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**Pilot Plant Study - Phase I
Task 5**

**Topical Report
September 1994 - June 1995**

July 1995

Work Performed Under Contract No.: DE-AC21-93MC30168

U.S. Department of Energy
Office of Environmental Management
Office of Technology Development
Washington, DC

For

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Babcock and Wilcox Company
Contract Research Division
Alliance, OH 44601

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Morgantown, West Virginia 26507-0880

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Contract Research Division
1562 Beeson St.
Alliance, Ohio 44601

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EXECUTIVE SUMMARY

This work is being performed in response to DOE's request for research on methodologies for the decontamination of process equipment. Requirements of the decontamination technology being developed in this program were: (1) removal of as much contamination as possible in a cost effective manner, (2) minimization of the volume of secondary waste generated, and (3) minimization of worker exposure. The specific objective of this task of the test program was to take the developed process and apply it on a pilot plant scale system to pieces of metal actually contaminated with uranium. A second part of this task was to attempt to recover the spent solvent and remove uranium from the aqueous phase using techniques developed during the earlier program tasks. Both objectives of this task were successfully completed.

Two chemical cleaning solvents were developed in the earlier portions of the test program. The first solution contained 20 grams per liter ammonium carbonate, pH adjusted to 9.0 with ammonium hydroxide, with hydrogen peroxide added. The second solvent was similar to the first except it also had the chelating agent ethylenediaminetetraacetic acid (EDTA) added to the formulation. The addition of the EDTA improved the solvent's performance for contamination buried deeper into the components. The EDTA made the solvent more versatile and would likely be the solvent of choice for field use.

Three test runs were made with the pilot system (two with the EDTA/carbonate solvent and one with the carbonate-only solvent). Contaminated metals used in the test program were stainless steel pipe brackets and several pieces of carbon steel floor grating. All stainless steel components subjected to the cleaning solvent showed a decontamination removal efficiency of greater than 99%. Decontamination factors for the carbon steel components subjected to the cleaning solvents were considerably less; however, a large percentage of the carbon steel surface areas subjected to the solvent were covered with a tar-like coating. It is believed the coating shielded the uranium from the solvent, thus reducing the effectiveness of the solvent for the dissolution of uranium.

Recovery tests were also quite successful. EDTA was recovered from solution by precipitation and the dissolved uranium reduced by ion exchange to a level between 11 and 144 pCi/L for the four (4) batches of waste solvent treated. This was equivalent to a uranium removal rate in excess of 99.4% for all of the waste processed. Heavy metals (iron) were also removed by the cation exchange column to acceptable discharge levels.

Process application modifications to the test rig were identified during the testing as being required prior to a field demonstration. The test rig needs to be modified for the field application to improve cooling during the H_2O_2 spikes and to control solvent aeration to reduce the ferric ion corrosion during process application. H_2O_2 analyses were not obtained during Task 5; however, a field applicable procedure was identified.

1.0 INTRODUCTION

The Department of Energy (DOE) is now faced with the task of meeting decontamination and decommissioning obligations at numerous facilities by the year 2019. Due to the tremendous volume of material involved, innovative decontamination technologies are being sought that can reduce the volumes of contaminated waste materials and secondary wastes requiring disposal. With sufficient decontamination, some of the material from DOE facilities could be released as scrap into the commercial sector for recycle, thereby reducing the volume of radioactive waste requiring disposal. Although recycling may initially prove to be more costly than current disposal practices, rapidly increasing disposal costs are expected to make recycling more and more cost effective (Reference 1). Additionally, recycling is now perceived as the ethical choice in a world where the consequences of replacing resources and throwing away reusable materials are impacting the well-being of the environment.

Current approaches to the decontamination of metals most often involve one of four basic process types: (1) chemical, (2) manual and mechanical, (3) electrochemical, and (4) ultrasonic (Reference 2). "Hard" chemical decontamination solutions, capable of achieving decontamination factors (Df's) of 50 to 100, generally involve reagent concentrations in excess of 5%, tend to physically degrade the surface treated, and generate relatively large volumes of secondary waste. "Soft" chemical decontamination solutions, capable of achieving Df's of 5 to 10, normally consist of reagents at concentrations of 0.1 to 1%, generally leave treated surfaces in a usable condition, and generate relatively low secondary waste volumes. Under contract to the Department of Energy, the Babcock & Wilcox Company is developing a chemical decontamination process using chelating agents to remove uranium compounds and other actinide species from process equipment. This report describes the technical approach being taken to achieve project objectives, and presents the results of Task 5 of the program, "Pilot Plant Testing."

2.0 BACKGROUND/OBJECTIVES

2.1 Overall Program Background/Goals

This work is being performed in response to DOE's request for research on methodologies for the decontamination of process equipment. At the time of project initiation, DOE offered equipment from the gaseous diffusion plant at Oak Ridge, Tennessee, for use in the full scale demonstration of the developed technology. For this reason, the selected technical approach was to develop a process suitable for application to process equipment contaminated in this manner.

Internal components of equipment utilized in the uranium enrichment process were in contact with uranium hexafluoride (UF_6) gas at elevated temperatures over many years of operation. It is suspected that inleakage of air during operations and after plant shutdown have resulted in deposits of other uranium compounds, possibly UO_2F_6 and UF_4 . Additionally, occasional outleakage of process gas has left small radioactive deposits on external surfaces.

The compressor internals are expected to not only have surface contamination, but, due to long exposures at high temperatures, it is anticipated that the radioactive contaminants have penetrated the grain boundaries of the base metal. The Allis Chalmers centrifugal compressors in the K-27 building typically have housings constructed of carbon steel with less than 0.001 inch of internal nickel plating. The rotors are typically made of Monel; the shafts, of carbon steel.

DOE's preliminary evaluation of the potential for recycling the compressor materials was that some equipment parts, such as the compressor base and rotor shaft, might be surface contaminated only, and, as such, releasable for unrestricted use under existing guidelines (eg. NRC Regulatory Guide 1.86, DOE Order 5400.5). Other parts, such as the compressor housing, rotor, and piping, were expected to be bulk contaminated with radionuclides, preventing unrestricted release and making the equipment attractive for reuse within the DOE complex. Requirements of the decontamination technology applied to the compressors were: (1) removal of as much contamination as possible in a cost effective manner, (2) minimization of the volume of secondary waste generated, and (3) minimization of worker exposure. The technical approach and test plan for this program were developed in accordance with this information.

2.2 Results - Solvent Screening/Refinement Tests

During Task 2 of this program, a large number of candidate solvents were evaluated for uranium dioxide dissolution and base metal corrosion response (Reference 3). The combination of chelant, ammonium carbonate, and hydrogen peroxide at a pH of 9.0 (adjusted with ammonium hydroxide) was found to effect virtually 100% dissolution of the uranium dioxide placed in the test flask, within the first two hours of exposure. The solvent was effective in uranium dissolution at room temperature.

Based on the results of the screening and refinement test program, two solvent systems were concluded to provide optimum uranium dioxide dissolution:

- (1) EDTA, ammonium carbonate, and hydrogen peroxide: pH 9.0 with NH_4OH
- (2) ammonium carbonate and hydrogen peroxide: pH 9.0 with NH_4OH .

Testing during Task 2 of this program indicated that the basic solvent systems were effective over a wide range of concentrations. This can allow for tailoring the solvent for differing levels of contamination and to minimize chemical usage.

Based on the Task 2 testing, the recommended application scenario for the process was as follows:

1. 2 Hours at room temperature with either solvent
2. Heatup to 66°C or 93°C and hold for approximately 4 hours
3. Cooldown to room temperature
4. Inject peroxide to remove additional uranium contamination uncovered by the high temperature exposure
5. 2 Hours at room temperature.

By starting with an initial low temperature application, readily available uranium contamination is easily removed. Heatup to 93°C (200°F) appears to dissolve the remaining readily available uranium contamination. The 93°C application results in higher corrosion rates than the 66°C (150°F) application. This is necessary to expose contamination buried more deeply into the surface of the component. Even at 200°F , the corrosion is uniform in nature.

Note that at the time of the Task 3 testing, both the 150°F and 200°F application scenarios were under consideration. Data with spent solvents using both application scenarios is presented in this report. The ultimate process recommendation was to use the 200°F application scenario.

2.3 Results - Solvent Recycle/Contaminant Volume Reduction Testing

As mentioned previously, one requirement of the developed process was to minimize the secondary waste generation from the decontamination process. After the decontamination process has been performed, removed radionuclides will be present as dissolved species in the chelating solution. The objective of Task 3 of this project was to develop a process to break the chelant-contaminant bond, remove the dissolved contaminants from solution, and to regenerate the chelant solution.

The ammonium carbonate solvent recovery test program resulted in five successful methods for removing uranium from the spent ammonium carbonate solvent with an efficiency of greater than 99.9%. The five successful recovery methods were:

1. acidification to pH 1.0 followed by the use of lime to a pH of 9.8 then caustic to a pH of 12.5
2. solvent pH reduction to 1.0 followed by the application of strong acid cation resin regenerated in the hydrogen form
3. application of strong base anion resin regenerated in the carbonate form at the existing solvent pH
4. application of strong base anion resin regenerated in the hydroxide form at the existing solvent pH
5. a precipitation technique encompassing application of trisodium phosphate after reducing the solvent pH to 2.0

The treatment process using anion resin in the carbonate form appeared to have the best merit for recovery applications because it removed only uranium from solution. All other processes were considered acceptable and considered equal.

Only one method was found that could be used with the EDTA/ammonium carbonate decontamination solvent. This method consisted of reducing the solvent pH to less than 2.0 followed by the application of a uranium selective cation resin (Purolite S-940) in the hydrogen form. No precipitation techniques provided acceptable results with the EDTA/carbonate solvent system. It was recommended in the Task 3 report (Reference 4) that if a combination of the two solvent systems were used, that this method (pH reduction followed by ion exchange with Purolite S-940) be utilized. This was the method chosen for the recovery portion of the pilot plant testing.

2.4 Specific Objectives - Task 5 Pilot Plant Testing

The purpose of the pilot plant scale tests was to evaluate the solvent system developed in the refinement tests and bench scale tests on a larger scale using actual pieces of uranium contaminated metal. These tests were to simulate field conditions on a small scale. The same solvent preparation procedures and test parameters as those used in the laboratory were applied to the pilot plant tests.

Carbon steel corrosion test coupons were also installed in the mix tank during each pilot scale test. The coupons were placed in the system to monitor the corrosion rates of the solvent and to provide information on whether uranium within the grain structure of the metal could be removed.

