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**Chemical Decontamination Of Process Equipment Using
Recyclable Chelating Solvent
Phase I**

**Final Report
September 1993 - June 1995**

October 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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Office of Fossil Energy
Morgantown Energy Technology Center
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Contract Research Division
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TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
EXECUTIVE SUMMARY	1
CHELANT SCREENING/REFINEMENT TESTING	1
FOAM APPLICATION TESTING	3
PROCESS APPLICATION TESTING	3
SOLVENT RECYCLE/CONTAMINANT VOLUME REDUCTION	4
BENCH SCALE TESTING	4
PILOT PLANT TESTING	5
CONCLUSIONS	6
RECOMMENDATIONS	7
1.0 INTRODUCTION	8
2.0 BACKGROUND/OBJECTIVES	10
2.1 Overall Program Background/Goals	10
2.2 Specific Task 2 (Chelant Screening/Refinement) Objectives	11
2.3 Specific Task 3 (Solvent Recycle/Contaminant Reduction) Objectives	11
2.4 Specific Task 4 (Bench Scale Testing) Objectives	11
2.5 Specific Task 5 (Pilot Plant Study) Objectives	11
3.0 TASK 2 - CHELANT SCREENING/REFINEMENT TESTING	12
3.1 Introduction	12
3.2 Chelant Screening Tests	12
3.2.1 Test Procedure	13
3.2.2 Results - Solvent Screening Tests	13
3.3 Solvent Refinement Tests	15
3.3.1 Results - Solvent Refinement Tests	17
3.3.2 Foam Application Testing	19
3.3.3 Process Application Testing	21

TABLE OF CONTENTS (continued)

<u>SECTION</u>	<u>PAGE</u>
4.0 TASK 3 - SOLVENT RECYCLE/CONTAMINANT VOLUME REDUCTION	23
4.1 Introduction	23
4.2 Treatment of Spent Ammonium Carbonate Solvent	24
4.3 Treatment of EDTA/Ammonium Carbonate Solvent	26
4.4 Task 3 - Solvent Recycle Recommendations	29
5.0 TASK 4 - BENCH SCALE TESTS	30
5.1 Introduction	30
5.2 Test Program	30
5.3 Test Apparatus	31
5.5 Summary of Results - Bench Scale Testing	31
5.5 Conclusions - Bench Scale Testing	36
6.0 TASK 5 - PILOT PLANT TESTING	37
6.1 Introduction	37
6.2 Overall Approach - Pilot Plant Decontamination Testing	37
6.3 Summary of Results - Pilot Plant Decontamination Test 1	39
6.4 Summary of Results - Pilot Plant Decontamination Test 2	40
6.5 Summary of Results - Pilot Plant Decontamination Test 3	41
6.6 Pilot Plant Corrosion Results	43
6.7 Approach - Pilot Scale Solvent Recovery Testing	43
6.8 Results - Pilot Scale Solvent Recovery Testing	44
6.9 Conclusions - Pilot Plant Tests	45
7.0 PHASE II SITE DEMONSTRATION	47
8.0 CONCLUSIONS	48
9.0 RECOMMENDATIONS	51
10.0 REFERENCES	52

APPENDIX A - COSTS ASSOCIATED WITH PHASE II SITE DEMONSTRATION

APPENDIX B - LETTER OF SUPPORT FOR PHASE II SITE DEMONSTRATION

LIST OF TABLES

<u>TITLE</u>	<u>PAGE</u>
1 Results - Treatment of Spent Ammonium Carbonate Solutions By Precipitation Techniques	24
2 Results - Treatment of Spent Ammonium Carbonate Solutions By Ion Exchange Techniques	25
3 Results - Treatment of Spent EDTA/Ammonium Carbonate Solutions By Precipitation Techniques	26
4 Results - Treatment of Spent EDTA/Ammonium Carbonate Solutions By Conventional Ion Exchange Techniques	27
5 Dissolved Metal Analysis - Bench Scale Test #3	35
6 Corrosion Results - Bench Scale Testing	36
7 Application Scenario - Pilot Plant Decontamination Test 1	39
8 Analytical Results - Pilot Scale Test #1	40
9 Decontamination Results - Pilot Scale Test #3	42
10 Total Uranium Results - Pilot Scale Solvent Recovery Testing	44

LIST OF FIGURES

<u>TITLE</u>	<u>PAGE</u>
1 Schematic of Typical Solvent Screening Test Flask Arrangement	14
2 Comparison of Uranium Dioxide Dissolution for Solvent With and Without Carbonate	16
3 Comparison of Uranium Dioxide Dissolution for Varying Solvent Compositions . . .	18
4 Effect of Coupons and Peroxide Concentration On Uranium Dissolution	20
5 Schematic of Bench Scale Test Loop	32
6 Total Uranium Dissolved - DOE Bench Scale Test Number 1	33
7 Total Uranium Dissolved - DOE Bench Scale Test Number 2	34
8 Schematic of Pilot Plant System	38

EXECUTIVE SUMMARY

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.

Under contract to the Department of Energy (DOE Contract Number DE-AC21-93MC30168), the Babcock & Wilcox Company (B&W) is developing a chemical decontamination process using chelating agents to remove uranium compounds and other actinide species from process equipment. The generic goal of this program is to develop a solvent capable of chelating uranium and other actinides, while having little or no effect on base metal constituents. This selectivity is required to eliminate the potential for the chelating capacity of the solvent to be exhausted by metallic species, such as iron, which might be present in overpowering quantities. A second requirement of the process is the ability to control corrosion of the base metal. In cases where materials are surface contaminated only, and reuse of the equipment is a possibility, corrosion should be controlled at a low rate. However, in cases where contamination has migrated into the grain boundaries of the base metal, a more aggressive solvent is required, to corrode away base metal and expose the radioactive species for removal. A third objective of the program is to recycle the chelating solvent, thereby minimizing the generation of secondary waste streams.

This project is divided into two separate phases:

Phase I - Process Development

Phase II - Field Demonstration

The report contained herein describes the results of the Phase I Development effort, which covers the initial solvent screening and recycle testing through pilot scale application of the developed process.

CHELANT SCREENING/REFINEMENT TESTING

The program initiated with a series of beaker tests to determine the optimum solvent and application process to achieve the objectives of the test program. Based on an extensive literature search, the screening tests were initiated using three readily available chelating agents; namely, EDTA (ethylenediaminetetraacetic acid), HEDTA (hydroxyethylethylenediaminetriacetic acid), and DTPA (diethylenetriaminepentaacetic acid). These chelants are known to form strong

complexes with uranium. The choice of these three candidates was consistent with contractual program objectives, which specified evaluation of readily available, cost effective chelants with a well developed knowledge base regarding their application.

The deposit material chosen for dissolution testing was uranium dioxide (UO_2), since it was felt to represent one of the least soluble contaminants potentially present. Each candidate chelant was subjected to several screening tests, run at varying pH's with various additives. The initial tests were performed at 93°C (200°F) with unacceptable dissolution results. A decision was then made to test chelants in conjunction with hydrogen peroxide and carbonate salts. The combination of chelant, ammonium carbonate, and hydrogen peroxide at an initial pH of 9.0 (adjusted with ammonium hydroxide) applied at room temperature was found to effect virtually 100% dissolution of the uranium dioxide placed in the test flask, within the first two hours of exposure. Results were equivalent for each of the three tested chelants.

Further testing was then performed using an EDTA/ammonium carbonate/hydrogen peroxide solvent. EDTA was selected as the most favored of the three candidate chelants based on its lower cost and the large information base regarding its application, developed for chemical cleaning applications. Several tests were performed to determine the effect of the chelant on the dissolution process. Results indicated that dissolution was 95% to 100% complete using a solvent containing peroxide and carbonate only; dissolution occurred slightly more rapidly, and to 100% completion, with the solvent containing chelant. These results were considered to be excellent.

The effect of carbonate on the dissolution process was evaluated. A solvent containing just chelant and peroxide was found to dissolve only 16% of the uranium dioxide placed in the test flask. These results indicated that complexation of the uranium by carbonate was essential to the dissolution process. Two basic solvent systems were found that met the objectives of the program:

Solvent A 50 g/L EDTA
 20 g/L $(\text{NH}_4)_2\text{CO}_3$
 5.0 g/L H_2O_2
 pH 9.0 with ammonium hydroxide

Solvent B 20 g/L $(\text{NH}_4)_2\text{CO}_3$
 5.0 g/L H_2O_2
 pH 9.0 with ammonium hydroxide

The solvent constituent concentrations were varied during the test program, and it was found that the basic solvent system was effective over a wide range of concentrations. This could allow for tailoring the solvent for removal of differing levels of contamination and for minimization of chemical usage. Results of the test program demonstrated the importance of tailoring the solvent system to different process application conditions.

Variations in the system metal content also had an effect on uranium dissolution. This necessitated an increase in the initial H_2O_2 concentration. The presence of the metal surfaces helped to catalyze the H_2O_2 decomposition, which could result in a peroxide concentration too low to effect complete dissolution. This surface to volume ratio needs to be factored into the solvent formulation as it is being tailored for a specific application.

FOAM APPLICATION TESTING

A secondary part of the refinement testing was to run a series of tests with the selected solvents to determine if they could be used effectively in the foam state. The foaming tests were successful in showing that uranium dioxide can be dissolved by the EDTA/carbonate/peroxide solvent in the foam state. However, a significant portion of the deposit was dissolved after it dislodged from the coupons onto which it had been baked, and dropped into the liquid. Although the foaming tests were considered as a qualified success, the lack of a suitable binder for immobilizing uranium dioxide on coupons for the foam tests limited the broad applicability of the test results. The results were, however, sufficiently promising to warrant further investigation of the foaming process.

It is recommended that additional foam tests be performed with a more suitable test coupon. This could be actual contaminated material, if available. The low application temperature and the relatively short time required for uranium dioxide dissolution make the EDTA/carbonate/peroxide solvent particularly adaptable to foam cleaning.

