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1

SELECTIVE DISSOLUTION AND RECOVERY OF DEPLETED URANIUM FROM ARMOR PLATE

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The impacted armor targets used in testing high density armor-piercing ammunition containing depleted uranium (DU) are subject to disposal as low level radioactive waste. Because of the costs associated with disposal of the entire armor plate and the limited use of secured commercial sites in the future, the U.S. Army is seeking to identify and evaluate new technologies for decontaminating these armor plates. The objectives of this Phase I SBIR program are two-fold, namely:

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19. Abstract (Continuation)

- To develop a selective solvent that can decontaminate impacted armor targets containing DU for disposal or recycle.
- To identify and characterize technologies that can remove depleted uranium from the solvent for solvent recycle and uranium recovery for easier hazardous waste disposal. (Keywords:

All of the objectives of this program have been achieved.

← over

This program has demonstrated the technical feasibility of using a hydrochloric acid:phosphoric acid solvent to dissolve depleted uranium fragments from contaminated metal targets for disposal or recycle as non-radioactive material. Decontamination testing on targets characterized as containing residual entrained penetrator fragments is necessary to determine if all of the radioactivity associated with penetrator holes in the metal target material can be removed.

The hydrochloric:phosphoric acid solvent completely and very rapidly dissolved a DU alloy pellet inserted in a pre-drilled bore hole in a simulated metal target, while the target plate remained intact with less than 1 percent of its total weight dissolved. In less than 30 minutes, the acid solvent reduced the average contamination of a hot spot on a real penetrated target by 86 percent, while reducing the overall contamination of the rest of the plate by 99.5 percent; the phosphoric acid in the combined solvent inhibited excessive corrosion of the target plate resulting in about a one percent total weight loss.

Three methods of recovering uranium from the chemical decontamination solvent for recycle were identified, namely ion exchange, solvent extraction, and precipitation. Ion exchange, using an aminophosphonic chelating resin, Duolite ES-467, appeared to be the most feasible technically for removing and concentrating the depleted uranium from the acid solvent. A conceptual flow sheet, based on preliminary test data, suggested that uranium could be extracted from the acid solvent while at the same time recycling the acid solvent. The resin could be eluted with ammonium carbonate solutions, ultimately recovering stable U_3O_8 ("yellow cake") for hazardous waste disposal. This technique can completely separate the depleted uranium from the target allowing the target to be disposed of as trash or salvage and generate a small volume of contaminant for disposal as low level radioactive waste.

It is recommended that further work be carried out in a small pilot plant to demonstrate that:

- Complete target decontamination can be achieved in large residual bulk penetrator material.
- Chelate ion exchange can continuously remove DU from the acid solvent for solvent recycling and can recover and concentrate DU for easier hazardous waste disposal.

PREFACE

This report was prepared by Foster-Miller, Inc., 350 Second Avenue, Waltham, MA 02254 under Contract No. DAAD03-86-C-0017. This study was performed between 26 June 1986 and 5 May 1987. The work was sponsored by the U.S. Army Jefferson Proving Ground, Madison, IN 47250-5100 under the Small Business Innovative Research (SBIR) Program, Phase I, Department of Defense Solicitation No. 86.1. The Army Project Officers were Dr. Norman Wykoff and Mr. Richard H. Herring.

The report represents the results of laboratory investigations pertinent to depleted uranium target plate decontamination using selective chemical solvents followed by solvent recycle.

The authors acknowledge the following individuals for significant contributions to the program:

- Mr. Benjamin F. Casole, III, Radiation Protection Officer, Combat Systems Test Activity, Aberdeen Proving Ground, MD, for his assistance in obtaining the penetrated targets used to characterize the decontamination characteristics of the selective solvents. We also acknowledge and greatly appreciate his help in obtaining information pertaining to the contaminated target disposal problems and current solutions conveyed during numerous conversations.
- Mr. Frank J. Vumbaco, Manager, Health and Radiation Safety, and Mr. Donald A. Barbor, Manager, Hazardous Waste, Nuclear Metals, Inc., Concord, MA, for providing a detailed protocol on the health, physics and waste management aspects of this project. We appreciate their assistance in disposing of the low level radioactive waste generated during the project, as well as supplying radioactive detection equipment and other personal protection clothing and devices.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the general public, including foreign nationals, after 5 May 1989, subject to the License Rights Legend on the inside front cover. This technical report has been reviewed and is approved for publication.