2.5 Specific Objective - Solvent and Uranium Recovery Process

The purpose of the solvent recovery phase of Task 5 of this test program was to determine if the Task 3 recovery process could be successfully applied on a pilot scale. Specifically, it was necessary to determine if the EDTA could be recovered from the spent solvent and made available for reuse, and to determine if dissolved uranium and heavy metals could be removed from solution, which would allow discharge of the treated solvent.

3.0 TEST PROGRAM AND PROCEDURES

3.1 Overall Approach

The first phase of Task 5 was to perform pilot scale tests using the two solvents developed for removing uranium from contaminated materials. A pilot scale test facility was designed and fabricated that would support both the decontamination and recovery parts of Task 5. The pilot plant was equipped with mix tanks, recovery and storage tanks, pumps, cooling coils, mixers, heaters, ion exchange column, filter, reaction tank and control panel.

Three pilot scale decontamination tests were run using the two candidate solvents developed in Task 2. Two tests were run using the EDTA solvent and one test was run with the carbonate-only solvent. The composition of these solvents was as follows:

EDTA Solvent:

50 g/L Ethylenediaminetetraacetic Acid (EDTA)
20 g/L Ammonium Carbonate $((\text{NH}_4)_2\text{CO}_3)$
5 g/L Hydrogen Peroxide (H_2O_2)
pH Adjusted to 9.0 with Ammonium Hydroxide (NH_4OH)

Carbonate-only Solvent:

20 g/L Ammonium Carbonate $((\text{NH}_4)_2\text{CO}_3)$
5 g/L Hydrogen Peroxide (H_2O_2)
pH Adjusted to 9.0 with Ammonium Hydroxide (NH_4OH)

Actual pieces of uranium contaminated metal were used in the pilot scale test plant. Contaminated metal (stainless steel and carbon steel) was taken from two of B&W's manufacturing facilities. The stainless steel components were primarily pipe supports which measured less than 3 feet long and 8 inches wide. The carbon steel components consisted of floor decking with part of the support beam attached. The part of the beam attached to the floor decking was painted. The pieces of decking measured 2 to 3 inches in width by approximately 2.5 feet in length. A large percentage of the surface area of both types of carbon steel components were coated with either paint or a black tar-like substance. These components were not considered ideal specimens due to the coating, but were what was available at the time of testing.

Recovery testing was performed based on the laboratory testing for recovery and treatment of the contaminated solvent (Reference 4). Both solvent systems were treated in the same manner. The solution pH was reduced to less than 1.5. This accomplished two things: one, it precipitated the EDTA present in those samples containing EDTA; and two, it liberated the carbonate present in the samples as carbon dioxide, prior to treatment with ion exchange.

Lowering the pH of solvents containing EDTA resulted in breakage of the chelate bond between EDTA and the heavy metals, including uranium. EDTA is insoluble at the low pH and precipitates from solution as free EDTA. Test results showed very low levels of heavy metals and uranium in the EDTA precipitate. The precipitated EDTA was recovered as a slurry, which was then filtered and washed to remove excess moisture and contaminants. The filter cake of EDTA is to be reused in the Phase II field test.

The supernatant solution was pumped through a filter and cation ion exchange column for removal of uranium and heavy metals. As will be presented later, test results showed exceptionally low concentrations of uranium and heavy metals in the treated solution.

3.2 Test Apparatus

The pilot plant was skid mounted and contained all the necessary equipment to perform both the decontamination and recovery tests. Figure 1 shows a schematic of the pilot plant system. All tanks, piping and tubing associated with the system were fabricated of stainless steel and wrapped with insulation. Two fifty-five gallon mix tanks were provided for mixing chemicals and were also used as reservoirs during decontamination testing. Both tanks were equipped with mixers, submersed cooling coils and two 3,000 watt band heaters. The reaction chamber consisted of a thirty gallon stainless steel tank. This tank was elevated above the mix tanks to allow gravity overflow.

The recycle pump took suction from the mix tanks through one-inch stainless steel lines and discharged solvent into the bottom of the reaction tank. The recycle pump output was approximately 15 gallons per minute. Solvent rose through the reaction tank, which contained the contaminated components, and overflowed by gravity back to the mix tank. The gravity overflow design was not sufficient to accommodate the full pump output; therefore, the pump output had to be throttled so solvent would not overflow the reaction chamber. Solvent flow through the reaction chamber was estimated to be approximately 10 gallons per minute. This flow equates to a velocity of approximately 1 foot per second past the components being cleaned.

The storage tanks were provided so that a number of decontamination test runs could be made before treatment of the waste solvent was required. Waste solvent could be pumped from the mix tanks to either storage tank, and waste in both the storage tanks and mix tanks could be pumped to the pH adjustment and precipitation tank. The solvent treatment system basically consisted of the pH adjustment tank, a process pump (rated the same as the recycle pump), a filter, ion exchange column and a treated effluent storage tank. Because the effluent from the ion exchange had to be analyzed for uranium prior to discharge, the system had the capability to send the treated solvent back to the solvent storage and mix tanks, so that up to five batches of solvent could be processed before solvent discharge was necessary.

Figure 2 is a photograph of the front of the pilot plant. The two fifty-five gallon drums without insulation in the foreground were the storage tanks and the one fifty-five gallon tank immediately behind the storage tanks was one of the mix tanks. The elevated tank with insulation was the reaction tank. The white lines coming off the two mix tanks and the reaction tank were vent lines for removal of ammonia vapors during the solvent heating cycle.

Figure 1
Schematic of Pilot Scale System

Figure 2

Photograph of Front of Pilot Plant

Figure 3

Photograph of Back Side of Pilot Plant

Figure 4

Photograph of Reaction Vessel With Lid
Removed and Solvent Circulating

Figure 5

Photograph of Reaction Vessel Several
Minutes After Peroxide Addition

Figure 6

Photograph of Reaction Vessel and Test
Specimens After Test #3

Figure 3 is a photograph of the back side of the pilot plant. The elevated tank with insulation was the reaction vessel. The tank to the left of the reaction vessel is the pH adjustment tank, and the one in the lower left is the treated storage tank. The resin column was not installed in the system at the time of this photograph.

Figure 4 is a photograph of the reaction tank with the lid removed and solvent circulating. Figure 5 is a photograph several minutes later after the addition of hydrogen peroxide. Because there was foaming associated with peroxide addition, the injection rate was adjusted so that the peroxide was added over a period of 10 minutes.

Figure 6 shows the components in the reaction chamber after the completion of test run number three. The solvent was drained from the chamber, the components rinsed with demineralized water, and the lid on the reaction chamber left off over night so the components could dry. The component propped up on the rim of the chamber was one of the pieces of carbon steel floor grating. The dark area in the center of the grating was the tar-like substance previously described.

This particular piece of metal was cut with a torch which burned off the tar coating around the edges. The edges of this piece of metal were exceptionally clean after exposure to the decontamination solutions.

3.3 Test Procedures

Detailed test procedures with step-by-step sign-offs were used to control all operations of the pilot plant test program. Copies of the test procedures are included as Appendix A to this report.

3.3.1 Decontamination Procedure

The following is an outline detailing the major steps used for the decontamination phase of the pilot plant test program.

1. Prepare a radiation work permit (RWP) for handling and controlling radioactive materials associated with the pilot plant.
2. Survey the radioactive test specimens to determine starting levels of uranium contamination. Load the metal pieces into the reaction chamber.
3. Prepare solvent according to the appropriate procedure.
4. Align the system valves to allow for recycling from the mix tank through the pump and reaction chamber and back to the mix tank.
5. Start the recycle pump, add hydrogen peroxide and recirculate the solvent for a period of 2 hours at ambient temperature. Take pH and temperature data at half-hour intervals and take duplicate solvent samples hourly.

6. Turn on the drum heaters and heat the solvent to 93°C (200°F) and maintain this temperature for a period of 4 hours.
7. Turn on the cooling water and cool the solvent down to less than 29.5°C (85°F). Add appropriate amount of hydrogen peroxide and recirculate for an additional 2 hours. Continue collecting solvent samples.
8. Shut down the pump, realign the system valves, and pump the remaining solvent in the reaction tank back to the mix tank.
9. Remove the reaction tank lid, rinse the excess solvent on the metal components, and pump the rinse water back to the mix tank.
10. After air drying overnight, survey the test specimens to determine ending levels of uranium contamination.
11. Align system valves and transfer spent solvent to a solvent storage tank.

3.3.2 Solvent Recovery Tests

The following is an outline detailing the major steps used for the recovery phase of the pilot plant test program.

1. Align system valving and transfer spent solvent from a storage tank to the pH adjustment tank.
2. Turn on the pH adjustment tank mixer and add sufficient acid to drop solution pH to 1.5 or less.
3. Turn off the mixer. Wait 2 hours for the precipitated EDTA to settle.
4. Align system valving to pump pH adjusted solvent from the pH mix tank through the filter, ion exchange column, and to the process storage tank.
5. Use a drop line to pull suction from the supernatant in the pH adjust tank. Do not pull the EDTA precipitate into the hose, as it will overload the filter.
6. Start pumping treated solvent through the ion exchange column. Throttle the pump discharge to provide a flow rate of 2 gpm through the ion exchange column.
7. Collect column effluent samples after pumping solvent for 10 and 15 minutes. Collect a sample from the storage tank after processing all the spent solvent.
8. Transfer the treated solvent to another storage tank and repeat the process.

9. Submit the solvent samples for activity surveys. When test results are completed, discharge the treated solvent to the waste system.

All contaminated components used in the pilot tests were surveyed for total uranium by Alpha Spectroscopy before and after testing. Several pieces of metal in each test were also checked for smearable uranium before and after testing.

All the solvent samples collected for both the decontamination and recovery tasks were analyzed for pH, free EDTA, and for Isotopic/Total Uranium by Alpha Spectroscopy. Most of the samples collected from the recovery tests were analyzed for total iron.

4.0 RESULTS AND DISCUSSION - PILOT SCALE DECONTAMINATION TESTS

As previously stated, three pilot scale decontamination tests were run using the solvents developed in the screening phase of this test program. Two test runs were made using the EDTA solvent and one was made with the carbonate-only solvent. Uranium contaminated metal components from B&W shops were used to evaluate the solvents in the test program. The results of each of these three tests are presented in this section. The results of the solvent recovery phase of the pilot plant test program are presented in Section 5.0.