PROCESS APPLICATION TESTING

As a final phase of the refinement testing, various application scenarios were simulated to evaluate their effect on dissolution and corrosion. The results of these final tests were used to develop the recommended process for the bench scale and pilot scale testing. Based on this testing, the following process application scenario was recommended for further evaluation.

1. Two hours at room temperature
2. Heatup to 93°C and hold for approximately four hours
3. Cooldown to room temperature
4. Inject peroxide to remove additional uranium contamination uncovered by the high temperature exposure
5. Two hours at room temperature.

By starting with an initial low temperature application, readily available uranium contamination was easily dissolved. Heatup to 93°C appeared to dissolve the remaining available uranium contamination. The 93°C application resulted in higher corrosion rates than a 66°C application. This level of corrosion will be necessary to expose contamination buried more deeply in component surfaces. Even at 93°C , the corrosion was uniform in nature.

SOLVENT RECYCLE/CONTAMINANT VOLUME REDUCTION

As mentioned previously, one requirement of the developed process was to minimize the secondary waste generation from the decontamination process. The objective of this task in the program was to accomplish waste minimization by means of recycling of the spent solvent. After the decontamination process has been performed, removed radionuclides will be present as dissolved species in the chelating solution. The objective of the tests performed in this program was to develop a process to break the chelant-contaminant bond, remove the dissolved contaminants from solution, and to regenerate the chelant solution.

A combination of precipitation and ion exchange techniques were successful in achieving the project recycle objectives. The ammonium carbonate solvent recycle test program resulted in five successful methods for removing uranium from the spent ammonium carbonate solvent. In each case the uranium content was reduced to less than the detectable limit of 3.0 ppm as determined by ICP (greater than 99.9% removal). The preferred methods of recycle were:

1. solvent pH reduction to 1.0 followed by the application of strong acid cation resin regenerated in the hydrogen form
2. application of strong base anion resin regenerated in the carbonate form at the existing solvent pH

The treatment process using anion resin in the carbonate form appeared to be most suitable for recovery applications, because it removes only uranium from solution. This method is relatively simple to apply and regenerates the solvent for reuse.

Recycle of the spent EDTA/ammonium carbonate solution proved much more difficult than the recycle of the carbonate-only solvent. Precipitation techniques were not successful in achieving the desired removal efficiency so that the solvent could be reused. Conventional ion exchange techniques were successful in achieving greater than 99.9% removal efficiency; however, resin usage was considered excessive.

Purolite S-940 cation resin in the hydrogen form was found to achieve the desired removal efficiency of greater than 99.9%. This uranium selective resin also provided an adequate exchange capacity. Since this is a cation exchange resin, it was first necessary to drop the solvent pH to expel carbonate prior to passing the solvent through the ion exchange column. Gas blockage of the columns occurred with cation resins if solvent was passed at its as-received pH of about 9.0. Therefore, reduction in pH was required prior to treatment. This technique could be used to recycle either solvent system.

BENCH SCALE TESTING

The purpose of bench scale tests was to evaluate the solvent system developed in the refinement testing under dynamic test conditions that more closely simulated the conditions of actual field application. The test procedures developed during this testing were to be used as the basis for procedures for the planned pilot plant testing.

Testing was performed in B&W's low temperature chemical cleaning velocity test apparatus. The basic flow loop was found to be adequate to apply and control the process. Hydrogen peroxide could easily be spiked, and temperature control could be maintained. It was important to have on line cooling capabilities during the low-temperature phase of the process. This was especially true during the final H_2O_2 spike when dissolved metal ions were present to catalyze the various exothermic reactions.

There was essentially no corrosion without EDTA being present in the solvent system. Thus, it was shown that EDTA will be required to effect consistent base metal corrosion for release of contamination below the surface of the equipment being decontaminated. EDTA also appeared to stabilize the dissolved uranium, preventing it from dropping out of solution during the cooldown phase of the process.

PILOT PLANT TESTING

The purpose of the pilot scale tests was to evaluate the solvent system on a larger scale using actual pieces of process equipment contaminated with uranium. These tests were to simulate field conditions on a small scale. The test procedures developed for the pilot plant were to be used as models for the Phase II field demonstration. A second objective of this testing was to determine if the solvent recovery process developed earlier in the program could be successfully applied on a pilot scale.

Testing was performed in a pilot plant facility designed and fabricated for this purpose. The test rig was found to be adequate to apply the process, although some limitations were noted. Solvent cooling immediately after a peroxide spike, when the solvent contained relatively high levels of dissolved ions, was only marginally effective, resulting in rapid H_2O_2 decomposition. Thus, a need for on-line cooling capability immediately after the peroxide injection point in the system was identified.

During the pilot scale testing, contaminated stainless and carbon steel components were exposed to the two solvents, using the chosen application scenario. All stainless steel material showed decontamination removal efficiencies of greater than 99%. Decontamination efficiencies for the carbon steel components were considerably less; however, much of the carbon steel surface was covered with a tar-like coating or iron oxide layer. It is believed that the coating and oxide layers shielded the uranium from the solvent, thus reducing its dissolution efficiency. The removal of oxides by the solvent system could easily be enhanced by modifying application parameters. Removal of tar and paint layers is beyond the scope of the developed solvent system; however, it is unlikely that inside surfaces of process equipment and piping would be coated. It is anticipated that the contaminated material available at the Phase II demonstration site will be representative of process equipment requiring decontamination throughout the DOE complex.

Essentially no corrosion occurred with the carbonate-only solvent. It was demonstrated that EDTA is required for consistent base metal corrosion; therefore, the EDTA/carbonate/peroxide formulation would likely be the solvent of choice for field use.

Pilot scale solvent recovery tests were successful. EDTA was recovered from solution by precipitation, and the dissolved uranium concentration in spent solvent was reduced by at least 99.4% using ion exchange techniques. Heavy metals (specifically iron) were also removed by cation exchange to acceptable discharge levels.

Hydrogen peroxide concentration was shown to be an important process variable that needs to be monitored and controlled during solvent application. An analytical procedure suitable for use with this process was identified.

CONCLUSIONS

Based on the results of the Phase I testing, two solvent systems are 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 .

From the data generated in this program, it appears that the carbonate/peroxide solvent should be effective for removal of surface uranium contamination. This solvent is also easier to recycle than the solvent containing EDTA. The addition of chelant is necessary for decontamination of material with contamination buried deeper in the metal surfaces. In such cases, the EDTA results in the required higher base metal corrosion during high temperature application of the solvent.

Based on this rationale, the application scenario for the process developed in this program is as follows:

1. Two hours at room temperature
2. Heatup to 93°C and hold for approximately four hours
3. Cooldown to room temperature
4. Inject peroxide to remove additional uranium contamination uncovered by the high temperature exposure
5. Two hours at room temperature.

Recycle of the solvent with a combination of precipitation and ion exchange techniques is feasible. Various techniques can be used with the carbonate-only solvent. Purolite S-940 cation resin in the hydrogen form was found to achieve the desired removal efficiency of greater than 99.9% with either the EDTA/carbonate solvent or the carbonate-only solvent system. This uranium-selective resin also provided an adequate exchange capacity. Since this is a cation exchange resin it is necessary to drop solvent pH, to expel carbonate, prior to passing the solvent through the ion exchange column.

The process application equipment requires the capability to spike hydrogen peroxide into the flowing stream, and to maintain temperature control. It is important to have on-line cooling capabilities during the low temperature phase of the process. This is especially true during the final H_2O_2 spike, when dissolved metal ions may be present to catalyze the various exothermic reactions.

RECOMMENDATIONS

Because of the excellent results obtained in this program it is recommended to continue to the field demonstration phase of this program (Phase II). A DOE site with a specific need for this technology is Fernald, which has extensive uranium contamination, along with a variety of equipment and piping systems. The contamination levels are suitable for a demonstration of the developed process. B&W and FERMCO have worked successfully together at this site. Therefore, the recommended site for the field demonstration is Fernald. Information on the cost of equipment and chemicals required for the demonstration are included as Appendix A.

Both of the basic solvent systems described in the preceding discussion should be considered for the field demonstration. The carbonate-only system is applicable to removal of surface uranium contamination on process equipment. If the contamination is more difficult to reach, or if the nature of the contamination is unknown, it is recommended that the EDTA/carbonate solvent system be utilized.

It is further recommended that the solvent be recycled for the field demonstration by first adjusting the pH to less than 2.0 and subsequently treating the solution with Purolite S-940 cation resin, regenerated in the hydrogen form. Note that if a carbonate-only solution is used, it is also acceptable to recycle the solvent without pH adjustment using a strong base anion resin regenerated in the carbonate form.

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 (DOE Contract Number DE-AC21-93MC30168), the Babcock & Wilcox Company (B&W) is developing a chemical decontamination process using chelating agents to remove uranium compounds and other actinide species from process equipment. The objective of the program is to develop a process to (1) reduce the level of surface contamination on process equipment to a level allowing for recycle of the materials of construction, (2) to reduce the volume of contaminated material and, hence, reduce disposition costs, and (3) to recycle the chelating solvent, thereby minimizing the generation of secondary waste streams. This project is divided into two separate phases:

Phase I - Process Development

Phase II - Field Demonstration

Phase I is further divided into four major technical tasks as follows:

Task 2 - Chelant Chemistry/Process Optimization

Task 3 - Solvent Recycle/Contaminant Volume Reduction Tests

Task 4 - Bench Scale Testing

Task 5 - Pilot Plant Study

Task 1 encompassed the generation of NEPA information required prior to the start of testing.

Volume 1 of this report describes the technical approach utilized, and summarizes results of Phase I activity under DOE contract DE-AC21-93MC30168. Volume 2 contains the individual Topical Reports on Tasks 2 through 5 of Phase I. Information included in the Topical Reports includes detailed descriptions of the test procedures and test apparatus utilized in each Task, as well as the raw data generated, discussion and interpretation of results, conclusions and recommendations.

2.0 BACKGROUND/OBJECTIVES

2.1 Overall Program Background/Goals

The work described herein was 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. This equipment may or may not be used for the full scale demonstration. However, it was used as the basis for the project plan. 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.