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TABLE OF CONTENTS

TABLE OF CONTENTS (CONCLUDED)

LIST OF FIGURES

LIST OF TABLES

SECTION I
INTRODUCTION

OBJECTIVES

The primary objective of this project was to develop a selective solvent that can decontaminate impacted armor targets containing depleted uranium. The ideal solvent would reduce the radiation in the plates to a lovel that allows the disposal of the plate to commercial non-hazardous burial sites. The decontaminated plates can also be reused or recycled, if desired.

The best approach for the final disposition of the solvent containing the dissolved low level radioactive waste is to recover the depleted uranium from the solvent as a uranyl salt or oxide of acceptable concentration and purity for recycling by a refiner. If recycling is undesirable, the recovered uranium can be inexpensively disposed of in its volume reduced state as low-level radioactive waste. In either case, the solvent may be recycled. A secondary objective was devoted to identifying and characterizing technologies for removing DU from the solvent.

These objectives were met by carrying out the work in two experimental phases:

(1) Selective solvent dissolution studies relating the functional relationship between preferential uranium removal and process parameters including solvent composition, concentration, volume, temperature and immersion time, and

(2) The use of ion exchange, solvent extraction and precipitation technologies were investigated in order to evaluate the efficiency of precipitating agents and selective ligands to form readily extractable or insoluble uranium complexes that can be selectively removed from the acid solvent.

BACKGROUND

The impacted armor targets used in testing high density armor-piercing ammunition containing depleted uranium (DU) are subject to disposal as low level radioactive waste. Depleted uranium, a low level radioactive by-product of the nuclear fuel enrichment process, is recognized as an outstanding material for use in kinetic energy armor piercing projectiles. Each branch of the U.S. Department of Defense has ordnance programs that utilize DU because of its superior armor penetrating capabilities and cost effectiveness. In current production, DU penetrators are the principal ammunition for the U.S. Army's 105 mm M-1 tank main cannon.

The various ballistic ranges have a great deal of armor that has been shot at with DU ammunition. The armor is normally in 4 ft x 4 ft (122 cm x 122 cm) sizes and varies in thickness from 0.5 in. (1.3 cm) thick to 4 in. (10.2 cm) thick. These plates have a varying number of holes in them; most of the holes are completely through the armor plate. In each case, the surface of the hole has been contaminated with DU. As the projectile passed through or even just impacted the target, the DU becomes molten and an adhesive bond is created on the surface. In some cases, the DU contamination penetrates into the armor plate.

Armor-piercing munitions are specifically designed to defeat armored targets through the primary target of a high-density, non-explosive penetrator. If DU is used as the penetrator material, its pyrophoric nature will cause the projectile to burst into burning fragments upon impact with armor. These fragments are dispersed into the air, the sand butts, and into the armor plate target. In the latter case, a eutectic alloy is formed with the mixed oxide, U_3O_8, and the iron from the steel target plate.

Depleted uranium is classified as a low-level radioactive material and, as such, must be handled in accordance with Nuclear Regulatory Commission (NRC) guidelines for low-level radioactive waste. The armor plates used in testing munitions containing DU are subject to disposal as low-level radioactive waste. The plates cannot be refined in their contaminated state and at the present time there are no operational alternatives to sending these plates to commercial disposal sites for burial. Because of the cost associated with disposal of the entire armor plate as low-level radioactive waste and the limited use of secured commercial sites in the future, the U.S. Army is seeking to identify and evaluate feasible solvents that selectively remove fragments of uranium imbedded in armor plate as a result of firing DU penetrators into the target material.

The problem is to decontaminate the target plate to meet state and Federal requirements so that they can be safely disposed of off-site in unsecured land fills or can be returned to the ranges for other uses.

Mechanical and physical techniques for removing imbedded DU fragments that require isolating the penetrated area by cutting or melting is not only time consuming but also dangerous. Small uranium fragments are extremely pyrophoric, creating a potential fire hazard. The most deleterious health consideration comes from ingesting and inhaling fire uranium dust and therefore precludes fragment removal by cutting out the contaminated area. Dissolution of the entire armor target is possible, but the reagent cost of treating hundreds of targets and difficulties associated with uranium recovery make this method impractical.

SCOPE

The major effort of the Phase I program focused on developing a selective solvent that preferentially attacks the areas on the armor target contaminated with DU, leaving the armor plate unaffected and intact. A secondary effort was devoted to the removal of DU from the solvent. The volume of the spent solvent solution can actually exceed the volume of the treated armor plate. The greatest advantage of the process developed for the removal of the DU from the solvent is the volume reduction of DU requiring disposal. Once the DU is recovered, the treated solvent is available for reuse and can be returned to treat additional impacted targets.

