fish or aquatic life- **applicable or relevant and appropriate**	Rules of the TDEC chap. 1200-4-3-.03(3)(g)
	May not exceed 200 ppt in surface water- **applicable or relevant and appropriate**	Rules of the TDEC chap. 1200-4-3-.03(3)(g)
	Water shall not contain other pollutants in quantities that may have a detrimental effect on recreation- **applicable or relevant and appropriate**	Rules of the TDEC chap. 1200-4-3-.03(3)(g)

ALARA=as low as reasonably achievable

ARAR=applicable or relevant and appropriate requirement

TDEC= Tennessee Department of Environment and Conservation

EDE=Effective Dose Equivalent

Table A.2 Action-Specific ARARs Guidance for the Selected Remedy, S-3 Ponds

Action/Medium	Requirements	Prerequisite	Citation(s)
Activities causing storm water runoff (e.g. clearing, excavation)	Implement good construction management techniques (including sediment and erosion controls, and structural control) in accordance with the substantive requirements of General permit No TNR10-0000, to ensure that storm water discharge:	Dewatering or storm water runoff discharges from land disturbed by construction activity-disturbance of > than one acre total-**applicable**	TCOA 69-3-108(J) Rules of the TDEC Chap. 1200-4-10-.03(2)
	does not violate water quality criteria as stated in TDEC 1200-4-30.03 including but not limited to prevention of discharges that cause a condition in which visible solids, bottom deposits, or turbidity impair the usefulness of waters of the state for any of the designated uses for the water body	Storm water discharges from construction activities	General permit No TNR10-0000
	Does not contain distinctly visible floating scum, oil, or other matter		General permit No TNR10
	Does not cause and objectionable color contrast in the receiving stream		General permit No TNR10
	Results in no incremental increase of materials hazardous or otherwise detrimental to human, livestock, wildlife, plant life, or fish and aquatic life		General permit No TNR10
Water treatment and discharge of groundwater, transfer of collected dewatering, decontamination, etc			
Discharge of treated groundwater	Shall receive the degree of treatment or effluent reduction necessary to comply with water quality standards and will comply with the standard of performance as required by the Tennessee Water Quality Control Act.	Point source discharge(s) of pollutants into surface water-**applicable**	TCA 69-3-103(30) Rules of the TDEC Chap 1200-4-3-.05(6)
	Is not prohibited from land disposal is such wastes are managed in a treatment system that subsequently discharges to waters of the United States pursuant to a permit issued under sect. 402	Restricted RCRA characteristically hazardous waste intended for disposal-**applicable**	40 CFR 268.1 (c)(4)(i) Rules of the TDEC Chap 1200-1-11-.10(1)(a)(3)(iv)(I)

	of the CWA, unless the wastes aree subject to a specified method of treatment other than DEACT in 40 CFR 268.40 or are D003, reactive cyanide.		
	Absorbed dose to native animal aquatic organisms must not exceed 1 rad/day	Discharge of radioactive materials in liquid waste to surface water at a DOE facility	DOE Order 5400.5(II)(3)(a)(5)
Waste generation, characterization, segregation, and storage-excavated soils, sludge, sediments, building debris, secondary wastes			
Characterization of hazardous waste (all primary and secondary wastes)	Must obtain a detailed chemical and physical analysis on a representative sample of the waste(s), which at a minimum contains all the information that must be known to treat, store, or dispose of the waste in accordance with pertinent sections of 40 CFR 264 and 268	Generation of RCRA hazardous waste for storage, treatment, or disposal-**applicable**	40 CFR 264.13(a)(1) Rules of the TDEC chap. 1200-1-11-.06(2)(d)(1)
	Must determined the underlying hazardous constituents (as defined in 40 CFR 268 et seq. by testing in accordance with prescribed methods or use of generator knowledge of waste.		40 CFR 268.7 Rules of the TDEC Chap. 1200-1-11-.10(1)(i)(1)
	Must determine each EPA Hazardous Waste number (waste code) to determine the applicable treatment standards under 40 CFR 268.40 et seq.		40 CFR 268.9(a) Rules of the TDEC Chap 1200-11-.06(2)(i)(1)
Characterization of low level waste (LLW)	Shall be characterized using direct or indirect methods and the characterization documented in sufficient detail to ensure safe management and compliance with the WAC of the receiving facility	Generation of LLW for storage or disposal at a DOE facility	DOE M 435.1-1(IV)(I)
	Characterization data shall, at a minimum, include the following information relevant to the management of the waste:		
	-Physical and chemical characteristics;		DOE M 435.1-1(IV)(I)(2)(a)
	-Volume, including the		DOE M 435.1-1(IV)(I)(2)(b)

	waste and any stabilization or absorbent media;		
	-Weight of the container and contents;		DOE M 435.1-1(IV)(I)(2)(c)
	-identities, activities, and concentration of major radionuclide		DOE M 435.1-1(IV)(I)(2)(d)
	-characterization date;		DOE M 435.1-1(IV)(I)(2)(e)
	-generating source; and		DOE M 435.1-1(IV)(I)(f)
	-any other information that may be needed to prepare and maintain the disposal facility performance assessment , or demonstrate compliance with performance objectives		DOE M 435.1-1(IV)(I)(2)(g)

APPENDIX B

Analysis of the remedial action plan using the nine NCP criteria:

1. Protection of human health and the environment: The remedial plan recommended in this RAWP has a positive effect on human health and the environment because it reduces contaminant concentrations in the groundwater to acceptable levels.

2. Compliance with Applicable or Relevant and Appropriate Requirements (ARARs): The technology suggested in this remedial plan satisfies regulatory requirements for both installation activities and reductions in contaminant concentrations.

3. Long-term effectiveness and performance: Ethanol injection technology satisfied the initial performance criteria. The residual risk associated with the waste stream has not been evaluated, and the nature and magnitude of the waste streams generated over the long term is not yet known.

4. Reduction of toxicity, mobility, or volume: The groundwater contamination will be reduced as well the uranium mobility.

5. Short-term effectiveness: The effectiveness of the ethanol technology was demonstrated in a small scale-short term. Performance over the long term will require continuing evaluation.

6. Implementability: Implementation of a technology in the field.

7. Cost: Cost is lower compared with other technologies; however, cost for long term is still undefined.

8. State (support agency) Acceptance: A DQO session will be schedule to present the RAWP to the regulators

9. Community acceptance: Community acceptance issues are not identified with the in-situ experiments using this technology.