The generic goal of this program was to develop a solvent capable of chelating uranium and other actinides, while having little or no effect on base metal constituents. This selectivity is required to eliminate the potential for the chelating capacity of the solvent to be exhausted by metallic species, such as iron, which might be present in overpowering quantities. A second requirement of the process is the ability to control corrosion of the base metal. In cases where materials are surface contaminated only, and reuse of the equipment is a possibility, corrosion should be controlled at a low rate. However, in cases where contamination has migrated into the grain boundaries of the base metal, a more aggressive solvent is required, to corrode away base metal and expose the radioactive species for removal.

2.2 Specific Task 2 (Chelant Screening/Refinement) Objectives

The specific goal of this task was to first perform laboratory screening tests to identify the best solvents for the selective chelation of uranium. The best solvents from the screening test program were then carried forward into the refinement phase of this task. The specific objective of the refinement tests was to optimize the solvent application parameters and to define the process application sequence for the subsequent bench scale and pilot plant tests.

2.3 Specific Task 3 (Solvent Recycle/Contaminant Volume Reduction) Objectives

The objective of this task in the program was to accomplish waste minimization by means of recycling the spent solvent. After the decontamination process has been performed, removed radionuclides will be present as dissolved species in the chelating solution. The objective of the tests performed under this task was to develop a process to break the chelant-contaminant bond, remove the dissolved contaminants from solution, and to regenerate the chelant solution.

2.4 Specific Task 4 (Bench Scale Testing) Objectives

The purpose of the bench scale tests was to evaluate the solvent systems developed in Task 2 under dynamic test conditions that more closely simulate the actual field application. This was the first set of tests required for scale up of the candidate processes. The test procedures developed from the testing were also used as models for the Task 5 pilot plant testing.

2.5 Specific Task 5 (Pilot Plant Study) Objectives

The pilot plant testing involved the application of the developed process to contaminated equipment from B&W's Naval Nuclear Fuel Division. One step in the development of any decontamination process is testing on an artifact that closely approximates the material requiring decontamination. The goal of this task was to verify the performance of the developed process on a pilot scale, as applied to actual contaminated scrap.

3.0 TASK 2 - CHELANT SCREENING/REFINEMENT TESTING

3.1 Introduction

The use of chelating agents for the chemical cleaning and decontamination of nuclear steam generating equipment is well known. Ethylenediaminetetraacetic acid (EDTA)-based solvents are currently state-of-the-art technology for the dissolution of magnetite (Fe_3O_4), copper, and other metals and metal oxides from the secondary side of nuclear steam generators. Technologies developed for the decontamination of commercial nuclear power reactors (eg. LOMI and CANDEREM processes) also utilize chelating agents; these processes have been tailored for the removal of metal oxides which are radioactive either from having spent time in-core or from incorporation of radioactive ions in solution into the oxide lattice as it grows on the metal surface. Thus, the vast majority of information available on cleaning and decontamination using chelants does not specifically apply to the removal of actinides.

The approach taken in this program was to build on the chemical cleaning expertise acquired by Babcock & Wilcox during the development and qualification of the Electric Power Research Institute/Steam Generator Owners Group (EPRI/SGOG) chemical cleaning process (Reference 3). The mechanism of the technology proposed for development was similar to that of the referenced process, and entails the formation of stable complexes between the chelant and contaminant species. Metal ions possess reactive sites at which the activity of the metal is centered. To inhibit the reaction of a metal ion, it is necessary to introduce a material which forms a stable complex with metal ions, and thus, blocks the reactive sites of the metal ion. When used appropriately, chelating agents can effectively stabilize a metal ion in solution. Stabilization of the metal ion in solution also shifts the metal to ion equilibrium and allows chelating solutions to continuously promote dissolution of metals into the solution phase (Reference 4). Chelating agents have been successfully used for a number of years in the chemical cleaning industry for deposit dissolution.

A series of beaker tests were performed to determine the optimum solvent and application process to achieve the objectives of the test program. A detailed description of the Task 2 test results can be found in the Task 2 topical report, which, along with the other task specific reports, can be found in Volume 2 of this report. The following is a summary of the task results.

3.2 Chelant Screening Tests

The goal of this subtask was to perform laboratory screening tests to identify the best solvent for the selective chelation of uranium. As a first part of this task, a literature search was conducted to select organic chelating agents for screening. The criterion for selection was the ability of the chelant to complex the various forms of uranium expected to be present on the compressor surfaces. Numerous references were located that described laboratory evaluations of the stability constants of uranium chelates (References 5-18).

Attempts were made to procure several chelating agents described in the literature as forming stable complexes with various forms of uranium. The majority of these compounds were not available for purchase from organic chemical vendors; of those that were available,

most were too expensive for practical application to decontamination requirements of the magnitude identified. A third consideration in the selection of candidate chelating agents was the status of EPA approval for utilization of the chemical; in the planning stages of the project, DOE personnel indicated that EPA approval was a requirement for application of the process in the field demonstration.

Based on these considerations, the screening tests were initiated using three readily available chelating agents; namely, EDTA (ethylenediaminetetraacetic acid), HEDTA (hydroxyethylethylenediaminetriacetic acid), and DTPA (diethylenetriaminepentaacetic acid). All three of these chelants are known to form strong complexes with uranium. The choice of these three candidates was consistent with contractual program objectives, which specified evaluation of readily available, cost effective chelants with a well developed knowledge base regarding their application.

Proprietary chelants were also included in the test program. The goal of the program was always to utilize readily available nonproprietary compounds, if possible. However, to provide the best chance for success, it was necessary to draw upon all available resources. As presented in the Task 2 topical report, none of the proprietary chelants outperformed the basic, readily available chelants. Therefore, no data will be presented in this summary report with regards to the proprietary products (the detailed data is available in Volume 2).

3.2.1 Test Procedure

The purpose of the screening tests was to select three solvents for refinement testing, based strictly on their ability to chelate uranium. The deposit material chosen for dissolution testing was uranium dioxide (UO_2), since it was felt to represent one of the least soluble contaminants potentially present on contaminated process equipment. Each candidate chelant was subjected to several screening tests, run at varying pH's with different additives. The screening tests were conducted in three-liter four-neck reaction flasks. A schematic of a typical solvent screening test flask arrangement is shown in Figure 1.

Prew weighed corrosion test specimens of carbon steel, Monel 400 and Nickel 200 were placed in the reaction flask prior to solvent injection, for corrosion monitoring by weight loss determination. These materials were selected based on the equipment from the gaseous diffusion plant at Oak Ridge, Tennessee, which was being used as the preliminary basis for development of the solvent systems.

3.2.2 Results - Solvent Screening Tests

The main criterion used for selecting solvent systems for further evaluation was rate of uranium dissolution, as determined by dissolved uranium analysis of the samples removed from the test flasks. These values were confirmed by the total amount of uranium dissolved, based on weight loss of the deposit added to the test flask. The absence of localized corrosion attack was also a selection criterion. As previously stated, details of all of the screening tests can be found in Volume 2 of this report.

Figure 1
Schematic of Typical Solvent Screening
Test Flask Arrangement

Each of the three candidate chelants (EDTA, HEDTA, DTPA) and select proprietary chelants were initially tested at 93°C (200°F) at an initial pH of 5.5, 7.0, and 9.0. The results were similar for all of these tests; only a small amount of the uranium dioxide added to the test flask (1%-4%) dissolved, generally during the first few hours of exposure. In an attempt to improve the uranium dissolution, the follow-on tests were then performed at a lower pH (2.5-3.2), achieved by adding citric or formic acid to the solvent formulation. These organic acids have also been used in the chemical cleaning industry successfully for removal of deposits from power generating equipment. These formulations, however, showed no improvement in uranium dissolution.

A decision was then made to test chelants in conjunction with hydrogen peroxide and carbonate salts. The combination of peroxide and carbonate has been applied to the dissolution of uranium compounds in the mining industry (oxidation of uranium to the +6 valence state by peroxide, followed by complexation with carbonate, References 19-21), and to the dissolution of copper compounds in the chemical cleaning industry. The testing was performed at room temperature, due, in part to the known potential for violent reaction between peroxide and organic materials. In addition, it is easier to maintain oxidizing conditions with H₂O₂ at lower temperatures.

The combination of chelant, ammonium carbonate, and hydrogen peroxide at an initial 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. Results were equivalent for each of the three tested chelants.

Further testing was then performed using an EDTA/ammonium carbonate/hydrogen peroxide solvent. EDTA was selected as the most favored of the three candidate chelants based on its lower cost and the large information base regarding its application, developed for chemical cleaning applications. Several tests were performed to determine the effect of the chelant on the dissolution process. Results indicated that dissolution was 95% to 100% complete using a solvent containing peroxide and carbonate only; dissolution occurred slightly more rapidly, and to 100% completion, with the solvent containing chelant. These results are shown graphically in Figure 2.

3.3 Solvent Refinement Tests

The original test plan allowed for three solvents to be carried forward from the screening to the refinement portion of the program. Based on screening results, it was decided that two solvents would be carried forward on the basis of their performance. Those selected for development were:

- (1) EDTA, ammonium carbonate, and hydrogen peroxide: pH 9.0 with NH₄OH
- (2) ammonium carbonate and hydrogen peroxide: pH 9.0 with NH₄OH.

The third solvent chosen for refinement testing was a proprietary formulation that had not dissolved uranium effectively during screening tests. The manufacturer had requested that a

Figure 2
Comparison of Uranium Dioxide Dissolution for
Carbonate/Peroxide Solvent With and Without Chelant

reformulation of the solvent be further tested. Additionally, during screening, this solvent had exhibited corrosivity toward carbon steel, a secondary requirement of the developed process. During refinement testing, however, none of the proprietary formulations matched the performance of the two basic solvent systems and will not be discussed herein. As previously stated, details of all testing can be found in Volume 2 of this report.

The purpose of refinement testing was to vary solvent parameters in an attempt to optimize solvent effectiveness. The goal was to optimize performance while minimizing the amount of chemicals used to reduce costs as well as the generation of secondary waste. Parameters investigated were alternate oxidants, solvent constituent concentrations and application scenarios.