4.1 Pilot Plant Decontamination Test #1

Test Number 1 was run using the EDTA solvent which was initially formulated as follows:

50 g/L EDTA
20 g/L $(\text{NH}_4)_2\text{CO}_3$
pH 9.0 with NH_4OH
0.5% H_2O_2 at the beginning of each low temperature step

Approximately 50 gallons of EDTA solvent was prepared for this test. Eight pieces of contaminated metal were placed in the reaction chamber and the recycle pump was started. After recirculation was started and the flow balanced to prevent solvent overflow from the reaction chamber, 2760 mL of 30% hydrogen peroxide was added to the solvent by direct addition to the pump suction. The solvent was recycled for 2 hours. During this time the temperature was maintained at less than 24°C (75°F). After the two hour low temperature exposure, the heaters were turned on and the solvent was heated to 93°C (200°F) and maintained at this temperature while recycling for a period of 4 hours. The solvent was then cooled to less than 29.5°C (85°F), followed by the addition of 3680 mL of 30% hydrogen peroxide. The solvent was recirculated for an additional 2 hours and the test was then terminated. The application scenario for pilot plant scale Test 1 is summarized in Table 1.

Table 1
Application Scenario - Pilot Scale Testing
Test #1

- 2 Hours At Room Temperature
- 4 Hour Ramp Up To 93°C
- 4 Hours At 93°C
- 0.25 Hour Cooldown To Room Temperature
- Spike With Hydrogen Peroxide
- 2 Hours At Room Temperature

The initial free (i.e. uncomplexed) EDTA concentration of the solvent was 50.5 g/L prior to the initial injection of hydrogen peroxide. Immediately after hydrogen peroxide addition the EDTA dropped to 50 g/L and by the end of the eight hour test period it had dropped to 35g/L. This drop was due to chelation of metals and to destruction resulting from oxidation by the

hydrogen peroxide. Total dissolved iron concentration of the solvent at the end of the test was 45.9 milligrams per liter, or approximately 8.3 grams of total iron. Solvent samples were collected hourly during the test run and the samples analyzed for pH, free EDTA, total uranium and total iron. The test results for the solvent samples collected during the test run are presented in Table 2.

Examination of the Table 2 data indicated that the majority of the uranium dissolution occurred either during the initial low temperature application or during the heatup from room temperature to 93°C (200°F). This was consistent with the results of the bench scale testing (Reference 5). From the dissolved iron values, it was evident that the majority of the corrosion occurred during the high temperature phase of the process. Again, this was consistent with the process development testing (Reference 3) and the bench scale testing (Reference 5).

Note the absence of hydrogen peroxide values in Table 2. The H₂O₂ analysis was attempted by the pilot plant operators using the colorimetric method used in the previous testing (References 3 and 5). This method of H₂O₂ analysis is very time consuming. The pilot plant operators did not have the necessary time to run the loop properly and to also perform the H₂O₂ analysis. As recommended in the bench scale testing (Reference 5), it is necessary to develop an analytical method for H₂O₂ analysis that can provide more "real time" results and can be used during the Phase II field demonstration. Subsequent to the pilot plant testing, a search was made for such a method. Determination of H₂O₂ concentration by potentiometric titration appeared to be well-suited for this purpose. Preliminary investigations verified this to be true. Details of this procedure can be found in Appendix B.

Table 2
Analytical Results - Pilot Scale Test #1

Sample I.D.	pH	Free EDTA (g/L)	Total U (pCi/L)	[Fe] (mg/L)
Initial	9.0	50.5	219	0.55
After H ₂ O ₂ Add	8.9	50.0	38,096	1.70
1 Hr @ 75°F	9.0	49.1	50,813	1.86
2 Hr @ 75°F	9.4	49.1	56,357	2.15
0 Hr @ 200°F	9.5	46.5	132,865	17.8
1 Hr @ 200°F	9.5	44.7	136,699	25.3
2 Hr @ 200°F	9.1	43.0	146,833	32.2
3 Hr @ 200°F	9.1	37.7	150,096	38.7
4 Hr @ 200°F	9.0	36.0	148,928	45.2
1 Hr @ 85°F	8.9	36.0	147,753	45.6
Final	8.8	35.0	151,052	45.9

Table 3 presents the decontamination data for the eight metal components subjected to the test solvent. Test data showed that decontamination efficiencies of greater than 99.0% were achieved for both alpha and beta activity for the 7 stainless steel components subjected to the solvent. The beta decontamination efficiency was greater than 99.9% for all test materials. The carbon steel drum ring, which consisted of two half circles, showed only 41.7% efficiency in removing alpha activity, while, as previously stated, the beta decontamination efficiency was greater than 99.9%. Overall, these results were considered excellent.

It is interesting to note that the carbon steel drum rings were heavily coated with iron oxide prior to decontamination and that the majority of iron oxide was still present after treatment with the decontamination solvent. It is theorized that the alpha contamination that was not removed was masked from the solvent by the iron oxide. Presumably, a longer duration at the elevated temperature would have improved iron oxide dissolution, which would, in turn, have improved the alpha decontamination efficiency. Note that this solvent (EDTA) at a pH of about 9.0 dissolves iron oxides at a relatively slow rate at 93°C (Reference 6). This reaction rate can be increased by the addition of hydrazine or by an increase in temperature to above 100°C (References 6 and 7).

Table 3
Decontamination Results - Pilot Scale Test #1

Description of Test Piece	Material	Starting Direct α (dpm)	Starting Direct β (dpm)	% α Decon	% β Decon
Thin Bracket	SS*	14,000	20,000	99.0	> 99.9
Bracket #30	SS	38,000	46,000	99.5	> 99.9
Bracket #4	SS	46,000	56,000	> 99.9	> 99.9
Tank Piece	SS	26,000	58,000	99.7	> 99.9
Bracket #1	SS	46,000	64,000	99.8	> 99.9
Bracket #2	SS	22,000	28,000	99.1	> 99.9
Bracket #3	SS	42,000	46,000	99.7	> 99.9
Drum Ring (2-Pieces)	Carbon Steel	1,200	3,600	41.7	> 99.9

* - Stainless Steel

Based on weight loss, the corrosion of the carbon steel coupon placed in Test 1 was 7 mils (178 μ m). This was greater than observed in previous tests with this solvent (References 3 and 5). However, corrosion was uniform in nature, as expected and as is required (Reference 3). The corrosion response of the coupons will be discussed in more detail in Section 4.3 of this report.

4.2 Pilot Plant Decontamination Test #2

Test Number 2 of the pilot scale test program was performed with the carbonate-only decontamination solvent:

20 g/L $(\text{NH}_4)_2\text{CO}_3$

pH 9.0 with NH_4OH

0.5% H_2O_2 at the beginning of each low temperature step

Table 4 lists the nominal process application scenario used for Test 2.

Table 4
Application Scenario - Pilot Scale Testing
Test #2

- 2 Hours At Room Temperature
- 3 Hour Ramp Up To 93°C
- 4 Hours At 93°C
- 0.25 Hour Cooldown To Room Temperature
- Spike With Hydrogen Peroxide
- 2 Hours At Room Temperature

Eight pieces of contaminated metal were used in this test. Seven of the metal pieces were carbon steel floor grating. The remaining piece was a stainless steel pipe bracket. The floor grating consisted of narrow (2 to 3 inches) strips of metal approximately 2 feet long. All of the grating was coated with a tar-like substance except for a narrow strip around the edges which was burned off during the cutting process.

As noted above, the initial concentration of the ammonium carbonate was 20 grams per liter. As with past tests with this solvent, the carbonate concentration was not monitored during the test run (References 3 and 5). Solvent pH was checked hourly during the test run and there was essentially no change in pH during the entire test run (consistent with the References 3 and 5 data for this solvent system). All of the analytical data obtained during Test number 2 is presented in Table 5.

Table 5
Analytical Results - Pilot Scale Test #2

Sample I.D.	pH	Total U (pCi/L)	[Fe] (mg/L)
After H ₂ O ₂ Add	9.1		0.21
1 Hr @ 75°F	9.1		1.1
2 Hr @ 75°F	9.1	8367	0.98
0 Hr @ 200°F	9.1		1.4
1 Hr @ 200°F	9.5		1.1
2 Hr @ 200°F	9.5		0.65
3 Hr @ 200°F	9.5	29,367	0.51
4 Hr @ 200°F	9.4		0.75
1 Hr @ 85°F	9.4		0.89
Final	9.4	25,823	0.89

Table 6 lists the decontamination data for the metal components subjected to the carbonate solvent. Decontamination efficiency for the alpha activity of the seven carbon steel pieces ranged from 23.3 to 82% while the beta decontamination factor ranged between 24% and 92%. Decontamination for the stainless steel bracket was 97.1% for alpha and 93.5% for the beta. These results were much lower than achieved with the Test 1 solvent containing EDTA. This data indicated that the carbonate solvent was less effective in dissolving uranium than the EDTA/carbonate solvent. Note, however, that the mix of specimens in Test 2 was different than used in Test 1. Most of the Test 2 specimens were carbon steel with coatings on their surface.

Analysis of the solvent samples showed 25,823 pCi/L total uranium dissolved in the solvent at the completion of the test run. Total iron in the carbonate solvent was only 0.89 mg/L. These values were relatively low in comparison to the values reported for Test 1 which showed 151,052 pCi/L total uranium and 45.9 mg/L total iron. Again, this was an indication that the carbonate-only solvent was less effective than the EDTA/carbonate solvent, especially if the contamination is shielded by coatings or an oxide layer.

The carbon steel coupon exhibited essentially no corrosion, as determined by weight loss. This was consistent with past tests using the carbonate-only solvent system (References 3 and 5).

Table 6
Decontamination Results - Pilot Scale Test #2

Description of Test Piece	Material	Starting Direct α (dpm)	Starting Direct β (dpm)	% α Decon	% β Decon
Plate	CS*	20,000	30,000	82.0	76.7
Decking #1	CS	54,000	70,000	37.0	31.4
Decking #3	CS	38,000	50,000	23.3	24.0
Decking #4	CS	46,000	60,000	52.3	50.0
Decking #5	CS	40,000	50,000	95.0	92.0
Decking #6	CS	40,000	54,000	50.0	48.1
Bracket	SS**	36,000	46,000	97.1	93.5
Decking #8	CS	74,000	92,000	46.0	43.0

* - Carbon Steel/** - Stainless Steel

4.3 Pilot Plant Decontamination Test #3

Because uranium dissolution with the carbonate-only solvent in Test 2 was poor, all but one carbon steel component was returned to the reaction chamber and subjected to the EDTA plus carbonate solvent as part of Test Number 3. The stainless steel component was replaced with two new stainless steel pipe brackets, and an additional piece of carbon steel floor grating was added to the reaction vessel. The nominal composition of the solvent for Test number 3 was the same as used for Test number 1:

50 g/L EDTA
 20 g/L $(\text{NH}_4)_2\text{CO}_3$
 pH 9.0 with NH_4OH
 0.5% H_2O_2 at the beginning of each low temperature step

Table 7 presents the solvent application scenario used for Test number 3. The test procedure was modified from the previous two tests. The same initial 8 hour solvent exposure procedure was followed. After 8 hours, the system was shut down and 3 pieces of metal were surveyed for uranium activity. These metal components were placed back in the reaction chamber and the test continued. Before restarting the test, the solvent was replenished to a concentration of 47.9 g/L free EDTA. The solvent was reheated to 93°C (200°F) and circulated for 2 hours at temperature, followed by system cool down, peroxide injection, and two hours of solvent recirculation at a target temperature of 29.5°C (85°F).

