Decontamination of Process Equipment Using Recyclable Chelating Solvent

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Introduction

The Department of Energy (DOE) is now faced with the task of meeting decontamination and decommissioning obligations at numerous facilities by the year 2019. Due to the tremendous volume of material involved, innovative decontamination technologies are being sought that can reduce the volumes of contaminated waste materials and secondary wastes requiring disposal. With sufficient decontamination, some of the material from DOE facilities could be released as scrap into the commercial sector for recycle, thereby reducing the volume of radioactive waste requiring disposal.

Although recycling may initially prove to be more costly than current disposal practices, rapidly increasing disposal costs are expected to make recycling more and more cost effective (Reference 1). Additionally, recycling is now perceived as the ethical choice in a world where the consequences of replacing resources and throwing away reusable materials are impacting the well-being of the environment.

Current approaches to the decontamination of metals most often involve one of four basic process types: (1) chemical, (2) manual and mechanical, (3) electrochemical, and (4) ultrasonic (Reference 2). "Hard" chemical decontamination solutions, capable of achieving decontamination factors (Df's) of 50 to 100, generally involve reagent concentrations in excess of 5%, tend to physically degrade the surface treated, and generate relatively large volumes of secondary waste. "Soft" chemical decontamination solutions, capable of achieving Df's of 5 to 10, normally consist of reagents at concentrations of 0.1 to 1%, generally leave treated surfaces in a usable condition, and generate relatively low secondary waste volumes.

Under contract to the Department of Energy, the Babcock & Wilcox Company is developing a chemical decontamination process using chelating agents to remove uranium compounds and other actinide species from process equipment. This paper describes the technical approach taken to achieve project objectives, and briefly discusses results obtained to date.
Objective

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

Internal components of equipment utilized in the uranium enrichment process were in contact with uranium hexafluoride (UF₆) gas at elevated temperatures over many years of operation. It is suspected that in-leakage of air during operations and after plant shutdown have resulted in deposits of other uranium compounds, possibly UO₂F₆ and UF₄. Additionally, occasional out-leakage 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.

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 (e.g., 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.

Approach

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 (Fe₃O₄), 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 (e.g., 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
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. When used appropriately, chelating agents can effectively stabilize a metal ion in solution. Stabilization of the metal ion shifts the metal to ion equilibrium and allows chelating solutions to continuously promote dissolution of metals into the solution phase (Reference 4).

**Project Description**

The goal of this program is to develop a solvent capable of selectively chelating uranium and other actinides. 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.

The third requirement of the process is that the spent solvent can be regenerated through destruction of the contaminant-chelant complex, thereby regenerating the chelant for subsequent reuse and reducing the volume of secondary waste generated.

Based on these requirements, a test program was developed that included: laboratory-scale chelant screening tests, to identify solvents capable of solubilizing uranium; refinements tests, in which process application parameters were varied to optimize solvent effectiveness; solvent recycle tests, aimed at development of a process to break the chelant-metal bond and free the chelant for reuse; bench scale testing, involving application of the developed solvent system under dynamic conditions simulating field application; and a pilot plant study, in which the process developed and refined in previous tasks was applied, on a pilot scale, to actual contaminated scrap material. This Phase I activity has been completed. Planned activity for Phase II of this project includes a field demonstration of the developed technology at a DOE site.

**Results**

**Chelant Screening Tests (Task 2.1)**

The goal of this task 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.

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, or 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 Phase II site demonstration.

Based on these considerations, the screening tests were initiated using three chelating agents that had been previously applied to the chemical cleaning of power generating equipment, namely EDTA (ethylenediaminetetraacetic acid), HEDTA (hydroxyethyl-ethylenediaminetriacetic acid), and DTPA (diethylenetriaminepentaacetic acid). All three of the chelants are known to form strong complexes with uranium.

The purpose of the screening tests was to select two or three solvents for refinement testing, based strictly on their ability to chelate uranium. The deposit material chosen for dissolution testing was uranium dioxide (UO₂), 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. Other conditions, including chelant concentration, temperature, and exposure time, were held constant throughout initial stages of the screening test program. The 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. The procedure for testing involved addition of a known quantity of uranium dioxide to the test flask, followed by exposure to solvent for eight hours at 93°C in a controlled temperature water bath.