3.3.1 Results - Solvent Refinement Tests

The effect of carbonate on the dissolution process was evaluated. A solvent containing just chelant and peroxide was found to dissolve only 16% of the uranium dioxide placed in the test flask. These results indicated that complexation of the uranium by carbonate was essential to the dissolution process. It is likely that a mixed chelate complex was formed in the presence of carbonate and EDTA (Reference 22); this assumption was supported by color differences observed between solutions containing uranium dissolved by carbonate alone, and by mixed carbonate/EDTA solvents.

Further testing was also performed to evaluate the possibility of using an oxidant other than hydrogen peroxide in the solvent. Oxidants evaluated included air, oxygen, sodium nitrite, potassium bromate and ferric chloride. Limited success was achieved with bromate and ferric chloride; however, application temperature had to be increased to 66°C.

Figure 3 shows graphically the comparative effectiveness of three different solvent compositions. Solvent containing chelant, carbonate, and peroxide effected 100% dissolution within four hours. The same solvent, minus carbonate, dissolved 16% of the available UO_2 . Solvent containing chelant and carbonate, applied with an oxygen sparge, dissolved only 5% of the deposit in the test flask.

At this stage of testing the basic solvent formulation was as follows:

100 g/L EDTA
15 g/L $(\text{NH}_4)_2\text{CO}_3$
2.5 g/L H_2O_2
pH 9.0
Room Temperature Application

The solvent constituent concentrations were then varied and it was found that the basic solvent system was effective over a wide range of concentrations. This could allow for tailoring the solvent for differing levels of contamination and to minimize chemical usage. Results of the test program demonstrated the importance of tailoring the solvent system to different process application conditions.

Figure 3
Comparison of Uranium Dioxide Dissolution for
Varying Solvent Compositions

One of the refinement tests with corrosion coupons (designated as Test 64 in Volume 2) used the carbonate-only system with all solvent constituents at their lowest tested concentration:

10 g/L $(\text{NH}_4)_2\text{CO}_3$
2.5 g/L H_2O_2
pH 9.0
4 g/L UO_2 Deposit Added To Test Flask
Room Temperature Application

The test duration was eight hours. Corrosion loss was low and uniform. The 1018 carbon steel corrosion was $0.86 \mu\text{m}$ (0.034 mils). This calculates to the very low corrosion rate of $0.11 \mu\text{m/hr}$. The corrosion loss on the Nickel 200 and Monel 400 were both $0.05 \mu\text{m}$ (0.002 mils).

The surprising result from Test 64 was the low uranium oxide dissolution. Less than 60% of the UO_2 added to the test flask was dissolved. Based on the previous testing, 100% dissolution was expected. The low corrosion rate of the coupons was not expected to affect the overall UO_2 dissolution effectiveness.

Closer examination of the data revealed rapid H_2O_2 depletion during Test 64, as compared to earlier tests. It was theorized that the presence of the metal coupons helped to catalyze the H_2O_2 decomposition, resulting in a peroxide concentration too low to effect complete dissolution. This theory was investigated further in follow on testing. These results are graphically presented in Figure 4.

From Figure 4, it is evident that the addition of corrosion coupons affected the uranium dioxide dissolution. An increase in metal surface area in the system necessitated an increase in the initial H_2O_2 concentration in order to maintain a peroxide level sufficient to effect complete dissolution. This fact will need to be factored into the solvent formulation as it is being tailored for a specific application.

3.3.2 Foam Application Testing

A secondary part of the refinement testing was to run a series of tests with the selected solvents to determine if they could be used effectively in the foam state. Some of the process equipment requiring decontamination at DOE sites is very large; foam cleaning is an industrial process used to clean large components. Additionally, foam decontamination technology is currently being developed, as it has shown waste reduction of 70% over present decontamination methods (Reference 23). In this method of solvent application, the foam is the transport medium which carries the solvent to the metal surfaces, reducing the amount of solution required for coverage. The normal procedure for generating foam is to add a surfactant to the solvent and inject air (or an inert gas) below the liquid surface. Bubbles formed by the sparge are directed to the vessel or component to be cleaned by the slight positive pressure of the sparge gas.

Figure 4
Effects of Coupons and Peroxide Concentration
On Uranium Dissolution

A series of laboratory tests was run to determine if the selected solvents could be applied in the foam state. These tests are described in detail in Volume 2 of this report. The foaming tests were successful in showing that uranium dioxide can be dissolved by the EDTA/carbonate/peroxide solvent in the foam state. However, a significant portion of the deposit was dissolved after it dislodged from the binder coupons, and dropped into the liquid. Several tests were subsequently run in an attempt to develop an improved binder which would hold the deposit on the test specimen while dissolution took place. However, an appropriate binder was not generated by this study.

The foaming tests were considered as a qualified success. From the limited data generated in this phase of the program, it appeared that the EDTA/carbonate/peroxide solvent developed in this program could be effectively applied in the foam state. The lack of a suitable test coupon to bind the uranium dioxide for the foam tests limits the broad applicability of the test results. The results were, however, sufficiently promising to warrant further investigation of the foaming process.

It was recommended that additional foam tests be performed with a more suitable test coupon. This could be actual contaminated material, if available. The low application temperature and the relatively short time required for uranium dioxide dissolution make the EDTA/carbonate/peroxide solvent particularly adaptable to foam cleaning.

3.3.3 Process Application Testing

As a final phase of the refinement testing, various application scenarios were simulated to evaluate their effect on dissolution and corrosion. The results of these final tests were used to develop the recommended process for the bench scale and pilot scale testing. Two solvents were selected for process development testing. The compositions of the two solvents were as follows:

Solvent A 50 g/L EDTA
 20 g/L $(\text{NH}_4)_2\text{CO}_3$
 5.0 g/L H_2O_2
 pH 9.0 with ammonium hydroxide

Solvent B 20 g/L $(\text{NH}_4)_2\text{CO}_3$
 5.0 g/L H_2O_2
 pH 9.0 with ammonium hydroxide

The purpose of the process development testing was to simulate several potential solvent application scenarios in order to evaluate their effect on uranium dissolution and corrosion. The two application scenarios tested were as follows:

Scenario #1 - Application of solvent two hours at room temperature (to dissolve surface uranium contamination), followed by heatup to 93°C (or 66°C) and hold for four hours (to corrode and remove base metal), then cooldown to room temperature, spike with peroxide and hold two hours (to chelate remaining uranium),

and

Scenario #2 - Application of solvent at 93°C (or 66°C) for four hours (to remove base metal), followed by cooldown to room temperature, spike with peroxide and hold four hours (to chelate uranium).

The results of testing on Scenario #1 indicated that requirements for uranium dissolution efficiency could be met by either solvent using this application sequence. The carbonate-peroxide solvent exhibited negligible corrosion rates as applied; the EDTA solvent showed general corrosion rates sufficient to remove 1.5 mils (38 μ m) of carbon steel during a four hour exposure at 93°C.

The results of testing on Scenario #2 indicated that requirements for uranium dissolution efficiency could be met if hydrogen peroxide were included in solvent formulation during the heatup to high temperature application. However, uranium dissolution after the high temperature step with the EDTA solvent was complicated due to the high level of dissolved metal ions produced by the corrosion of base metal during the application. The presence of these metal ions makes it more difficult to maintain the concentration of hydrogen peroxide required for uranium dissolution. Additionally, corrosion rates observed for the EDTA solvent using this scenario were somewhat erratic.

It was therefore recommended that Scenario #1 be utilized for the bench- and pilot-scale testing of the selected solvent systems:

1. Two hours at room temperature
2. Heatup to 93°C and hold for approximately four hours
3. Cooldown to room temperature
4. Inject peroxide to remove additional uranium contamination uncovered by the high temperature exposure
5. Two hours at room temperature.

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

4.0 TASK 3 - SOLVENT RECYCLE/CONTAMINANT VOLUME REDUCTION

4.1 Introduction

As mentioned previously, one requirement of the developed process was to minimize the secondary waste generation from the decontamination process. The objective of this task in the program was to accomplish waste minimization by means of recycling the spent solvent. After the decontamination process has been performed, removed radionuclides will be present as dissolved species in the chelating solution. The objective of the tests performed in this program was to develop a process to break the chelant-contaminant bond, remove the dissolved contaminants from solution, and to regenerate the chelant solution.

B&W has performed laboratory research on the removal of iron from EDTA chemical cleaning solutions. Two approaches were applied. The first technique, in which solution pH was increased to 11, resulted in a filter cake of precipitated contaminant and a regenerated solvent solution. A second method broke the chelant-contaminant bond by reducing the solution pH to < 1.5 , resulting in formation of the insoluble tetraacid EDTA. It was demonstrated that the precipitated EDTA could be filtered and stored for reuse.

Another technique which was investigated during this study is ion exchange. Ion exchange is the process of removing ions from solution in an equivalent exchange for other, preferred, ions supplied by a solid material having a special structure to do this. This solid ion exchange material (resin) must either be recharged periodically with the preferred ions or discarded. For this application, the likely preferred approach would be to discard the resin as a solid radioactive waste.

Tests were run to evaluate whether these techniques could be used on the selected solvent systems for regeneration of the spent solution. Primary emphasis was placed on removing the contaminants from solution and regenerating the solvent.

As described in Section 3, 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 .

Recycle testing was performed separately on the two decontamination solutions. A summary of the results of the testing are presented separately in the following sections. Details of all of the recycle testing can be found in Volume 2 of this report. The dissolved uranium content of the test solutions was analyzed before and after treatment. The success criteria established for this testing was a dissolved uranium removal efficiency from the solvent of greater than 99.9%.

4.2 Treatment of Spent Ammonium Carbonate Solvent

The first set of recovery tests was run on the spent solvent containing only the ammonium carbonate. The solvent was treated by means of pH adjustment, to effect precipitation, and also by ion exchange. Spent ammonium carbonate solvent from Task 2 of this program was used for testing under this task. The initial pH of the test solution ranged from 9.0 to 9.1. The dissolved uranium content of this spent solvent was 3778 ppm. In all cases the treated solvent was analyzed for dissolved uranium for comparison to this original dissolved uranium content.