The laboratory research plan involved screening candidate solvents for their ability to dissolve DU pellets containing 0.75 percent titanium (the same composition used for ammunition production). Solvents passing the initial screening criteria were tested for uranium selectivity by evaluating their ability to dissolve a DU-0.75 percent Ti pellet from a simulated test target. Testing on simulated targets provided valuable selectivity data until actual targets were obtained. The most promising solvent was evaluated using actual penetrated targets.

The feasibility of removing the dissolved uranium from the spent solvent was demonstrated using precipitation, ion exchange, and solvent extraction technologies. The advantages and disadvantages of the techniques were assessed and are discussed in this report.

The program plan under the Phase I SBIR program consisted of three tasks described as follows:

Literature Search

A literature search was made to determine what solvents, combination of solvents, and combinations of solvents and oxidants (catalysts) will selectively attack (dissolve) uranium-titanium alloys, and other eutectoid alloys that may be formed upon projectile impact. Emphasis was placed on literature pertaining to uranium-selective chelating agents.

The range of operating parameters, such as solvent composition, solvent concentration and the reaction temperature at which selective dissolution of the uranium takes place, was initially defined based on the existing literature and past experience. Other characteristics of the solvent system, such as compatibility with the target material, flammability, and toxicity, were discussed when appropriate.

Based on the dissolution properties of the solvents, a list of candidate solvent systems was developed and have the potential of meeting the criteria for selective dissolution of uranium-alloyed fragments from steel plate targets.

Decontamination Studies

The solvents selected as potential selective candidates were subjected to dissolution studies with weapon grade uranium to evaluate their performance as solvents for the DU-0.75 percent Ti alloy. Candidates meeting the initial screening criteria were evaluated to determine their selectivity characteristics for DU alloy fragments imbedded in simulated test fragments. The most promising solvent was evaluated using the actual penetrated targets. The selectivity and rate of dissolution of the solvents were conducted according to the recommended methods of total immersion testing for ferrous metals described by Uhlig (1). When necessary, the testing procedures were amended to meet the technical objectives.

According to this procedure, the simulated and actual test targets are placed in the test apparatus and covered with the solvent. Chelate additives are also added, if appropriate. Test variables controlled included solvent composition, concentration, and volume; temperature and test duration.

Solvent selectivity was determined from elemental analysis of the solvent following the test.

Solvent Recycle and Uranium Recovery/Waste Reduction

The successful dissolution of DU from the target plates transfers the uranium disposal problem to the solvent solution. Removal of the DU from the solvent reduces the volume of disposal uranium and allows reuse of the solvent.

Three techniques considered for removing the DU from the solvent solution were precipitation, ion exchange and solvent extraction. The separation of uranium from solution by precipitation is based on the formation of sparingly soluble compounds. The purity of the uranium compounds is dictated by the resulting solvent containing dissolved uranium and the choice of precipitant. The recovery of uranium from the selective solvents was greatly influenced by pH. Increasing the pH of the acid solvent for uranium recovery neutralizes the solvent and precludes the opportunity for solvent recycle.

The feasibility of removing uranium from spent solvents using selective chelate ion exchangers was assessed using commercially available products. This was demonstrated by reacting liquid and solid ion exchangers by selectively removing uranium from a spent solvent without excessive extraction of other solution contaminants such as iron. Successful uranium recovery was achieved from an acid chloride/phosphate combination using the aminophosphonic acid chelating resin, Duolite ES 467. The effect of solvent composition and concentration on the capacity of the ion exchanger was assessed by comparing the uranium concentration in the solvent before and after treatment. The distribution coefficients for uranium and other metals dissolved by the solvent were calculated, from which the selectivity factors were determined.

SECTION II

LITERATURE REVIEW

During the process of penetration of armor targets, DU penetrators undergo severe fragmentation. Flash temperatures reached during impact of DU penetrators with armor plate have been shown to fall in the range of 3037 °C to 3093 °C over the entire range of impact test velocities. Such heat generation following impact causes the formation of molten uranium, uranium oxides, and eutectoid alloys with the steel plate. X-ray analysis confirms that airborne DU particles, formed when DU projectiles (99.25 percent DU, 0.75 percent titanium) impact armor targets, contain an extremely high iron content (2). It is reasonable to assume that the morphological characteristics of the uranium fragments imbedded in the armor targets will contain, not only DU, but also DU of a heterogeneous iron eutectoid composition.

The removal of DU from the target material is complicated by the presence of these uranium-iron eutectoid alloys. The dissolution of this eutectoid by a selective solvent was assessed using an impacted target contaminated with DU.