![Figure 1 - Typical Screening Test Flask Arrangement](image-url)
Periodically, samples of the solvent were removed from the test flask for analysis for dissolved uranium and for available chelant. At the conclusion of the test, the entire solution remaining in the test flask was filtered, and the filtered material was dried and weighed to evaluate the completeness of UO$_2$ dissolution.

Each of the three candidate chelants (EDTA, HEDTA, DTPA) was initially tested in this way at a pH of 5.5, 7.0, and 9.0. The results were similar for all 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. Further 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 subsequently 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 and chemical cleaning industries (Reference 5).

The testing was performed at room temperature, due to the known potential for violent reaction between peroxide and organic materials. 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.

Results were equivalent for each of the three tested chelating agents.

This type of solvent appeared to be 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. Since EDTA is known to be corrosive to metals at higher temperatures, the solvent could be applied in such a way as to remove base metal, thereby releasing contamination trapped within the grain boundaries.

3. The addition of carbonate and hydrogen peroxide did not complicate the secondary waste stream, since these are not hazardous materials.

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 approximately 95% complete using a solvent containing peroxide and carbonate only; dissolution occurred slightly more rapidly, and to 100% completion, with the solvent containing chelant.

The effect of carbonate on the dissolution process was also 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. The effects of chelant and carbonate on uranium dissolution are shown graphically in Figure 2.

These results indicated that a carbonate/peroxide solvent might be effective for removal of light surface uranium contamination. The addition of chelant would be required for decontamination of surfaces characterized by heavier deposits, to stabilize the uranium ions in solution and prevent precipitation from occurring during the cleaning process. Chelant would also be required to effect base metal corrosion for release of bulk contamination.

Solvent Refinement Testing (Task 2.2)

At this stage of screening, it was decided that two solvents would be carried forward to solvent refinement testing. Those selected for development were:

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

(2) ammonium carbonate and hydrogen peroxide: pH 9.0 with NH₄OH.

The purpose of refinement testing was to vary solvent parameters in an attempt to optimize solvent effectiveness. Parameters investigated included solvent constituent concentrations and application scenarios. The evaluation of solvent performance considered the rate of dissolution.
uranium dissolution, extent of dissolution, and the amount and type of corrosion to materials of interest.

Refinement tests were run using the same equipment arrangement and utilizing similar procedures as the screening tests.

Since refinement testing was also designed to characterize the corrosivity of both solvents, preweighed specimens of carbon steel, Monel, and nickel were placed in the reaction flask for the estimation of general corrosion by weight loss.

Initial tests were performed to determine the concentration of each constituent required to dissolve uranium dioxide effectively. Testing with varying solvent compositions showed that the basic solvent system was effective over a wide range of constituent concentrations.

However, the importance of tailoring the solvent system to process application conditions was demonstrated. Specifically, the surface area of metal exposed during testing affected uranium dissolution; increased metal content in the system necessitated an increase in the initial H₂O₂ concentration for complete dissolution to occur. These results showed that the metal surface area to solvent volume ratio must be factored into solvent formulation as it is tailored for a specific application. This information is shown graphically in Figure 3.

A secondary part of refinement testing was to evaluate the feasibility of applying the selected solvents in the foam state. Foam decontamination technology is currently being evaluated by DOE, as it has shown waste reduction of 70% over present decontamination methods (Reference 6).

![Figure 3](image_url)

**Figure 3**
Effects of Coupons and Peroxide Concentration On Uranium Dissolution
A paste of uranium dioxide was dried onto coupons, which were subsequently exposed to the foamed EDTA/carbonate/peroxide solvent. The tests showed that UO₂ could be dissolved by the solvent in the foam state, although some of the deposit was dissolved after it had dislodged from the coupon and dropped into the condensed foam. Further testing of foamed solvent with more appropriate test samples (material contaminated in service, if available) has been recommended.

In the final phase of refinement testing, process application 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 bench scale and pilot scale testing. Based on the results of testing, the following process application scenario was chosen for application in bench- and pilot-scale testing:

- Two hours at room temperature
- Heatup to 93°C and hold for four hours
- Cool to room temperature and inject peroxide
- Two hours at room temperature

The rationale for this application scenario is that readily available uranium will be dissolved during the initial low temperature exposure. The four-hour 93°C exposure will result in corrosion of base metal, thereby releasing contamination trapped in grain boundaries. This released contamination will be dissolved by the final low temperature exposure.