Table 1 contains a summary of representative tests performed using precipitation techniques to treat the spent ammonium carbonate solution. Removal of uranium by ion exchange resin was also evaluated using the spent ammonium carbonate solution. A 1 inch diameter column was loaded with 150 mL of resin. In some instances the spent solvent was pretreated. The same spent solvent as used in the precipitation phase of the program was used during the ion exchange phase (3778 ppm dissolved uranium). Table 2 contains a summary of the tests performed using ion exchange techniques to treat the spent ammonium carbonate solution.

Table 1
Results - Treatment of Spent Ammonium Carbonate Solutions
By Precipitation Techniques

Starting Solvent: 3778 ppm Dissolved Uranium - pH 9.1

Test #	pH Adjustment	pH Additives	Other Chemical Additives	Dissolved Uranium (ppm)	Removal Efficiency (%)
1	12.5	NaOH	None	1468	61
3	1.29/12.5	HCl/NaOH	None	10.3	99.7
5	9.8/12.5	Ca(OH) ₂ / NaOH	N ₂ H ₄	480	87.3
7	1.0/9.8/ 12.5	HCl/ Ca(OH) ₂ / NaOH	None	<3.0	>99.9
9B	2.0	HNO ₃	Na ₃ PO ₄	<3.0	>99.9

Table 2
Results - Treatment of Spent Ammonium Carbonate Solutions
By Ion Exchange Techniques

Starting Solvent: 3778 ppm Dissolved Uranium - pH 9.0

Test #	pH Adjustment	Resin Type	Resin Form	Dissolved Uranium (ppm)	Removal Efficiency (%)
10	None	Strong Acid Cation	Hydrogen	NA*	NA*
11	1.0 with H ₂ SO ₄	Strong Acid Cation	Hydrogen	<3.0	>99.9
12	None	Strong Base Anion	Hydroxide	<3.0	>99.9
13	None	Strong Base Anion	Carbonate	<3.0	>99.9

* Not Applicable, Gas Blockage of the Column - No Analysis Performed

Further discussion on these tests can be found in Volume 2 of this report. The ammonium carbonate solvent recycle test program resulted in five successful methods for removing uranium from the spent ammonium carbonate solvent. In each case the uranium content was reduced from 3778 ppm in the spent solvent to less than the detectable limit of 3.0 ppm as determined by ICP (greater than 99.9% removal). The five successful recycle 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 involving application of trisodium phosphate after reducing the solvent pH to 2.0.

The treatment process using anion resin in the carbonate form appears to have the best merit for recovery applications because it removes only uranium from solution. In essence this method regenerates the solvent for reuse, assuming there is not a large pickup of heavy metals such as copper and iron. The method of reducing the solvent pH followed by cation exchange complicates the process and removes both the uranium and carbonate from solution. The precipitation techniques also remove both the uranium and carbonate from solution.

4.3 Treatment of EDTA/Ammonium Carbonate Solvent

Spent EDTA/carbonate solvent from Task 2 of this program was used for testing under this task. The initial pH of the test solution ranged from 9.0 to 9.1. The dissolved uranium content of this spent solvent was 3704 ppm. In all cases the treated solvent was analyzed for dissolved uranium for comparison to this original dissolved uranium content.

Note that two laboratory test procedures were used in Task 2 with the solvent containing EDTA, ammonium carbonate and hydrogen peroxide. One procedure included a high temperature exposure of 66°C (150°F) and the other procedure included a high temperature exposure at a temperature of 93°C (200°F). Solvent recovery work used a considerable amount of solvent from both the 66°C and 93°C tests. It was found that the solvents exposed at the lower temperature were not adequately recovered while a procedure was developed to both remove the EDTA and uranium from the higher temperature tests. Note from Section 3, that the 93°C application became the preferred application scenario.

Table 3 contains a summary of representative tests performed using precipitation techniques to treat the spent EDTA/ammonium carbonate solution. Conventional ion exchange resins were also evaluated. The spent EDTA/carbonate solvent used in this ion exchange evaluation contained 3455 ppm dissolved uranium. Table 4 contains a summary of the results from these ion exchange tests.

Table 3
Results - Treatment of Spent EDTA/Ammonium Carbonate
Solutions By Precipitation Techniques

Starting Solvent: 3704 ppm Dissolved Uranium - pH 9

Test #	pH Adjustment	pH Additives	Other Chemical Additives	Dissolved Uranium (ppm)	Removal Efficiency (%)
15	<2.0/12.5	HCl/NaOH	None	3704	0
17	12.5/<2.0	NaOH/HCl	CaF ₂	3704	0
18	<2.0	HCl	NaOCl	1108	70.1
22	<2.0	HCl	Heat*	162	95.6

* Solution heated to 93°C (200°F) and held for 2 hours prior to pH adjustment

Table 4
Results - Treatment of Spent EDTA/Ammonium Carbonate
Solutions By Conventional Ion Exchange Techniques
Starting Solvent: 3455 ppm Dissolved Uranium - pH 9.0

Test #	pH Adjustment	Resin Type	Resin Form	Dissolved Uranium (ppm)	Removal Efficiency (%)
24	None	Strong Base Anion	Hydroxide	2000	42.1
25	<2.0 with H ₂ SO ₄	Strong Base Anion	Hydroxide	<3.0	>99.9%*
26	<2.0 with H ₂ SO ₄	Strong Base Anion	Carbonate	19.8	99.4
27	None	Strong Base Anion	Hydroxide	<3.0	>99.9%*
28	None	Strong Base Anion	Carbonate	60.2	98.3
29	<2.0 with H ₂ SO ₄ - 12.5 with NaOH	Strong Base Anion	Hydroxide	133	96.2

* Although >99.9% removal efficiency was achieved, the resin capacity was limited

The data from Tests 25 and 27 indicate that the required removal efficiency was achieved. However, the Table 4 values are for effluent samples collected after passing 150 to 200 mL of solvent through each column. Flow was continued through the columns and additional samples collected after processing more solvent. Test results showed unacceptable dissolved uranium levels after the additional flow. For example the Test 27 effluent was at 51.4 ppm dissolved uranium after processing a total of 450 mL of solvent. These tests show that uranium can be effectively removed by ion exchange. However, the resin has a very low capacity for uranium.

All testing up to this point with the spent EDTA solvent had shown that precipitation was not effective in reducing uranium content to less than 3.0 ppm and that conventional ion exchange resins were not economically feasible due to their low exchange capacity for uranium. Ion exchange was shown to be effective in removing uranium but the high dissolved ion content of the solvent rapidly depletes the resin capacity. At this point a number of resin vendors were

contacted to determine the availability of resins which have a high selectivity for uranium. A number of uranium selective resin samples were received and evaluated in this test program. Results of these tests are contained in Volume 2 of this report. One resin in particular provided excellent results.

These successful ion exchange tests were performed using a Purolite cation resin designated as S-940. This resin is classified as a chelating type with aminophosphonic acid functional groups. The resin is shipped in the sodium form, at a cost of \$345 per cubic foot. Per the manufacturer's instructions for this use, it was converted to the hydrogen form prior to testing. The resin regeneration level was 6 pounds of sulfuric acid per cubic foot. The spent solvent was first pH adjusted to <2.0 with sulfuric acid and the precipitate filtered. Solvent flow through the ion exchange column was established at 8 - 15 ml per minute. Samples of the resin column effluent were collected after passing 500 mL of solvent through the column. Uranium analysis showed the samples to contain less than 3 ppm dissolved uranium. The test was repeated several times with similar results. The 500 mL samples indicated that this resin had the capability of greater than 99.9% uranium removal efficiency with an associated reasonable capacity.

In summary, recycle of the spent EDTA/ammonium carbonate solution proved much more difficult than the recycle of the carbonate-only solvent. Precipitation techniques were not successful in achieving the desired removal efficiency so that the solvent could be effectively reused. Conventional ion exchange techniques were successful in achieving greater than 99.9% removal efficiency, however resin usage was considered to be excessive.

Purolite S-940 cation resin in the hydrogen form was found to achieve the desired removal efficiency of greater than 99.9%. Laboratory tests showed the S-940 to have a very adequate total exchange capacity of 0.19 pounds per cubic foot of resin. These tests were run using an exhausting solution containing only uranium in the solvent matrix. The uranium ion exchange capacity of the resin may be lower in the presence of other ions, such as iron and nickel.

Since the Purolite S-940 is a cation exchange resin, it is first necessary to drop the solvent pH to expel the carbonate prior to passing the solvent through the ion exchange column. Note that gas blockage of the column occurs with cation resins if the solvent is passed at its as-received pH of about 9.0. Therefore, reduction in pH prior to treatment is required.

When treating an EDTA/carbonate solvent that has experienced a high temperature exposure (minimum of two hours at 200°F), reducing the pH to less than 2.0 results in precipitation of EDTA. The precipitated material is not considered a waste stream, since it is in a form suitable for reuse in the solvent. The precipitation operation, in conjunction with the Purolite S-940 resin, allows for recycle of the solvent. The volume of secondary waste generated by the process is, therefore, the volume of ion exchange resin needed to remove the required amount of uranium from the spent solvent. This figure was not determined during the reported testing, but could be calculated by running sufficient spent solvent through a column to cause breakthrough of uranium. It is probable that the required resin volume is not greater than that which would be generated by precipitation of uranium.

4.4 Task 3 - Solvent Recycle Recommendations

If a carbonate-only solution is used for decontamination, it is recommended to recycle the solvent with a strong base anion resin regenerated in the carbonate form. If an EDTA/carbonate solution is used for decontamination, it is recommended to recycle the solvent by first adjusting pH to less than 2.0 and subsequently treating the solution with the Purolite S-940 cation resin regenerated in the hydrogen form.

If a combination of the two solvents is used, it is recommended to recycle the solvents by first adjusting pH to less than 2.0 and subsequently treating the solution with the Purolite S-940 resin. Based on the data generated in this program, this technique will be successful in obtaining greater than 99.9% uranium removal with either solvent system.