Table 7
Application Scenario - Pilot Scale Testing
Test #3

- 2 Hours At Room Temperature
  - 3 Hour Ramp Up To 93°C
  - 4 Hours At 93°C
  - 0.25 Hour Cooldown To Room Temperature
  - Spike With Hydrogen Peroxide
  - 2 Hours At Room Temperature
- Examine Vessel Contents/Adjust Solvent Composition
- Ramp Up to 93°C
  - 2 Hours At 93°C
  - 0.25 Hour Cooldown To Room Temperature
  - Spike With Hydrogen Peroxide
  - 2 Hours At Room Temperature

As will be presented later, the dissolved iron in solution at the start of the second exposure (after the interim examination) was about 400 mg/L. After the 2-hour exposure at 93°C the dissolved iron had increased to over 700 mg/L. It is known that dissolved iron in solution can catalyze the H_2O_2 decomposition reactions. Visually, rapid decomposition of the peroxide did occur. Note that peroxide injection occurred at the pump suction. The solvent then flowed through the test chamber and back to the mix tank for cooling (refer to Figure 1). To ensure that the test chamber did not overflow, due to the H_2O_2 decomposition reactions, it was necessary to slow the peroxide injection rate. Injection occurred over a 15 minute span.

Using this approach, solvent temperature was maintained under 35°C (95°F). However, it was suspected that the H_2O_2 was depleted below the level required for uranium dissolution during the first solvent change-out in the test chamber. A more appropriate delivery scheme might have been to have cooling capability in-line after the pump and just before the test chamber.

Table 8 presents the decontamination efficiency for the 3 metal components removed after the normal 8 hour test period and at the completion of the test. The stainless steel bracket showed very little change in decontamination efficiency between the two steps in the test run. However, the overall decontamination factor was greater than 98.8% (98.8% α removal and >99.9% β removal). This result is essentially a duplication of the results obtained on stainless steel components decontaminated in Test number 1.

As with Test number 1, the carbon steel decontamination efficiency was less than that achieved with the stainless steel. As previously noted, these carbon steel components had a tar-like coating which apparently limited solvent access. The carbon steel plate showed 66.6% alpha removal and 54.2% beta removal after the first step in Test 3. This efficiency increased to 73.6% (for α) and 77.1% (for β) after the second step. The number 9 decking specimen

showed a similar increase in alpha removal efficiency between the two steps (58.8% up to 64.7%). However, beta removal remained constant after the first step. Overall, the second step was marginally effective in improving contamination removal efficiency. It is possible that an improved peroxide injection scheme would have improved the efficiency of the second step.

Table 8
Decontamination Results - Pilot Scale Test #3
Comparing Efficiency After First Step and After Both Steps

Description of Test Piece	Material	First Step % α Decon	First Step % β Decon	Both Steps % α Decon	Both Steps % β Decon
Plate	CS*	66.6	54.2	73.6	77.1
Decking #9	CS	58.8	60.9	64.7	60.9
Pipe Bracket #10	SS**	98.7	>99.9	98.8	>99.9

* - Carbon Steel/** - Stainless Steel

Table 9 contains the decontamination efficiencies for all test materials exposed during pilot plant scale Test 3 after the complete process. Excellent decontamination efficiencies were obtained for the stainless steels, with lesser efficiencies seen on the carbon steel components. This duplicated the Test 1 results. The tar-like coating on the carbon steel components obviously limited solvent access. Note, however, that many of the carbon steel components were previously exposed during Test 2 with the carbonate-only solvent. The starting contamination for these components was that determined as the ending level of contamination after Test 2. The removal efficiencies shown in Table 9 reflect an increase in decontamination using the EDTA-carbonate solvent versus the carbonate-only solvent system.

Chemistry results from Test number 3 are presented in Table 10. During the initial low temperature phase of the test and the first hour at 93°C, the dissolved iron was tracking with Test 1. However, during Test 3, dissolved iron increased rapidly after the two-hour point at 93°C and continued to increase at a relatively rapid rate for the remainder of the high temperature exposure. The reason for this significant increase in dissolved iron was unknown. However, it was theorized that a relatively large portion of the carbon steel materials became exposed between the 1 and 2 hour mark (some of the tar like coating was removed). This exposed more carbon steel surface to the solvent, resulting in more dissolved iron from corrosion. The dissolved iron stopped increasing when the solvent was lowered in temperature.

Table 9
Decontamination Results - Pilot Scale Test #3

Description of Test Piece	Material	Starting Direct α (dpm)	Starting Direct β (dpm)	% α Decon	% β Decon
Plate*	CS**	3,600	7,000	73.6	77.1
Decking #1*	CS	34,000	48,000	64.7	66.6
Decking #3*	CS	28,000	38,000	67.1	57.9
Decking #4*	CS	22,000	30,000	66.3	53.3
Decking #6*	CS	20,000	28,000	40.0	42.9
Decking #8*	CS	40,000	52,000	65.0	61.5
Decking #9	CS	34,000	46,000	64.7	60.9
Bracket #10	SS	16,000	22,000	98.8	> 99.9
Bracket #11	SS	36,000	46,000	99.7	> 99.9

* - Previously Exposed During Test Number 1

** - CS = Carbon Steel/SS = Stainless Steel

After the first step, the solvent was reconstituted with free EDTA. This resulted in a dilution effect, thereby reducing the level of dissolved iron. Once temperature was increased, the dissolved iron again began to increase at a rapid rate. During this second exposure, the dissolved iron increased even during the lower temperature exposure. It is theorized that the rapid H_2O_2 decomposition discussed earlier resulted in a condition where the carbon steel components were not properly passivated, as normally occurs with the low temperature application. This fact, plus the previously discussed problems with temperature control, resulted in corrosion during the final lower temperature application. Judging from the dissolved uranium values, the rapid H_2O_2 decomposition also limited the decontamination effectiveness of the final step.

Table 10
Analytical Results - Pilot Scale Test #3

Sample I.D.	pH	Free EDTA (g/L)	Total U (pCi/L)	[Fe] (mg/L)
Initial	8.8	60.0		2.04
After H ₂ O ₂ Add	8.8	59.0		2.35
1 Hr @ 75°F	8.8	51.0	6,182	2.33
2 Hr @ 75°F	8.8	49.0	7,715	2.15
0 Hr @ 200°F	9.4	43.6	17,427	15.9
1 Hr @ 200°F	9.4	38.3	21,468	25.3
2 Hr @ 200°F	9.2	29.8	23,539	193
3 Hr @ 200°F	9.0	23.4	25,916	341
4 Hr @ 200°F	8.9	19.1	25,647	433
1 Hr @ 85°F	8.6	19.1	27,280	432
2 Hr @ 85°F	8.6	17.0	26,626	427
Start of Second Step	8.7	47.9		391
1 Hr @ 200°F	8.4	38.2	25,608	574
2 Hr @ 200°F	8.5	35.1	25,698	736
1 Hr @ 95°F	8.3	32.9	24,138	871
2 Hr @ 95°F	8.0	29.8	27,450	910

The corrosion coupon exhibited extensive corrosion during this test. Corrosion was calculated to be 33.8 mils (859 μm). This was much higher than the 7 mils (178 μm) experienced during Test 1. The corrosion during both Test 1 and Test 3 of the pilot plant testing was significantly higher than the corrosion determined for the EDTA/carbonate solvent in past testing (References 3 and 5). During earlier testing the corrosion was less than 1.5 mils (38 μm). This higher corrosion during the pilot plant testing has been attributed to the location of the coupon, the pilot plant system design, and ferric ion corrosion.

Ferric ion corrosion is defined by the following equation (Reference 6):

Ferric ion is a known strong oxidizer that results in corrosion of carbon steel materials. In a closed system, ferric ion corrosion is limited by the stoichiometry of the reactions. Once the ferric ion is consumed according to the above equation, ferric ion corrosion stops. However, if the solvent is oxidized, the ferrous ion can be converted back to ferric ion and the corrosion reactions will continue.

In the pilot plant loop, the solvent was returned to the mix tank above the solvent level. This configuration would fully oxygenate the solvent. During the bench scale testing the solvent was returned below the solvent level (Reference 5). During the initial beaker testing the solvent was tested in a closed beaker system (Reference 3). The corrosion coupon was placed in the solvent mix tank. This would be the location of the most corrosive solvent. The difference between pilot plant Tests 1 and 3 was the amount of dissolved iron in solution (as a result of corrosion of a greater number of carbon steel specimens undergoing decontamination). The higher dissolved iron in Test 3 resulted in more ferric ion corrosion of the corrosion specimen. However, the ferric ion corrosion that occurred in Test 1 was still greater than that experienced during the earlier testing.

5.0 RESULTS AND DISCUSSION - PILOT SCALE SOLVENT RECOVERY TESTS

5.1 Approach

The second part of Task 5 was to treat the spent solvent, with primary emphasis on the recovery of EDTA and the removal of dissolved uranium from the remaining solvent. This task was accomplished using the pilot scale test rig.

At the completion of the three decontamination test runs the total volume of spent solvent and rinse water was between 180 and 200 gallons. About fifty gallons of solvent were used for each test run. The remaining approximately forty gallons of waste water was generated by the rinsing of metal components at the completion of each test run and also rinsing of the system piping and mix tank between test runs. Every attempt was made to segregate the solvents. However, due to the limited tank storage space, some mixing of the EDTA solvent, carbonate solvent and rinse water occurred when the solvents were pumped to storage.

The treatment process used was the same as recommended from the Task 3 testing for a mixed EDTA/carbonate solvent system. The initial step was to reduce the solvent pH to less than 1.5, followed by treatment with Purolite S-940 chelating cation exchange resin. The solution pH was reduced to effectively remove EDTA from solution by forming the insoluble tetraacid form, to expel carbonate from solution as carbon dioxide gas, and to achieve optimized solution pH for efficient uranium removal by the resin. A copy of the test procedure for the treatment of the spent waste solutions is attached as Appendix C.