Using this application sequence for the EDTA/carbonate/peroxide solvent, 100% of available UO₂ was dissolved and a carbon steel corrosion rate of 1.4 mils in four hours was achieved. These results exceeded the established success criteria for the solvent developed in this task, those being 90% dissolution of uranium present in the system in less than eight hours, and capability of a carbon steel corrosion rate greater than two mils per eight hours. These results are shown graphically in Figure 4.

![Figure 4: Chelant/Carbonate/Peroxide Solvent](image)

**Figure 4**
Chelant/Carbonate/Peroxide Solvent
Room Temperature → 93°C → Room Temperature
Solvent Recycle/Contaminant Reduction Testing (Task 3)

As mentioned previously, one requirement of the developed process is 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 this task was to develop a process to break the chelant-contaminant bond, and to precipitate the contaminants as the insoluble metal hydroxides. The end result was to be a filter cake of contaminants and a regenerated chelant solution.

Methods for recycling both the EDTA/carbonate/peroxide and EDTA/carbonate solvents were evaluated. Spent solvents from Task 2 of the program were used for this testing. Dissolved uranium content of the test solutions before and after treatment was used to evaluate the effectiveness of each recycle process tested.

The EDTA/carbonate solvent recycle test program resulted in five successful methods for removing uranium from the spent solvent with an efficiency of greater than 99.9%:

1. acidification to pH 1 followed by addition of lime and caustic to pH 12.5
2. pH reduction to 1.0 followed by application of hydrogen-form strong acid cation resin
3. application of carbonate-form strong base anion resin at existing solvent pH
4. application of hydroxide-form strong base anion resin at existing solvent pH
5. precipitation by application of trisodium phosphate after reducing solvent pH to 2.

The process utilizing anion resin in the carbonate form appeared to be most viable, because it removed only uranium from solution. All other processes were acceptable and considered equal.

Only one method was found to be successful with the EDTA/carbonate/peroxide solvent. This method consisted of reducing solvent pH to less than 2, followed by application of a uranium selective cation resin in the hydrogen form. No precipitation techniques provided acceptable results with the EDTA/carbonate solvent system.

Bench Scale Testing

The purpose of bench scale tests was to evaluate the solvent system developed in the solvent refinement test under dynamic test conditions that simulate the actual field application. The tests were conducted in the B&W Alliance Research Center’s low temperature chemical cleaning velocity test apparatus. Ceramic plugs containing uranium dioxide and corrosion coupons of nickel, carbon steel, and Monel 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 on a periodic basis and were analyzed for dissolved uranium, iron, copper, nickel, and available chelant.

The first phase of the task was development of a suitable binder for making UO₂ test plug that would release uranium slowly throughout the dynamic
exposure, in order to simulate the cleaning of scrap material with uranium contamination embedded in base metal grain boundaries. Plugs consisting of various combinations of calcium carbonate, trisodium phosphate, silicon dioxide, and mortar, were evaluated with both solvents. For the first portion of bench scale testing, uranium dioxide was added to a formulation that appeared to produce a plug deteriorating slowly throughout the test exposure.

Results of initial testing indicated that the plugs were more robust than testing without UO₂ in the formulation had indicated, and decomposed at a significantly slower rate than anticipated. Additional testing was performed using smaller plugs made from a formulation with an increased ratio of uranium dioxide to binder.

The application scenario utilized in the bench-scale testing was that qualified in the refinement testing:

- Two hours @ room temperature
- Heatup to 93°C; hold four hours
- Cooldown to room temperature and inject peroxide
- Hold @ room temperature two hours.

Initial testing consisted of two tests using the original plug formulation; one test with each of the two candidate solvents. The test plugs used did not disintegrate to the extent predicted by plug formulation testing. For this reason, some of the encapsulated uranium did not become accessible to the solvents, and, hence, was not dissolved. The EDTA/carbonate/peroxide solvent dissolved 25% of the added uranium; the carbonate/peroxide solvent dissolved about 18%.

As mentioned above, the plugs were then reformulated for additional bench scale testing. Two tests were run with the smaller, modified-formulation plugs; one test with each of the two candidate solvents. The EDTA-containing solvent attacked the reformulated plugs more aggressively than it did the original formulation; 75% of the added uranium was dissolved. The carbonate/peroxide solvent dissolved only 10% of the added uranium. Based on the low dissolved calcium values observed, the revised plug formulation appeared to be very resistant to this solvent.