5.0 TASK 4 - BENCH SCALE TESTS

5.1 Introduction

The purpose of bench scale tests was to evaluate the solvent system developed in the solvent refinement test under dynamic test conditions that more closely simulated the actual field application. This was the first set of tests required for scale up of the candidate processes. The test procedures developed from this testing were used as the models for the pilot plant testing performed in Task 5. Corrosion coupons and plugs of uranium dioxide were loaded into a sealed reaction chamber. Solvent was circulated through the reaction chamber at a velocity approaching one foot per second. Samples were taken periodically and analyzed for dissolved uranium, iron, copper, nickel, and available chelant.

5.2 Test Program

The first phase of this task was to develop a suitable binder to use to make the UO_2 test plug. It was suspected that if loose UO_2 powder were used in the testing, it would immediately dissolve in the test solvents. A slower release of the UO_2 was desired to ensure the solvent remained active over a longer period under the dynamic test conditions. The use of UO_2 baked onto coupons was attempted during the foam testing in Task 2 of this program (see Task 2 Topical Report in Volume 2), but with little success. Plugs consisting of calcium carbonate, trisodium phosphate, silicon dioxide and mortar were evaluated and found to meet the objectives of the test program. The results of this plug evaluation are presented in Volume 2 of this report.

Two tests with each of the two candidate solvents were performed:

Solvent 1 (used in tests designated 1 and 3):

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)

Solvent 2 (used in tests designated 2 and 4):

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)

The UO_2 plugs and corrosion coupons of carbon steel, Nickel 200, and Monel 400 were exposed to the solvents under dynamic flowing conditions. The test was performed over a temperature range from ambient to 93°C (200°F). The solvent was periodically sampled and analyzed. The results of these four dynamic tests are included in Volume 2 of this report. These tests are summarized in the following.

5.3 Test Apparatus

The dynamic tests were performed in B&W's low temperature chemical cleaning velocity test rig. A schematic of the rig is provided as Figure 5. The rig contained a solvent reservoir; the solvent volume used for testing was seven (7) liters. Immersion heaters and a cooling coil were contained in the reservoir for rapid heating and cooling of the solvent as required. The solvent was sampled via a sample line contained in the stainless steel reservoir.

The other major components of the rig were the centrifugal pump, the magnetic flowrator and the test vessel. The stainless steel test vessel housed the UO_2 plugs and corrosion coupons.

5.4 Summary of Results - Bench Scale Testing

Figure 6 shows the dissolved uranium versus time for Test 1 (EDTA/carbonate solvent). Also included in Figure 6 is a curve of the test temperature versus time. Uranium dissolved throughout the entire exposure period. The majority of the dissolution occurred at the lower temperatures. It appears that dissolution was still occurring at the end of test.

At the end of the test, approximately 25% of the uranium added to the system was dissolved. A substantial portion of the plug was retrieved at the end of testing. The plug served the purpose of slow dissolution during the test exposure, but proved more robust than originally expected. The data from this test and all of the bench scale tests clearly showed that the solvent was actively dissolving uranium as it became accessible to the solvent. The uranium not accessible to the solvent was retained in the plug matrix.

Figure 7 shows the dissolved uranium versus time for Test 2 (carbonate only). Also included in Figure 7 is a curve of the test temperature versus time. As with Test 1, the majority of the dissolution occurred at the lower temperatures. It appears that dissolution stopped during the 93°C portion of the exposure and never restarted, even after the reduction in temperature and the spike of additional H_2O_2 . Uranium dissolution stopped at the same time as the dissolved calcium stopped increasing (note: dissolved calcium was used as a tracer of plug dissolution). As with all tests, the uranium accessible to the solvent was dissolved. The uranium stabilized in the plug did not dissolve.

It was necessary to use the cooling capability of the loop for both the initial low temperature exposure and also during the final low temperature exposure during this and all bench scale tests. The cooling coil was turned off during the final hour of Test 2 to see if the reactions could be restarted with the heat generated by the pump and the hydrogen peroxide reactions. The maximum temperature achieved was 32.2°C (90°F). As previously described, the dissolution reactions did not appear to restart during this exposure period.

Table 5 contains a summary of the dissolved metal analysis taken during Test 3 (EDTA/carbonate). Note that dissolved calcium is included in Table 5. The source of the calcium is the plug material (CaCO_3 and the mortar). As expected, the calcium was readily chelated by the EDTA. The dissolved calcium values indicate slow dissolution of the plug through the initial stages of the test exposure. During the 93°C exposure, dissolution of the plug apparently ceased.

Figure 5
Schematic of Bench Scale Test Loop

Figure 6
Total Uranium Dissolved
DOE Bench Scale Test Number 1

Figure 7
Total Uranium Dissolved
DOE Bench Scale Test Number 2

From Table 5 it is evident that the majority of the iron, nickel, and copper went into solution during the 93°C exposure period. This indicates that the majority of the corrosion occurred during the high temperature exposure, consistent among all tests.

Table 5
Dissolved Metal Analysis - Bench Scale Test #3

Sample I.D	[U] (g/L)	[Fe] (g/L)	[Cu] (g/L)	[Ni] (g/L)	[Ca] (g/L)
1 hr @ R.T. ¹	1.392	0.011	0.002	0.003	0.830
2 hr @ R.T.	1.915	0.013	0.002	0.003	1.022
0 hr @ R.T.	2.484	0.021	0.004	0.006	1.401
1 hr @ 93°C	2.484	0.044	0.004	0.016	1.492
2 hr @ 93°C	2.663	0.068	0.008	0.051	1.656
0 hr @ R.T. ²	2.664	0.073	0.011	0.070	1.712
1 hr @ R.T.	2.591	0.071	0.011	0.068	1.717
2 Hr @ R.T.	2.600	0.070	0.010	0.066	1.712

¹ R.T. = Room Temperature Exposure

² Upon Return to R.T. Prior to H₂O₂ Spike

Based on dissolved uranium analyses during Test 4 (carbonate-only), some uranium appeared to be dropping out of solution during the final cool down and peroxide spike phases. Based on this observation and the results of all four tests, the addition of the EDTA provides more consistent results and helps to stabilize the dissolved uranium.

Table 6 summarizes the corrosion results from all four tests performed during this phase of the test program. In all cases, corrosion loss was uniform with no localized attack evident. Overall, the corrosion results with the EDTA/carbonate solvent were more consistent than those from the carbonate only solvent.

Table 6
Corrosion Results - Bench Scale Testing

Material	Mils Corrosion*			
	Test 1	Test 3	Test 2	Test 4
AISI-1018	0.531	0.406	0.000	0.000
AISI-1018	0.536	0.254	0.000	0.001
Nickel-200	0.225	0.351	0.001	0.004
Nickel-200	0.224	0.402	0.000	0.002
Monel-400	0.116	0.203	0.044	0.001
Monel-400	0.121	0.166	0.044	0.001

* Tests 1 and 3 used the EDTA/Carbonate solvent while Tests 2 and 4 used the Carbonate-only solvent

5.5 Conclusions - Bench Scale Testing

The basic test loop used during this testing was adequate to apply and control the process. Hydrogen peroxide could easily be spiked and temperature control could be maintained. It was important to have on line cooling capabilities during the low temperature phase of the process. This is especially true during the final H_2O_2 spike when dissolved metal ions may be present to catalyze the various exothermic reactions.

The plug system utilized in this test program shielded some of the uranium dioxide from the solvent system. It was concluded that all of the uranium dioxide accessible to the solvent was dissolved. Most of the dissolution occurred during the low temperature phase of the application.

There was essentially no corrosion without the EDTA present in the solvent system. The EDTA is required to effect consistent base metal corrosion for release of contamination below the surface of the equipment being decontaminated. The EDTA also appears to stabilize the dissolved uranium, preventing it from dropping out of solution during the cool down phase of the process. Finally, the basic test procedures developed from this testing were considered suitable as a model for the pilot plant testing to be performed in Task 5.

6.0 TASK 5 - PILOT PLANT TESTING

6.1 Introduction

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. The decontamination of the uranium contaminated metal constituted the first phase of the pilot plant scale testing. These tests were to simulate field conditions on a small scale. The same test procedures with respect to solvent preparation and test parameters used in the laboratory were applied to the pilot plant tests. The second phase of the pilot plant testing consisted of solvent recovery tests.

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.

6.2 Overall Approach - Pilot Plant Decontamination Testing

The first phase of Task 5 was to perform pilot scale tests using the 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. The pilot plant test rig is schematically shown in Figure 8.

Three pilot scale decontamination tests were run using the two candidate solvents. 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 ((NH₄)₂CO₃)
5 g/L Hydrogen Peroxide (H₂O₂)
pH Adjusted to 9.0 with Ammonium Hydroxide (NH₄OH)

Carbonate-only Solvent:

20 g/L Ammonium Carbonate ((NH₄)₂CO₃)
5 g/L Hydrogen Peroxide (H₂O₂)
pH Adjusted to 9.0 with Ammonium Hydroxide (NH₄OH)

Figure 8
Schematic of Pilot Plant System

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. A large percentage of the surface area of the 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 they were the best available at the time of testing. It is anticipated that the contaminated material available at the Phase II demonstration site will be representative of process equipment requiring decontamination throughout the DOE complex.

6.3 Summary of Results - Pilot Plant Decontamination Test 1

Detailed data from the Task 5 pilot plant tests can be found in Volume 2 of this report. The following summarizes the Task 5 test results. Test number 1 was run using the EDTA/carbonate/H₂O₂ solvent described in Section 6.2. Approximately 50 gallons of EDTA solvent was prepared for this test. Eight pieces of contaminated metal were placed in the reaction chamber. The application scenario for pilot plant scale Test #1 is summarized in Table 7.

Table 7
Application Scenario - Pilot Scale 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 test results for the solvent samples collected during the test run are presented in Table 8. Examination of the Table 8 data indicates 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). For these specimens, only a small percentage of the contamination was removed during the second low-temperature exposure. From the dissolved iron values, it is evident that the majority of the corrosion occurred during the high temperature phase of the process. Again, this is consistent with the process development testing and the bench scale testing.