5.2 Test Description

At the completion of decontamination testing, the two storage tanks and both solvent mix tanks were filled with mixtures of spent solvent and rinse water. The waste was processed in four batches. Batch 1 was primarily the carbonate-only solvent used in pilot plant Test 2. Batch 2 was primarily the EDTA/carbonate solvent used in pilot plant Test 1. Batch 3 was primarily the EDTA/carbonate solvent used in pilot plant Test 3. Batch 4 was primarily rinse water. These batches of solvent were processed in order (Batch 1 then Batch 2, Batch 3, and Batch 4).

Referring to Figure 1, fifty gallons of waste solvent was pumped into the pH adjust tank, the mixer turned on, and the solution pH reduced to <1.5 with sulfuric acid. At a pH of approximately 2.3 a precipitate of EDTA started to form. After the desired pH was achieved, the mixer was turned off and a minimum of two hours of settling time was allowed.

After the solvent settling period, the supernatant was pumped through the resin column at a rate of approximately two gallons per minute. The resin column contained 2 cubic feet of S-940 with a minimum bed depth of 30 inches. The column effluent was collected in a storage tank and later pumped back to the original storage tank awaiting solvent uranium analysis prior to solvent discharge. Each batch of solvent was sampled prior to pH adjustment and 2 hours after pH adjustment. The resin column effluent was sampled after 10 and 15 minutes of solvent pumping. The combined resin column effluent was also sampled after thorough mixing.

This sampling sequence was followed for all test batches with the following exceptions. Batch 1 of solvent did not form a precipitate after pH adjustment, since this batch was primarily the carbonate-only solvent. No sample was taken of this solvent after the pH adjustment. The fourth batch of processed solvent (primarily the rinse water) was not sampled at the column effluent during the run, because there were only about 30 gallons in this batch. Due to the large freeboard volume above the resin, it would have taken approximately 15 to 20 gallons of solvent to displace the residual solvent from the previous test.

After each test run, the sludge remaining in the bottom of the tank was drained into a 5 gallon bucket. The sludge was filtered using a Buchner funnel and Number 40 Whatman filter paper. The filter cake was then rinsed with demineralized water with the pH reduced to less than 1.5 to prevent dissolution of the EDTA. A sample of each of these filter cakes was taken.

All solvent samples and the two sludge samples were analyzed for total uranium activity and total dissolved iron. Select samples were also analyzed for free EDTA. The most important analyses were the EDTA concentration before and after pH adjustment and the uranium activity before and after the ion exchange column.

5.3 Results and Discussion

Results of the recovery testing are presented in Tables 11, 12, and 13. Uranium test results, presented in Table 11, showed that essentially no uranium was removed from solution with the precipitation of EDTA. These results were substantiated by the low uranium activity of the sludge cake. This means that the recovered EDTA had a very low uranium contamination, making it well suited for recycle.

The ion exchange column exhibited very high removal of uranium activity from the solvent. All four batches of waste solvent processed showed better than 99% uranium removal efficiencies. The first two batches of solvent showed greater than 99.99% removal efficiency, as expected from the Task 3 testing (Reference 4). A decrease in efficiency to 99.4% was observed during the processing of Batch 3. It was suspected that the relatively high amount of dissolved iron in this batch affected the efficiency of the ion exchange column, as the iron ions were competing for the ion exchange sites. It was suspected that the removal efficiency would have improved if the batch had been run back through the column to increase residence time.

Batch 4 showed a uranium removal efficiency of 99.6%. This was the last batch processed through the column. It is possible that the column was becoming loaded at this time with a combination of uranium and iron ions. Overall removal efficiencies were considered acceptable.

Table 11
Total Uranium Results - Pilot Scale Testing
Solvent Recovery Test

Sample I.D.	Total Uranium (pCi/L)			
	Batch 1	Batch 2	Batch 3	Batch 4
Before pH Adjustment	14,754	92,384	25,334	15,451
After pH Adjustment	No Sample	94,470	32,874	11,816
Column Effluent (10 Minutes)	14.39	78.25	101	No Sample
Column Effluent (15 Minutes)	< Minimum Detection	176.03	72.6	No Sample
Combined IX Column Effluent	11.44	88.85	144	60.29
Filter Cake Sludge	No Sample	67.11*	34.24*	No Sample
Decontamination Efficiency	99.99%	99.99%	99.40%	99.60%

* - Filter Cake Analyzed at pCi/gram rather than pCi/L

The dissolved iron analysis (Table 12) showed that very little iron precipitated during the pH adjustment phase. This was expected, since iron is extremely soluble at low pH values. The ion exchange column removed an extensive amount of the dissolved iron. As previously discussed, this may have had an effect on uranium removal efficiency. This could be investigated further in follow-on programs. If high iron concentrations exist it may be necessary to increase solvent pH to above 12 at some time in the processing prior to ion exchange. This would precipitate iron prior to the ion exchange treatment.

Results for the recovery of EDTA were also quite good, based on the amount of EDTA remaining in solution after acid addition (Table 13). Note that no attempt was made to recover, dry, and weigh the precipitated EDTA. Batch numbers 2 and 3 were the two solvents which were primarily the EDTA-based solvent from pilot plant Tests 1 and 3. The other two solvent batches contained significantly lower concentrations of EDTA. The EDTA in Batches 1 and 4 was primarily a result of mixing the solvents when transferring to waste storage. The EDTA results represent the concentration of uncomplexed (free) EDTA remaining in solution.

Table 12
Total Dissolved Iron Results - Pilot Scale Testing
Solvent Recovery Test

Sample I.D.	Total Dissolved Iron (mg/L)			
	Batch 1	Batch 2	Batch 3	Batch 4
Before pH Adjustment	0.70	29.1	678	30.5
After pH Adjustment	No Sample	28.3	787	33.4
Combined IX Column Effluent	0.26	1.03	34.0	9.41
Filter Cake Sludge	No Sample	0.99	20	No Sample

When the pH of the solvent is reduced to 1.5, both free and complexed EDTA are removed from solution. The metal chelate bond is broken and EDTA precipitates while the heavy metal stays in the acid solution (see Table 12). Results showed that the EDTA level in all solvents was reduced to 1.9 g/L or less. The lower limit of detection for the EDTA test is approximately 0.9 g/L. The resultant EDTA filter cake could be readily solubilized utilizing water and ammonia, and the resultant solution could then be reused in further decontamination efforts.

Table 13
Free EDTA Results - Pilot Scale Testing
Solvent Recovery Test

Sample I.D.	Total Free EDTA In Solution (g/L)			
	Batch 1	Batch 2	Batch 3	Batch 4
Before pH Adjustment	2.8	14.8	23.1	3.7
After pH Adjustment	No Sample	1.9	0.9	1.9
Combined IX Column Effluent	0.9	1.9	1.9	1.9

6.0 CONCLUSIONS

The following is a summary of the significant conclusions from the data generated during Task 5 of the DOE Program DE-AC21-83MC30168, "Chemical Decontamination of Process Equipment Using Recyclable Chelating Agents."

The basic test rig was adequate to apply the process, however some limitations were noted. The hydrogen peroxide could easily be spiked and the solvent quickly cooled between high and low temperature steps. However, cooling immediately after a spike, when the solvent had relatively high levels of dissolved ions, was marginally effective. This resulted in rapid H_2O_2 decomposition. It is important to have on line cooling capability after the peroxide injection point in the system.

Three test runs were made with the pilot system (two with the EDTA/carbonate solvent and one with the carbonate-only solvent). Contaminated metals used in the test program were stainless steel pipe brackets and several pieces of carbon steel floor grating. All stainless steel components subjected to the cleaning solvent showed a contamination removal efficiency of greater than 99%. Decontamination factors for the carbon steel components subjected to the cleaning solvents were considerably less; however, a large percentage of the carbon steel surface areas subjected to the solvent were covered with a tar-like coating. It is believed the coating shielded the uranium from the solvent, thus reducing the effectiveness of the solvent for the dissolution of uranium.

The addition of the EDTA improved the solvent's performance. The EDTA made the solvent more versatile and would likely be the solvent of choice for field use.

There was essentially no corrosion without the EDTA present in the solvent system. The EDTA is required to effect consistent base metal corrosion. The application sequence in the test rig continually aerated the solvent. This resulted in increased corrosion due to ferric ion attack of the carbon steel corrosion coupon and test materials.

Recovery tests were also quite successful. EDTA was recovered from solution by precipitation and the dissolved uranium reduced by ion exchange to a level between 11 and 144 pCi/L for the four (4) batches of waste solvent treated. This was equivalent to a uranium removal rate in excess of 99.4% for all of the waste processed. Heavy metals (iron) were also removed by the cation exchange column to acceptable discharge levels.

Hydrogen peroxide is an important variable that needs to be monitored and controlled during the process application. An analytical procedure suitable for use with this process was identified (Appendix B).

7.0 RECOMMENDATIONS

It is recommended to continue with Phase II of the test program, "Field Demonstration Test." The EDTA/carbonate solvent system appears more versatile and would be the solvent of choice, unless it could be verified that the contamination is readily available to the solvent. In this case, the carbonate-only solvent might be applicable. It is recommended that the basic procedures used for solvent application and recovery be used as the guide for the field demonstration test.

It is further recommended that the Appendix B H_2O_2 analytical procedure be used during the field demonstration. The test rig should be modified for the field application to improve cooling during the H_2O_2 spikes and to control solvent aeration to reduce the ferric ion corrosion during process application.

8.0 REFERENCES

- (1) "Decontamination and Decommissioning Integrated Demonstration Strategy," Draft for Review, November 1991, a product of the DOE Environmental Management D&D Workshop, August 12-16, 1991
- (2) W. J. Manion and T. S. LaGuardia, "Decommissioning Handbook," prepared for U.S. DOE by Nuclear Energy Services, Inc., November, 1980
- (3) Task 2 Topical Report, DOE Contract DE-AC21-93MC30168.
- (4) Task 3 Topical Report, DOE Contract DE-AC21-93MC30168.
- (5) Task 4 Topical Report, DOE Contract DE-AC21-93MC30168.
- (6) J.M. Jevic and W.S. Leedy, "Chemical Cleaning Solvent and Process Testing," EPRI Report NP-2976, Electric Power Research Institute, April 1983.
- (7) D. Schneidmiller and D. Stiteler, "Steam Generator Chemical Cleaning Process Development," EPRI Report NP-3009, Electric Power Research Institute, April 1983.