The corrosion losses on test specimens included in all four tests were uniform, with no localized attack evident. The application of the carbonate/peroxide solvent resulted in negligible corrosion of all three materials; application of the EDTA-based solvent resulted in average corrosion of 0.2 mils for Monel 400, 0.3 mils for Nickel 200, and 0.4 mils for carbon steel. It was thus shown that the addition of chelant is required to effect consistent base metal corrosion, which will be required for release of contamination below the surface of process equipment being decontaminated.

**Pilot Plant Study**

Upon completion of bench scale testing, a pilot study of the developed process was conducted at B&W's Lynchburg Technology Center. The purpose of this study was to verify operating parameters for the decontamination system to be used in the field demonstration, as well as to demonstrate the success of the process in decontaminating actual contaminated process equipment. The testing was performed in a skid mounted pilot-scale
The study was conducted using scrapped process equipment characterized by contamination felt to be representative of that to be cleaned in the Phase II field demonstration. The contaminated metal consisted of stainless steel pipe brackets and several pieces of steel floor grating.

Three tests runs were made with the pilot system: two with the EDTA/carbonate/ peroxide solvent and one with the carbonate/ peroxide formulation. The application scenario utilized was the same as that applied in bench-scale testing. All stainless steel components subjected to the cleaning solvent showed a decontamination removal efficiency greater than 99%. Decontamination factors for the carbon steel components subjected to the cleaning solvents were considerably less; however, a large percentage of the carbon steel surface areas subjected to the solvent were covered with a tar-like coating. It is believed that the coating shielded the uranium from the solvent, thereby reducing the effectiveness of the cleaning.

The pilot scale solvent recovery tests were also quite successful. EDTA was recovered from solution by precipitation and the dissolved uranium was 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 of greater than 99.4% for all of the waste processed. Iron was 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 pilot tests. These include improved cooling capabilities during hydrogen peroxide spikes and control of solvent aeration, to reduce the ferric ion corrosion occurring during process application. In addition, the need for real-time peroxide analysis was also identified.

Figure 5 - Schematic of Pilot Scale Test Rig
Application

Based on the results of 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 ammonium hydroxide


Since UO₂ is dissolved effectively by these solvents at room temperature, they can be utilized in surface decontamination applications without interference from chelation of iron, which does not occur readily at low temperatures.

Essentially no corrosion is observed without EDTA being present in the solvent system. The EDTA is required to effect consistent base metal corrosion for release of radioactive material below the surface of equipment requiring decontamination. The chelant also appears to stabilize the dissolved uranium in the presence of competing ions in solution.

From the information generated in Phase I, it is projected that the carbonate/peroxide solvent should be effective for removal of surface uranium contamination with a single low-temperature application. The addition of chelant will be necessary for decontamination of surfaces characterized by uranium contamination buried deeper in metal grain boundaries. In such cases, the presence of EDTA results in the necessary higher base metal corrosion during the 93°C application phase of the decontamination process.

Potential also exists for application of the solvents in the foam state, which would be useful for decontamination of large components. Further evaluation of a foaming decontamination process using these solvents has been proposed as part of Phase II.

Future Activities

Planned activity for Phase II of this program is a full scale demonstration of the developed decontamination and solvent recycle technology. Initially, the site demonstration was to take place at the gaseous diffusion plant at Oak Ridge. However, due to the level of enrichment of the uranium contamination represented, there were criticality concerns associated with the used of aqueous solvent systems for decontamination. For this reason, 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, which has accumulated an inventory of nuclear material, low-level radioactive waste, mixed wastes, and contaminated equipment/facilities. As a result of years of uranium metal production, equipment, buildings, soil, and ground water at this site have become contaminated and have the potential to impact public health and the environment.

The uranium contamination levels at Fernald are amenable to support the proposed project. Site conditions there are well characterized and documented to support completion of the test program. In addition, B&W's Nuclear Environmental Services, Inc., which will perform the field cleaning, already has a trained field
staff at this site. Prior environmental tests conducted by B&W NESI in cooperation with FERMCO at this site have received excellent support from FERMCO. For these reasons, B&W has recommended the Fernald site as the location for the Phase II demonstration.

References


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