Note the absence of hydrogen peroxide values in Table 8. The H₂O₂ analysis was attempted by the pilot plant operators using the colorimetric method used in the previous testing in this program. 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. The testing in this program showed that 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 was found to be well suited for this purpose. Preliminary investigations verified this fact. Details of this procedure can be found in Volume 2 of this report.

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 (see Volume 2 for details). The beta decontamination efficiency was greater than 99.9% for all test materials. The 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%.

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 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 pH 9 dissolves iron oxides at a relatively slow rate at 93°C (Reference 3). This reaction rate can be increased by the addition of hydrazine, or by an increase in temperature to above 100°C.

Table 8
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

6.4 Summary of Results - Pilot Plant Decontamination Test 2

Test number 2 of the pilot scale test program was performed with the carbonate-only decontamination solvent described in Section 6.2. The Test 1 application scenario was used for Test 2 (Table 7) with the exception that the heatup ramp to 93°C required only 3 hours. Again, 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. 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.

The Test 2 decontamination efficiency for the alpha activity of the seven carbon steel pieces ranged from 23.3 to 82% while the beta decontamination removal efficiency ranged between 24% and 92% (see Volume 2 for details). 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 indicates that the carbonate solvent is less effective in dissolving uranium than the EDTA/carbonate solvent. Note, however, that most of the Test 2 specimens were carbon steel with coatings on their surface.

6.5 Summary of Results - Pilot Plant Decontamination Test 3

Because there was very poor dissolution of uranium in Test 2 with the carbonate-only solvent, 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 EDTA/carbonate/H₂O₂ solvent described in Section 6.2 was used for pilot plant Test 3.

The Table 7 test procedure was modified for Test 3. 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, additional peroxide injection and two hours of solvent recirculation at a target temperature of 29.5°C (85°F).

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 H₂O₂ 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 then back to the mix tank for cooling (refer to Figure 8). To ensure that the test chamber did not over flow, due to the H₂O₂ decomposition reactions, it was necessary to slow the peroxide injection rate. Injection occurred over a 15 minute span. With this scheme, solvent temperature was maintained under 35°C (95°F). However, it is suspected that the H₂O₂ was depleted below the level required for uranium dissolution during the first solvent change out in the test chamber. A more appropriate delivery scheme may have been to have the cooling capability in-line after the pump and just before the test chamber.

Based on the three specimens used for the interim examination, the second step was marginally effective in improving decontamination removal efficiency. An average improvement of about 6% was obtained during the extended exposure (see Volume 2 for details). It is possible that an improved peroxide injection scheme would have improved the efficiency of the second step.

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 duplicates 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 the final 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.

After the initial step, the dissolved iron in solution was 427 mg/L. The origin of the dissolved iron was corrosion of the coupon and the carbon steel specimens. At this time, the solvent was reconstituted with free EDTA. This resulted in a dilution effect, reducing the dissolved iron to 391 mg/L. Once temperature was increased, the dissolved iron once again began to increase at a rapid rate (final value of 736 mg/L at the end of the 93°C step).

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 2

** CS = Carbon Steel / SS = Stainless Steel

During this second exposure the dissolved iron increased even during the lower temperature exposure (final value of 910 mg/L). 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.

6.6 Pilot Plant Corrosion Results

The carbon steel coupon exposed during Test 2 exhibited essentially no corrosion loss. This was expected and consistent with past tests using the carbonate only solvent system.

The corrosion coupon exposed during Test 3 exhibited extensive corrosion loss during this test. Corrosion was determined at 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 the earlier program testing (See Volume 2 for details). During the earlier testing, the corrosion was less than 1.5 mils (38 μm). This higher corrosion during the pilot plant testing was 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 3):

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. During the initial beaker testing the solvent was tested in a closed beaker system. During pilot scale testing, 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.

6.7 Approach - Pilot Scale Solvent Recovery Testing

Recovery testing was performed based on the laboratory testing for recovery and treatment of the contaminated solvent (Section 4.0). The solvent systems were all treated in the same manner. The solution pH was reduced to less than 1.5. The precipitated EDTA was recovered as a slurry which was then filtered and washed to remove excess moisture and contaminants. The supernatant solution was pumped through a filter and cation ion exchange column for removal of uranium and heavy metals.

At the completion of decontamination testing, the 2 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 before Batch 2 before Batch 3 before Batch 4).

6.8 Results - Pilot Scale Solvent Recovery Testing

Detailed results of the recovery testing can be found in Volume 2 of this report. These results are summarized in this section. The uranium test results are presented in Table 10. Uranium test results 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 EDTA recovered for recycle has a very low uranium contamination, making it well suited for recycle.

Table 10
Total Uranium Results - Pilot Scale Solvent Recovery Testing

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 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 (Section 4.0). A decrease in efficiency to 99.4% was observed during the processing of Batch 3. It is suspected that the relatively high amount of dissolved iron (about 700 mg/L) in this batch affected the efficiency of the ion exchange column.

The iron ions were competing for the ion exchange sites. It is suspected that the removal efficiency would have improved if the batch would have 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.

Results for the recovery of EDTA were also quite good based on the amount of EDTA remaining in solution after acid addition. Batch numbers 2 and 3 were the two solvents which were primarily the EDTA based solvents from pilot plant Tests 1 and 3. The EDTA in Batches 1 and 4 was primarily a result of mixing the solvents when transferring to waste storage. Results show that the EDTA level in all solvents was reduced from a value as high as 23 grams/liter to 1.9 g/L or less. The resultant EDTA filter cake can be readily solubilized utilizing water and ammonia and the resultant solution can then be reused in further decontamination efforts.

6.9 Conclusions - Pilot Plant Tests

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, and the remaining pieces were coated with iron oxide. It is believed that the coating and oxide layers shielded the contamination from the solvent, thus reducing the effectiveness of the solvent for the dissolution of uranium.

As discussed earlier, solvent application parameters could be adjusted (addition of hydrazine, higher temperature) to provide for enhanced removal of iron oxide layers during decontamination. The removal of tar-like coatings is beyond the scope of the developed solvent system, and would require an additional step in processing. However, it is unlikely that inside surfaces of process equipment and piping would be coated.

The addition of the EDTA improved the solvent's performance; it also stabilized the uranium in solution. The EDTA made the solvent more versatile and would likely be the solvent of choice for field use. The carbonate-only solvent appears applicable for readily available surface contamination that can be removed by a single low-temperature application.

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, required prior to a field demonstration, were identified during the testing. The test rig needs to be modified to improve cooling during the H_2O_2 spikes, and to control solvent aeration to reduce the ferric ion corrosion during process application. Excessive corrosion of the decontamination equipment itself during operation could necessitate the replacement of system components and lead to excessive down time. Implementation of the proposed engineering changes will circumvent this potential problem.

In addition, H_2O_2 analyses were not obtained during Task 5; however, a field applicable procedure was identified. Real time peroxide analysis will be required for proper process control during field application.

7.0 PHASE II SITE DEMONSTRATION

During the course of Phase I activity, efforts were made to identify a DOE site with a specific need for the developed technology, willing to sponsor a demonstration. One site that meets these criteria is Fernald. The Fernald Facility is owned by the U. S. DOE and is located in southwestern Ohio, approximately 17 miles northwest of downtown Cincinnati. The total site area of 1050 acres includes 136 acres of former production facilities.

The Fernald facility was built during the early 1950's by the U.S. Atomic Energy Commission to process uranium ore concentrates into high purity uranium-metal products. Between 1953 and 1988 a wide variety of chemical and metallurgical processes at Fernald supported other DOE sites and defense programs. At the end of this period, the demand for such products decreased, and Fernald production was reduced until suspension on July 10, 1989. In August 1991, the facility name was changed to Fernald Environmental Management Project (FEMP), signifying the change in site mission to environmental restoration, waste management, and technology development.

The Fernald site has accumulated an inventory of nuclear material, low-level radioactive waste, mixed (radioactive and hazardous) wastes, and contaminated equipment/facilities. As a result of years of uranium metal production, equipment, buildings, soil and groundwater at the Fernald site have become contaminated and have the potential to impact public health and the environment. Site conditions are well characterized and documented; a variety of equipment and piping systems are represented, with contamination levels that are amenable to support the proposed project.

In December 1991, DOE issued a Request for Proposal for an Environmental Restoration Management Contractor to replace the traditional Management and Operations contract arrangement at the Fernald site. A consortium led by Fluor Daniel, Inc. was awarded the contract on August 11, 1992, and its subsidiary FERMC0 assumed responsibility for the contract on December 1, 1992. Completion of remediation is anticipated by the year 2019. FERMC0 has agreed to support work on the B&W proposed field test for solvent decontamination of process equipment.

B&W recommends the Fernald site as the location for the Phase II tests on the basis that the site has a diversity of uranium contaminated process equipment which is being decommissioned; B&W already has a trained field staff at this site which will help extend the scope of testing which can be accomplished within the projected budgets; FERMC0 will make available site services, to provide operations support, and to assist in the collection of test data at no extra cost to the test program, and prior environmental tests conducted by B&W NESI in cooperation with FERMC0 at this site have received excellent support from FERMC0. Information on the cost of equipment and chemicals required for the demonstration are included as Appendix A.

Appendix B contains a letter from FERMC0's Vice President of Technology, communicating interest in and support of DOE-METC and contractors for the site demonstration of the developed technology.

8.0 CONCLUSIONS

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

None of the elevated temperature (93°C) chelant-only solvent systems provided acceptable uranium dissolution. This included the proprietary and commercially available solvents evaluated in the program.

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 Phase I testing, 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 .

This type of combined solvent is promising for several reasons:

- (1) Since uranium dioxide was dissolved effectively at room temperature, the solvent could be utilized in surface decontamination applications without interference from chelation of iron, which does not occur readily at low temperatures.
- (2) The addition of carbonate and hydrogen peroxide does not complicate the secondary waste stream, since these are not hazardous materials.