APPENDIX A

TASK 5 TOPICAL REPORT

DOE CONTRACT DE-AC21-93MC30168

**TEST PROCEDURES AND SIGN-OFF SHEETS
FOR PILOT SCALE DECONTAMINATION TESTS**

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE NO. 1

PREPARATION OF SOLUTION CONTAINING HYDROGEN PEROXIDE AND AMMONIUM CARBONATE

Prepared by: _____ Date _____

Approved by: _____ Date _____

1.0 Description

This procedure describes the preparation of 184 liters of solvent containing 20 grams of ammonium carbonate and 5 grams of hydrogen peroxide per liter. Other concentrations can be prepared by simple proportioning of the constituents.

2.0 Health and Safety Precautions

Follow instructions given in the RWP for the Recyclable Chelating Agent Pilot Plant.

3.0 Protective Equipment

Follow instructions given in the RWP for the Recyclable Chelating Agent Pilot Plant.

4.0 Training Required

4.1 Personnel performing work with radioactive materials must have received Level 2 LTC Site Training.

4.2 Personnel working in the pilot plant must be trained under the RWP for the Recyclable Chelating Agent Pilot Plant.

5.0 Equipment and Materials Required

5.1 Agitator

5.2 55-Gallon Mix Tank

5.3 Scales to weigh ammonium carbonate

5.4 Graduated cylinder to measure 20% ammonium hydroxide and 30% hydrogen peroxide

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE NO. 1

- 5.5 Standardized pH Meter
- 5.6 ACS Grade 20% Ammonium Hydroxide Solution
- 5.7 ACS Grade Ammonium Carbonate
- 5.8 ACS Grade 30% Hydrogen Peroxide Solution
- 6.0 Procedure
- 6.1 Add about 100 liters of deionized water to the Mix Tank (20" air space).
- 6.2 Start the agitator.
- 6.3 Add sufficient 20% ammonium hydroxide solution to the Mix Tank to bring the pH to at least 8.0. Measure the air space (AS) following the NH_4OH addition. (Stop the agitator and allow swirling to stop before measuring the air space.)
- 6.4 Add 3,680 grams of ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$ to the Mix Tank to prepare a solution containing 20 g $(\text{NH}_4)_2\text{CO}_3$ per liter.
- 6.5 Stir the solution well and determine the pH. Adjust the pH to 9.0 ± 0.1 with 20% ammonium hydroxide solution. Then adjust the volume to 184 liters (8" air space).
- 6.6 Determine the pH of the adjusted solution.
- 6.7 If the temperature of the solution is below 85° F, add 2,760 mL of fresh 30% hydrogen peroxide solution. Continue agitation for another five minutes and then stop the agitator. Continued agitation will promote decomposition of the solvent.
- 8.0 Record Control and Reporting

Record information and data as indicated on the attached form.

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE NO. 1

PREPARATION OF SOLUTION CONTAINING HYDROGEN PEROXIDE AND AMMONIUM CARBONATE

DATA AND INFORMATION FORM

Test No. _____	Date _____
Step	Reading
6.1 Add deionized water to the Mix Tank (20" air space).	Time _____
6.2 Start the agitator.	Time _____
6.3 Add ammonium hydroxide solution to the Mix Tank to bring the pH to at least 8.0. Measure the air space (AS) following the NH_4OH addition.	Time _____ Amount _____ pH _____ AS _____
6.4 Add ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$ to the Mix Tank.	Time _____ Amount _____
6.5 Determine the pH. Adjust the pH to 9.0 ± 0.1 with 20% ammonium hydroxide solution. Then adjust the volume to 184 liters (8" air space).	Time _____ Amount _____ pH _____ AS _____
6.6 Determine the pH of the adjusted solution.	Time _____ pH _____
6.7 If the temperature of the solution is below 85° F, add fresh 30% hydrogen peroxide solution. Continue agitation for another five minutes and then stop the agitator.	Time _____ Amount _____ pH _____ AS _____

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE NO. 1

PREPARATION OF SOLUTION CONTAINING
HYDROGEN PEROXIDE AND AMMONIUM CARBONATE

DATA AND INFORMATION FORM

Test No. _____

Date _____

COMMENTS

Operator _____

Date _____

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

PREPARATION OF SOLUTION CONTAINING EDTA, HYDROGEN PEROXIDE AND AMMONIUM CARBONATE

Prepared by: _____ Date _____

Approved by: _____ Date _____

1.0 Description

This procedure describes the preparation of 184 liters of solvent containing 50 grams of EDTA (ethylene diamine tetraacetic acid), 20 grams of ammonium carbonate, and 5.0 grams of hydrogen peroxide per liter. Other concentrations can be prepared by simple proportioning of the constituents.

2.0 Health and Safety Precautions

Follow instructions given in the RWP for the Recyclable Chelating Agent Pilot Plant.

3.0 Protective Equipment

Follow instructions given in the RWP for the Recyclable Chelating Agent Pilot Plant.

4.0 Training Required

4.1 Personnel performing work with radioactive materials must have received Level 2 LTC Site Training.

4.2 Personnel working in the pilot plant must be trained under the RWP for the Recyclable Chelating Agent Pilot Plant.

5.0 Equipment and Materials Required

5.1 Agitator

5.2 55-Gallon Drum

5.3 Scales to weigh EDTA and ammonium carbonate

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

- 5.4 Graduated cylinder to measure 20% ammonium hydroxide and 30% hydrogen peroxide
- 5.5 Hydrometer
- 5.6 Standardized pH Meter
- 5.7 ACS Grade 20% Ammonium Hydroxide Solution
- 5.8 ACS Grade EDTA
- 5.9 ACS Grade Ammonium Carbonate
- 5.10 ACS Grade 30% Hydrogen Peroxide Solution
- 6.0 Procedure
- 6.1 Add about 100 liters of deionized water to the Mix Tank (20" air space).
- 6.2 Start the agitator.
- 6.3 Add 4,900 mL of 20% ammonium hydroxide solution to the Mix Tank. Measure the air space (AS) following the NH_4OH addition. (Stop the agitator and allow swirling to stop before measuring the air space.)
- 6.4 Slowly add 9,200 grams of EDTA to the Mix Tank to prepare a solution containing 50 grams EDTA per liter. Continue agitation until all of the EDTA is dissolved. If the EDTA does not dissolve within 30 minutes, the pH may be too low.
- 6.5 Check the pH. If the pH is below 7.0, add sufficient 20% ammonium hydroxide solution to the Mix Tank to bring the pH to at least 7.0. The pH should be at or above 7.0 to aid in dissolution of the EDTA and to avoid loss of carbonate during subsequent steps.
- 6.6 Add 3,680 grams of ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$ to the Mix Tank to prepare a solution containing 20 g $(\text{NH}_4)_2\text{CO}_3$ per liter.
- 6.7 Stir the solution well and determine the pH. Adjust the pH to 9.0 ± 0.1 with 20% ammonium hydroxide solution. Then adjust the volume to 184 liters (8" air space).
- 6.8 Determine the pH of the adjusted solution.

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

- 6.9 Take a sample for analysis of EDTA concentration. Measure the specific gravity of the solution with a hydrometer.
- 6.10 If the temperature of the solution is below 85° F, add 2,760 mL of fresh 30% hydrogen peroxide solution. Continue agitation for another five minutes and then stop the agitator. Continued agitation will promote decomposition of the solvent.

7.0 Record Control and Reporting

Record information and data as indicated on the attached form.

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

PREPARATION OF SOLUTION CONTAINING HYDROGEN PEROXIDE AND AMMONIUM CARBONATE

DATA AND INFORMATION FORM

Test No. _____	Date _____
Step	Reading
6.1 Add deionized water to the Mix Tank (20" air space).	Time _____
6.2 Start the agitator.	Time _____
6.3 Add ammonium hydroxide solution to the Mix Tank. Measure the pH and air space following the NH_4OH addition.	Time _____ Amount _____ pH _____ AS _____
6.4 Slowly add EDTA to the Mix Tank. Continue agitation until all of the EDTA is dissolved.	Time _____ Amount _____
6.5 Check the pH. If the pH is below 7.0, add sufficient 20% ammonium hydroxide solution to the Mix Tank to bring the pH to at least 7.0.	Time _____ Amount _____
6.6 Add ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$ to the Mix Tank.	Time _____ Amount _____
6.7 Determine the pH. Adjust the pH to 9.0 ± 0.1 with 20% ammonium hydroxide solution. Then adjust the volume to 184 liters (8" air space).	Time _____ Amount _____ pH _____ AS _____
6.8 Determine the pH of the adjusted solution.	Time _____ pH _____
6.9 Take a sample for analysis of EDTA concentration. Measure the specific gravity of the solution with a hydrometer.	Time _____ EDTA _____
6.10 If the temperature of the solution is below 85° F, add fresh 30% hydrogen peroxide solution. Continue agitation for another five minutes and then stop the agitator.	Time _____ Amount _____ pH _____ AS _____

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

PREPARATION OF SOLUTION CONTAINING
HYDROGEN PEROXIDE AND AMMONIUM CARBONATE

DATA AND INFORMATION FORM

Test No. _____

Date _____

COMMENTS

Operator _____

Date _____

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

URANIUM DECONTAMINATION

Prepared by: _____ Date _____

Approved by: _____ Date _____

1.0 Description

This procedure describes the method for demonstrating the decontamination of equipment contaminated with uranium.

2.0 Health and Safety Precautions

Follow instructions given in the RWP for the Recyclable Chelating Agent Pilot Plant.

3.0 Protective Equipment

Follow instructions given in the RWP for the Recyclable Chelating Agent Pilot Plant.

4.0 Training Required

4.1 Personnel performing work with radioactive materials must have received Level 2 LTC Site Training.

4.2 Personnel working in the pilot plant must be trained under the RWP for the Recyclable Chelating Agent Pilot Plant.

5.0 Equipment and Materials Required

5.1 Heated 55-Gallon Mix Tank

5.2 Heated 30-Gallon Reaction Vessel

5.3 Circulating Pump

5.4 Cooling Coil

5.5 Scales to weigh EDTA and ammonium carbonate

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

- 5.6 Graduated cylinder to measure 20% ammonium hydroxide and 30% hydrogen peroxide
- 5.7 Hydrometer
- 5.8 Standardized pH Meter
- 5.9 ACS Grade 20% Ammonium Hydroxide Solution
- 5.10 ACS Grade EDTA
- 5.11 ACS Grade Ammonium Carbonate
- 5.12 ACS Grade 30% Hydrogen Peroxide Solution
- 6.0 Procedure
- 6.1 The specimens to be decontaminated must have been surveyed for radioactive contamination (smearable and direct α , smearable and direct β , and direct γ) and the results recorded.
- 6.2 The test solution must be ready to use. Submit a 100 mL sample of the fresh test solution for analysis for TCLP metals (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) and total uranium.
- 6.3 Inspect the Reaction Vessel to assure it is clean and empty.
- 6.4 Suspend the specimens to be decontaminated in the Reaction Vessel.
- 6.5 Open the drain valve and inlet valve on the Mix Tank to be used and the drain valve on the Reaction Vessel. (Assure the drain valve and the inlet valve on the other Mix Tank are closed.) Start pumping solution up through the Reaction Vessel and overflowing back to the Mix Tank.
- 6.6 Record the temperature of the solution in the Reaction Vessel at the start of the test and every half hour until the end of the test.
- 6.7 Record the pH of the solution in the Reaction Vessel at the start of the test and every hour until the end of the test.
- 6.8 Continue recirculating at room temperature for 2 hours.

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

- 6.9 At 2 hours, turn on the heating elements on the Mix Tank being used and the heating element on the Reaction Vessel. Heat the solution to 200°F and maintain this temperature for 4 hours. Record the time that 200°F is reached.
- 6.10 After 4 hours at 200°F, turn the heating elements off and turn on the cooling water to the cooling coil in the Mix Tank being used. Continue the recirculation for 2 more hours while the solution cools. Record the time that 75°F is reached.
- 6.11 When the temperature reaches 75°F, add 3,680 mL of fresh 30% H₂O₂ solution to the recirculating solution. Record the time of addition.
- 6.12 Turn off the recirculating pump. Allow the solution to drain from the Reaction Vessel back into the Mix Tank. When the Reaction Vessel is empty, close the drain valve and inlet valve on the Mix Tank and the drain valve on the Reaction Vessel.
- 6.13 Rinse the specimens to remove the decontamination solution, dry them, survey them for radioactive contamination (smearable and direct α , smearable and direct β , and direct γ) and record the results.
- 6.14 Submit a 100 mL sample of the fresh test solution for analysis for TCLP metals (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) and total uranium.
- 7.0 Record Control and Reporting

Record information and data as indicated on the attached form.

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

URANIUM DECONTAMINATION

DATA AND INFORMATION FORM

Test _____

Date _____

Step

Reading

- 6.1 Record data from surveys of specimens on the Specimen Survey Record (smearable and direct α , smearable and direct β , and direct γ).
- 6.2 Submit a 100 mL sample of the fresh test solution for analysis for TCLP metals (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) and total uranium.
- 6.3 Inspect the Reaction Vessel to assure it is clean and empty.
- 6.4 Suspend the specimens to be decontaminated in the Reaction Vessel.
- 6.5 Open the drain valve and inlet valve on the Mix Tank to be used and the drain valve on the Reaction Vessel. Start pumping solution up through the Reaction Vessel and overflowing back to the Mix Tank.
- 6.6 Record the temperature of the solution in the Reaction Vessel at the start of the test and every half hour until the end of the test on the Temperature and pH Record.
- 6.7 Record the pH of the solution in the Reaction Vessel at the start of the test and every hour until the end of the test on the Temperature and pH Record.
- 6.8 Continue recirculating at room temperature for 2 hours.
- 6.9 At 2 hours, turn on the heating elements. Heat the solution to 200°F and maintain this temperature for 4 hours. Record the time that 200°F is reached on the Temperature and pH Record.

Time _____

Time _____

Time _____

Time _____

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

URANIUM DECONTAMINATION

DATA AND INFORMATION FORM

Test _____

Date _____

Step

Reading

6.10 After 4 hours at 200°F, turn the heating elements off and turn on the cooling water to the cooling coil in the Mix Tank being used. Continue the recirculation for 2 more hours while the solution cools. Record the time that 75°F is reached on the Temperature and pH Record.

Time _____

6.11 When the temperature reaches 75°F, add fresh 30% H₂O₂ solution to the recirculating solution and record the time of addition.

Time _____

Amount _____

6.12 Turn off the recirculating pump. Allow the solution to drain from the Reaction Vessel back into the Mix Tank. When the Reaction Vessel is empty, close the drain valve and inlet valve on the Mix Tank and the drain valve on the Reaction Vessel.

Time _____

6.13 Rinse the specimens to remove the decontamination solution, dry them, survey them for radioactive contamination (smearable and direct α , smearable and direct β , and direct γ) and record the results on the Specimen Survey Record.

6.14 Submit a 100 mL sample of the used test solution for analysis for TCLP metals (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) and total uranium.

COMMENTS _____

_____

_____

_____

_____

_____

Operator _____ Date _____

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

URANIUM DECONTAMINATION

ANALYTICAL SAMPLE RECORD

Test _____

Date _____

<u>Sample No.</u>	<u>Analyte</u>	<u>Results</u>
<u>Fresh Decon Solution</u>	Arsenic	_____
	Barium	_____
	Cadmium	_____
	Chromium	_____
	Lead	_____
	Mercury	_____
	Selenium	_____
	Silver	_____
<u>Used Decon Solution</u>	Uranium	_____
	Arsenic	_____
	Barium	_____
	Cadmium	_____
	Chromium	_____
	Lead	_____
	Mercury	_____
	Selenium	_____
_____	Silver	_____
	Uranium	_____
	Arsenic	_____
	Barium	_____
	Cadmium	_____
	Chromium	_____
	Lead	_____
	Mercury	_____
	Selenium	_____
	Silver	_____
	Uranium	_____

Operator _____

Date _____

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

URANIUM DECONTAMINATION

SPECIMEN SURVEY RECORD

Test _____

Date _____

Specimen Description

Specimen No.

Survey Results

Direct α _____ dpm

Direct β _____ dpm

Direct γ _____ mR/hr

Smearable α _____ dpm

Smearable β _____ dpm

Direct α _____ dpm

Direct β _____ dpm

Direct γ _____ mR/hr

Smearable α _____ dpm

Smearable β _____ dpm

Direct α _____ dpm

Direct β _____ dpm

Direct γ _____ mR/hr

Smearable α _____ dpm

Smearable β _____ dpm

Direct α _____ dpm

Direct β _____ dpm

Direct γ _____ mR/hr

Smearable α _____ dpm

Smearable β _____ dpm

Direct α _____ dpm

Direct β _____ dpm

Direct γ _____ mR/hr

Smearable α _____ dpm

Smearable β _____ dpm

Operator _____

Date _____

RECYCLABLE CHELATING AGENT PILOT PLANT TEST PROCEDURE

URANIUM DECONTAMINATION

SPECIMEN SURVEY RECORD

Test _____

Date _____

Test	Temperature	pH
0:00		
0:30		
1:00		
0:30		
2:00		
0:30		
3:00		
0:30		
4:00		
0:30		
5:00		
0:30		
6:00		
0:30		
7:00		
0:30		
8:00		
0:30		

Time 200°F was reached

Time 75°F was reached

COMMENTS _____

Operator _____ Date _____

APPENDIX B

TASK 5 TOPICAL REPORT

DOE CONTRACT DE-AC21-93MC30168

**ANALYTICAL PROCEDURE FOR DETERMINATION OF
HYDROGEN PEROXIDE BY POTENTIOMETRIC TITRATION**

Babcock & Wilcox

Research and Development Division

TECHNICAL PROCEDURE

NUMBER ARC-TP-1276 REV. NO. 0

TITLE DETERMINATION OF HYDROGEN PEROXIDE IN EDTA SOLUTIONS BY POTENTIOMETRIC
TITRATION

PREPARED BY

J.S. Presley

10/3/95

APPROVED BY

APPROVED BY

DISTRIBUTED BY QUALITY ASSURANCE

RESEARCH AND DEVELOPMENT DIVISION
TECHNICAL PROCEDUREPROCEDURE NO. ARC-TP-1276PAGE NO. 2

REVISIONS		
REV. NO.	DATE	DESCRIPTION

0	9/19/95	Original Release

RESEARCH AND DEVELOPMENT DIVISION
TECHNICAL PROCEDUREPROCEDURE NO. ARC-TP-1276REV. NO. 0PAGE NO. 3DATE 9/19/95

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1.0 SCOPE

Residual hydrogen peroxide in EDTA cleaning solutions can be determined by potentiometric titration with cerium ammonium nitrate. Recoveries of hydrogen peroxide are 95% to 101% in these media and the practical determinable lower limit is 0.5 g/L. The relative precision of the method is 3% at 2 g/L and 0.5% at 20 g/L of hydrogen peroxide. Samples should be diluted and acidified immediately after collection to minimize decomposition of hydrogen peroxide.

2.0 PRINCIPLE

Hydrogen peroxide is titrated with ceric ammonium nitrate to a potentiometric end point. The reactions for this titration are as follows:

3.0 REAGENTS

Unless otherwise indicated, all reagents shall be of the quality known as reagent grade and conform, where applicable, to the specifications of the Committee on Analytical Reagents of the American Chemical Society.

3.1 Cerium (IV) ammonium nitrate [$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$]

3.2 Sulfuric acid (H_2SO_4), concentrated

3.3 Hydrogen peroxide (H_2O_2), 30%

3.4 Arsenic (III) trioxide (As_2O_3)

3.5 Sodium hydroxide (NaOH)

3.6 Iodine (I)

4.0 EQUIPMENT

4.1 Metrohm 716 DMS Titrino Autotitrator

5.0 SOLUTIONS

5.1 Standard Cerium (IV) Solution 0.5 N

Weigh 274 g of cerium (IV) ammonium nitrate (F.W. 548.2) into a 1500 mL beaker. Add 140 mL of concentrated sulfuric acid and stir until a smooth slurry is obtained. Very cautiously add 10 mL portions of deionized water with stirring. When the volume is about 500 mL, transfer the solution quantitatively to a 1000 mL volumetric flask and dilute to volume. Filter the solution through 2 Whatman glass fibre filters (GF/C), rinsing the filtering apparatus 3 times with the cerium (IV) sulfate solution to avoid dilution. Standardize as described in Section 7.0. Label the bottle "Standard Cerium IV Solution 0.5N".

5.2 Sulfuric Acid Solution 9N

Cautiously add 250 mL of concentrated sulfuric acid to 500 mL of deionized water with stirring. Dilute to 1L. Cool and store in a 1 L linear polyethylene wide mouth bottle. Label the bottle "H₂SO₄ solution 9N".