There was essentially no corrosion without the EDTA present in the solvent system. The EDTA is required to effect consistent base metal corrosion for release of contamination below the surface of the equipment being decontaminated. The EDTA also appears to stabilize the dissolved uranium in the presence of competing ions in solution.

From the data generated in this program, the carbonate/peroxide solvent should be effective for removal of surface uranium contamination with a single low-temperature application. It is the easier solvent to recycle. The addition of chelant is necessary for decontamination of surfaces where the contamination is buried deeper in the metal surfaces. In this case, the EDTA results in the necessary higher base metal corrosion during the 93°C application phase of the decontamination process. The EDTA also stabilizes the dissolved uranium in solution. The addition of EDTA results in an overall more versatile solvent.

Testing in 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. The addition of corrosion coupons in the beaker tests affected the uranium dioxide dissolution. This necessitated an increase in the initial H_2O_2

concentration. The presence of the metal coupons helped to catalyze the H_2O_2 decomposition which apparently resulted in a peroxide concentration too low to effect complete dissolution. This will need to be factored into the solvent formulation as it is being tailored for a specific application. Peroxide is an important variable that needs to be carefully applied for optimum performance. This was evident from all of the testing covered by this report.

The foaming tests were considered to be a qualified success. From the limited data generated in this phase of the program, it appeared that the EDTA/carbonate/peroxide solvent developed in this program could be effectively applied in the foam state. The lack of a suitable test coupon to bind the uranium dioxide for the foam tests limits the broad applicability of the test results. However, the results were sufficiently promising to warrant further investigation of the foaming process.

The application scenario for the process developed in this program is as follows:

1. Two hours at room temperature
2. Heatup to 93°C and hold for approximately four hours
3. Cooldown to room temperature
4. Inject peroxide to remove additional uranium contamination uncovered by the high temperature exposure
5. Two hours at room temperature.

By starting with an initial low temperature application, all readily available uranium contamination is easily removed. Heatup to 93°C dissolves the remaining readily available uranium contamination. The 93°C application with EDTA present results in acceptable uniform corrosion. This is necessary to expose contamination buried more deeply into the component.

The ammonium carbonate solvent recycle test program resulted in five successful methods for removing uranium from the spent ammonium carbonate solvent. In each case the uranium content was reduced to less than the detectable limit of 3.0 ppm as determined by ICP (greater than 99.9% removal). The five successful recycle 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 involving application of trisodium phosphate after reducing the solvent pH to 2.0.

The treatment process using anion resin in the carbonate form appears to have the best merit for recovery applications because it removes only uranium from solution. In essence this method regenerates the solvent for reuse assuming there is not a large pickup of heavy metals such as copper and iron. The method of reducing the solvent pH followed by cation exchange complicates the process and removes both the uranium and carbonate from solution. The precipitation techniques also remove both the uranium and carbonate from solution.

Recycle of the spent EDTA/ammonium carbonate solution proved much more difficult than the recycle of the carbonate only solvent. Precipitation techniques were not successful in achieving the desired removal efficiency so that the solvent could be effectively reused. Conventional ion exchange techniques were successful in achieving greater than 99.9% removal efficiency, however resin usage was considered to be excessive.

Purolite S-940 cation resin in the hydrogen form was found to achieve the desired removal efficiency of greater than 99.9%. This uranium selective resin also provided an adequate capacity. Since this is a cation exchange resin it is first necessary to drop the solvent pH to expel the carbonate prior to passing the solvent through the ion exchange column. Note that gas blockage of the column occurs with cation resins if the solvent is passed at its as-received pH of about 9.0. Therefore, reduction in pH prior to treatment is required. This was the technique used to successfully process the solvent streams from the Task 5 pilot plant tests.

The basic process application loop needs the capability to spike hydrogen peroxide into the flowing stream and to maintain temperature control. It is important to have on line cooling capabilities during the low temperature phase of the process. This is especially true during the final H_2O_2 spike when dissolved metal ions may be present to catalyze the various exothermic reactions. The loop also needs to be designed to control solvent aeration, in order to reduce ferric ion corrosion during process application. This modification is required to eliminate the potential for excessive corrosion damage to the process application loop.

9.0 RECOMMENDATIONS

Because of the excellent results obtained in this program it is recommended to continue to the field demonstration phase of this program (Phase II). The recommended site for the demonstration is Fernald. Both of the basic solvent systems should be considered for the field demonstration.

- (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 .

The carbonate only system is applicable to remove surface uranium contamination on process equipment. If the contamination is more difficult to reach or if the nature of the contamination is unknown, it is recommended to utilize the EDTA/carbonate solvent system.

The process application loop utilized for the field demonstration needs to incorporate lessons learned from this program (ie., in-line cooling and control of solvent aeration) for proper process control. In addition, the Phase II demonstration decontamination should utilize the potentiometric titration method described in the Volume 2/Task 5 report for hydrogen peroxide analysis.

It is further recommended that the solvent be recycled for the field demonstration by first adjusting the pH to less than 2.0 and subsequently treating the solution with the Purolite S-940 cation resin regenerated in the hydrogen form. Note that if a carbonate-only solution is used it is also acceptable to recycle the solvent without pH adjustment using a strong base anion resin regenerated in the carbonate form.

It is also recommended that additional foam tests be performed with a more suitable test coupon. This could be actual contaminated material from the field demonstration site, if available. The low temperature application temperature and the relatively short time required for uranium dioxide dissolution make the EDTA/carbonate/peroxide solvent particularly adaptable to foam cleaning.

Basic cost information on the chemicals and equipment required for the Phase II site demonstration is attached as Appendix A. A cost benefits/comparison between the developed process and competing hard chemical decontamination technologies is a deliverable, per the current contract, with the Phase II Final Report. A meaningful cost comparison could not be generated with the information obtained during execution of Phase I, but will be developed at the conclusion of Phase II activity, when more information regarding field application costs for the process will be available.

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APPENDIX A

PHASE I FINAL REPORT

DOE CONTRACT DE-AC21-93MC30168

COSTS ASSOCIATED WITH PHASE II SITE DEMONSTRATION

EQUIPMENT COSTS

Modification of Phase I Pilot Plant Equipment for Fernald Site Demonstration

B&W will modify the test equipment used in Phase I tests for use at the Fernald site (a schematic of the proposed field demonstration solvent delivery system appears on the next page). The anticipated modifications include the revision of cleaning solution delivery and return piping. Cleaning solutions may then be diverted from the cleaning vessel used in Phase I tests to a circulating system having increased flow and heating capacity, which is connected to a supply header or manifold with three outlet connections. Suitable connections will be run from this manifold to reducer fittings which will be mounted on the ends of the contaminated pipe specimens to be cleaned. Similar connections will be provided for the solvent return lines.

A suitable support rack will be provided by B&W for all the pipe specimens which will allow the test specimens to be oriented either vertically or horizontally during the tests, and will include provisions for filling, draining, and drying the test specimens and for connecting the radiation survey equipment. Thermal insulation and a supplementary thermostatically controlled electric heater will also be provided to reduce the heat load on the mixing tank heaters. Cooling capability will also be included at this point. This will ensure that sections being cleaned will operate at the target temperatures. This feature will also reduce the time required to warm the system to test temperature.

Tanks and transfer pumps included in the pilot scale facility will be utilized in the modified equipment. A higher capacity circulating pump, exhaust blower for removal of ammonia vapor, and appropriate connecting tubing, fittings, and isolation valves will be procured for the modifications.

Total cost for procurement of the equipment to be used in the Fernald Site Demonstration is approximately \$15,000.

Schematic of Field Demonstration
Solvent Delivery System

CHEMICAL & RESIN COSTS

The costs of the chemicals that will be used in the Site Demonstration, when purchased in 100-pound quantities, are as follows:

Ammonium carbonate	\$0.76/pound
Ammonium hydroxide	\$0.40/pound
Hydrogen peroxide	\$0.86/pound
EDTA	\$2.09/pound

Based on the expected solvent composition of 50 g/L EDTA, 20 g/L ammonium carbonate, 5 g/L hydrogen peroxide (spiked twice during process application), pH adjusted to 9.0 with ammonium hydroxide, the approximate chemical cost per gallon of solvent will initially be \$1.18. The most expensive component of the solvent, EDTA (\$0.87/gallon), will be recovered and reused, thereby minimizing total solvent costs.

The cost of the ion exchange resin that will be used in the Site Demonstration is as follows:

Purolite S-940 resin	\$345/ft ³
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Approximately four cubic feet of resin will be required, for a total cost of \$1380.

APPENDIX B

PHASE I FINAL REPORT

DOE CONTRACT DE-AC21-93MC30168

LETTER OF SUPPORT FOR PHASE II SITE DEMONSTRATION

Restoration Management Corporation P.O. Box 398704 Cincinnati, Ohio 45239-8704 (513) 738-6200

July 14, 1995

Fernald Environmental Management Project
Letter No. C:EET(TP):95-0097

Mr. Roy W. Haggard
Contract Management
The Babcock & Wilcox Company
Contract Research Division
Alliance Research Center
1562 Beeson Street
Alliance, OH 44601-2196

Dear Mr. Haggard:

DOE CONTRACT DE-AC21-93MC30168, PHASE II SITE DEMONSTRATION

This letter is to confirm previous verbal communications of FERMCO's strong interest and support of DOE-METC and contractors for the site demonstration of the subject contract. If the results of the field demonstration verify the laboratory results, the process under development would be expected to be put to use at the site to benefit the FEMP D&D activities.

The site has a variety of equipment and piping systems plus contamination levels that are amenable to support the proposed site demonstration. The site conditions are well characterized and documented to support completion of the test program.

As with the current B&W programs at Fernald, FERMCO will make every effort to supply the support required and will cooperate with B&W to ensure the timely completion of Phase II of B&W's DOE Contract DE-AC21-93MC30168. If you or your staff have any questions, or would like additional clarification, please call me at 513-648-6558.

Sincerely,

Paul J. Pettit
Vice President Technology

PJP:jap

c: D. L. Herman, MS81-2
R. E. Heath, MS81-2