6.0 STANDARDIZATION OF Ce (IV) TITRANT

6.1 Verify 716 DMS Titrino is setup for analysis. (ref. 10.2)

6.2 The Ce(IV) titrant is standardized with As₂O₃ as follows:

6.2.1 Accurately weigh about 0.3 g of As₂O₃ into an appropriate size mL beaker containing 2 g of sodium hydroxide dissolved in 25 mL of deionized water (25mL of 2 N NaOH).

6.2.2 When dissolution is complete, add two small flakes of iodine (about 10 mg), dissolve, and dilute to 100 mL with deionized water.

6.3 With stirring, add 10 mL of concentrated sulfuric acid and titrate as follows:

6.3.1 Verify the combination massive Pt electrode is connected to Ind 1 input at the back of the 716 DMS Titrino.

6.3.2 Place the electrode and the burette tip in the 716 DMS Titrino stand holding clamp. Before using the electrode, remove the plug from the electrolyte filling aperture.

6.3.3 Turn the 716 DMS Titrino on by pressing the red button on the back of the titrator.

6.3.4 Recall user method CeIV STD

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- 6.3.4.1 Press the number 3 key (user meth) on the separate key pad.
- 6.3.4.2 At the prompt > recall method press the enter key.
- 6.3.4.3 At the prompt method name press the select key until CeIV STD appears on the display, then press the ENTER key.
- 6.3.5 Position the sample in the center of the swing out magnetic stirrer.
- 6.3.6 Verify the platinum tip at the electrode is free of any tightly adhering white chalky substance. Lower the holding clamp such that the electrode and burette tip are immersed into the solution.
- 6.3.7 Check the clearance of the magnetic stir bar to ensure that it will spin freely. Turn on the magnetic stir plate by tipping the toggle switch and stir at a suitable rate (the solution must not vortex).
- 6.3.8 Press the START control key on either the 716 DMS Titrino or the separate key pad.
- 6.3.9 At the prompt id#1 or C21 input the id# using the separate key pad, then press the enter key (up to an eight digit number).
- 6.3.10 At the prompt sample size, input the mass of As_2O_3 in grams using the separate key pad, then press the enter key (up to a six digit number).
- 6.3.11 At the end of the titration the normality of the Ce(IV) solution will be displayed. Note the normality value displayed.
- 6.4 Updating the normality stored in the 716 DMS Titrino memory:
  - 6.4.1 Press the <CONFIGURATION> key on the key pad (~4 times) until "COMMON VARIABLES" is revealed on the display.
  - 6.4.2 Press the <ENTER> key until "C36" is displayed.
  - 6.4.3 Input the value for normality determined in Step 6.3.11. Press <ENTER> where done (will show zero).
  - 6.4.4 Press <QUIT> until method screen is displayed (~2 times).

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7.0 SAMPLE PREPARATION

- 7.1 If the sample contains 0-40 g H_2O_2 /L, then take a 5.00 mL aliquot of sample and add to a clean titration vessel containing a magnetic stir bar. (This aliquot size can vary depending on the concentration of the hydrogen peroxide. The total volume of sample and water should be kept at 50 mL by adjusting the volume of deionized water accordingly.)
- 7.2 With stirring add 45 mL of deionized water and 10 mL of 9N H_2SO_4 .
- 7.3 Rinse the electrodes thoroughly and immerse them in the solution to be titrated, centering the vessel on the magnetic stirrer.

8.0 AUTO TITRATION

- 8.1 Verify the combination massive Pt electrode is connected to Ind 1 input at the back of the 716 DMS Titrino.
- 8.2 Place the electrode and the burette tip in the 716 DMS Titrino stand holding clamp. Before using the electrode, remove the plug from the electrolyte filling aperture.
- 8.3 Turn the 716 DMS Titrino on by pressing the red button on the back of the titrator.
- 8.4 Recall user method H_2O_2 smp
  - 8.4.1 Press the number 3 key (user meth) on the separate key pad.
  - 8.4.2 At the prompt <recall method press the enter key.
  - 8.4.3 At the prompt method name press the SELECT key until H_2O_2 smp appears on the display, then press the ENTER key.
- 8.5 Position the sample in the center of the swing out magnetic stirrer.
- 8.6 Verify the platinum tip of the electrode is free of any tightly adhering white chalky substance. Lower the holding clamp such that the electrode and burette tip are immersed into the solution.
- 8.7 Check the clearance of the magnetic stir bar to ensure that it will spin freely. Turn on the magnetic stir plate by tripping the toggle switch and stir at suitable rate by adjusting the dial labelled 1-10 beside the switch.

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- 8.8 Press the START control key on either the 716 DMS Titrino or the separate key pad.
- 8.9 At the prompt id#1 or C21 input the id# using the separate key pad, then press the enter key (up to an eight digit number).
- 8.10 The result will be automatically displayed as RS1 in g/L H_2O_2 on the titrator and will be printed on the printer. Record this result along with the sample identification in the lab notebook.

9.0 RECORDS

- 9.1 All samples will be clearly identified in the laboratory notebook together with results read directly from the autotitrator display.
- 9.2 The dilution and sample size for all samples and standards will be recorded in the laboratory notebook.
- 9.3 Each set of samples and check standards analyzed will be designated in the laboratory notebook as belonging to a single set. This is to aid in the calculation by keeping all samples and check standards of a particular set identified as belonging to the same set.

10.0 REFERENCES

- 10.1 ORION Laboratory Products Group Bench Top pH/ISE Meter Instruction Manual, Models: 420A, 520A, 720A, and 920A.
- 10.2 "Installation/Checkout for 716 DMS Titrino". ARC-TP-1273

APPENDIX C

TASK 5 TOPICAL REPORT

DOE CONTRACT DE-AC21-93MC30168

**TEST PROCEDURE AND SIGN-OFF SHEET
FOR PILOT SCALE SOLVENT RECOVERY TESTS**

**RECYCLABLE CHELATING AGENT PILOT PROGRAM
RECOVERY OF EDTA AND URANIUM**

Revision No. 0

May 3, 1995

Prepared by: _____

Date: _____

Approved by: _____

Date: _____

RECYCLABLE CHELATING AGENT PILOT PROGRAM RECOVERY OF EDTA AND URANIUM

1.0 DESCRIPTION

This procedure describes the method to be used for recovering EDTA from spent chelating solvent by chemical precipitation and the removal of dissolved uranium from the solution by cation ion exchange.

2.0 HEALTH & SAFETY PRECAUTIONS

Follow instructions given in the RWP for the Recyclable Chelating Agent Pilot Program -Solvent Recovery Test.

3.0 PROTECTIVE EQUIPMENT

Follow instructions given in the RWP for the Recyclable Chelating Agent Pilot Program -Solvent Recovery Test.

4.0 TRAINING REQUIRED

- 4.1 Personnel performing work with radioactive materials must have received Level 2 LTC Site Training.
- 4.2 Personnel working in the pilot plant must have trained under the RWP for the Recyclable Chelating Agent Pilot Program - Solvent Recovery Test.

5.0 EQUIPMENT AND MATERIALS REQUIRED

- 5.1 Three (3) - Stainless Steel Storage Tanks
- 5.2 55-gallon Stainless Steel Mix Tank for pH Adjustment
- 5.3 Circulating Pump
- 5.4 Ion Exchange Column (5' long x 1' diameter)
- 5.5 Two (2) Cubic Feet of Purolite S 940 Cation Exchange Resin Regenerated in the Hydrogen Form
- 5.6 One (1) Liter Graduated Cylinder to Measure 95% Sulfuric Acid
- 5.7 Standardized pH Meter
- 5.8 100 Milliliter Poly Bottles

6.0 PROCEDURE

- 6.1 Load the 2 cubic feet of ion exchange material into the exchanger column. Bring the water level in the column up to the top of the flange.
- 6.2 Install the top flange and torque the bolts to the manufacturer specifications.
- 6.3 Add approximately 30 gallons of demineralized water to the pH adjust tank.
- 6.4 Align the system valves to pump demineralized water through the ion exchange column into the effluent storage tank.
- 6.5 Turn on the waste treatment recycle pump and pump demineralized water through the ion exchange column. Using the vent valve at the inlet to the column, vent the system. Set the water flow rate through the column at approximately 2.5 gallons per minute.
- 6.6 After ten minutes, sample the column effluent and monitor the solution pH. Solution pH should be 5.5 or above. If the solution pH is low, continue to rinse the system with demineralized water. Shut down the waste pump.
Initial:____ Time:____
- 6.7 Align the system valves and pump the spent solvent from one of the waste storage tanks to the mix tank labeled pH and precipitate tank per the attached schematic.
- 6.8 Collect two - 100 mL samples of the spent solvent. Submit one sample to the laboratory for total uranium and total iron analysis. The other sample will be analyzed for EDTA.
Initial:____ Time:____
- 6.9 Turn on the mixer for the pH adjustment tank.
- 6.10 The pH of the spent solvent must be reduced to less than 1.5 prior to treatment by ion exchanger. Reduce the solution pH by slowly adding 4,000 mL of concentrated sulfuric acid. After 20 minutes, check the solution pH and add more acid as required.
Initial:____ Time:____
- 6.11 Once the solution pH is adjusted below 1.5, allow 2 hours for complete precipitation of EDTA. If EDTA is absent from the solution, proceed with step 6.12.

- 6.12 The ion exchange column for uranium recovery will be installed in the piping system between the pH adjustment tank and the storage tank per the attached drawing. Align system valves to pump solvent from the pH adjustment tank through the ion exchange column to the storage tank.
- 6.13 Be sure the pump suction line from the pH adjustment tank is equipped with a floating header to prevent the pumping of precipitated EDTA. Start the discharge pump and adjust the flow through the ion exchange column to approximately 2.5 gallons per minute.
- 6.14 Collect two 100 mL samples of the column effluent every 5 minutes until the pump starts to pull the precipitated EDTA into the system. Shut down the pump.
Initial:____ Time:____
- 6.15 Thoroughly mix the treated solvent in the waste tank and collect two (2) 100 mL samples. Submit all solvent samples for analysis of total EDTA and total uranium.
- 6.16 With concurrence from HP, open the drain valve on the waste storage tank and dump the treated waste to the waste treatment system.
- 6.17 Open the bottom drain valve on the pH adjustment tank, and wash the precipitated EDTA into a 5 gallon bucket. Close the drain valve.
- 6.18 Filter the EDTA and wash the filter cake with demineralized water pH adjusted to <2.0 with sulfuric acid. Submit a sample of filter cake to the laboratory for uranium analysis.
Initial:____ Time:____
- 6.19 Place the remaining filter cake in a plastic bag for disposal.

SIGNATURE:_____ DATE:_____