Rodden (3) and Katz and Rabinowitch (4) describe methods used for dissolving uranium metal and high uranium alloy. However, no detailed information was found concerning dissolving bulk depleted uranium-titanium alloys alone or from other bulk base metals. Most of the discussions in the literature are confined to the dissolution of uranium metal and its alloys for the purpose of analysis, in which uranium is the principal constituent. Other literature sources describe methods for the complete dissolution of alloys in which only small percentages of uranium are contained in the metal sample, like reactor fuels.

In general, oxidizing acids, such as nitric acid and perchloric acid, as well as hydrochloric acid, react vigorously with elemental uranium. These acids are also likely to react with the homogeneous armor steel plate used for ammunition testing.

Mineral acids, like sulfuric and phosphoric acids, are slow to dissolve uranium. However, these acids used in high concentrations with the addition of catalysts and accelerators, have the potential to dissolve the uranium fragments and also passivate the target material. Partial dissolution of the target is beneficial in order to remove all traces of uranium and eutectoid uranium-iron alloys formed by projectile impact.

A list of acid solvent/solvent combinations that were considered as potential selective solvents is shown in Table 1.

NITRIC ACID

Probably the most common reagent for the dissolution of uranium metal and its alloys is nitric acid (HNO_3). Nuclear Metals, Inc. (Concord, MA), a manufacturer of the M744 armor piercing anti-tank round, dissolves DU-0.75 percent Ti scrap for recovery by converting the depleted scrap to the metal oxide with 8 Molar (M) HNO_3 and with 0.5 percent hydrogen hexafluorophosphate (HPF_6) as an accelerator. A pure uranyl peroxide product is recovered by H_2O_2 precipitation at an adjusted pH of 2 to 4 (5).

HYDROCHLORIC ACID

Uranium reacts with hydrochloric acid (HCl) very rapidly to form uranium (IV) chloride (UCl_4) and a black precipitate that is described as a hydrated (III-IV) oxide. In 1M HCl acid at 100 °C, a 10 gram bulk sample can be consumed in one hour; in 12M acid, the evolution of hydrogen is explosively rapid (6). The addition of an oxidizing agent (e.g., sodium chlorate, hydrogen peroxide, perchloric acid) reacts rapidly with uranium (IV) to form a uranyl halide solution that can be precipitated and recovered.

AQUA REGIA

Aqua regia, which has a relatively high hydrochloric acid:nitric acid ($HCl:HNO_3$) volume ratio (4:1), is used for dissolving uranium alloyed with one percent or more zirconium (a Class V element along with titanium), molybdenum, ruthenium, and rhodium (4). This presents the problem of solubilizing the very reactive uranium matrix material in the same acid as that used for the very

TABLE 1. Reagents for Dissolution of Uranium and its Alloys.

Description	HNO_3	Aqua Regia	HNO_3-HF	HCl+ Ox	HCl-EtOAc	NaOH-H_2O_2	H_2SO_4-H_2O_2-HCl	H_3PO_4 (hot)
U	S	S	S	S	S	S	S	S
U-Zr	N	N	S	N	N	N	N	-
U-Nb	N	N	S	N	N	S	N	-
U-Fe	S	S	S	S	S	N	S	S
U-Cr	N	N	N	S	S	N	-	-
U-Ru	N	S	N	N	N	N	-	-
U-Mo	N	S	N	S	N	S	-	-
U-Fissium[a]	N	S	N	N	N	N	-	-
U-Si	S	-	S	-	-	-	-	-
U-Pu	S	S	N	S	S	N	-	-

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[a] Alloys containing from 1 to 3 percent zirconium, molybdenum, ruthenium, rhodium, palladium and cerium.

inert alloying constituents. Alloys of this type have been satisfactorily dissolved in aqua regia when hydrofluoric acid is added in the appropriate amounts.

PERCHLORIC ACID

Uranium metal dissolves very rapidly and spectacularly in hot (160 °C), 70 percent perchloric acid ($HClO_4$) (4). The character of the perchloric acid dissolves much to be desired from a safety aspect and was given a low priority as a dissolution method.

PHOSPHORIC ACID

Rodden (3) studied the dissolution of uranium in phosphoric acid (H_3PO_4) and reported that the bulk uranium metal is attacked by 85 percent phosphoric acid at a moderate rate to form a clear uranium (IV) phosphate solution. A plethora of information is available in the literature for the selective recovery of the resulting uranyl phosphate complex, $UO_2H_2PO_4$, from wet process phosphoric acid solutions by a number of ion exchange resins, such as Duolite ES467, Lewatit M504, and Levextrel OC 1023.

SODIUM HYDROXIDE - HYDROGEN PEROXIDE

It may be necessary to use a basic medium to selectively dissolve uranium fragments from the target material, if the target is soluble in most acid solutions. The dissolution in sodium hydroxide (NaOH) - hydrogen peroxide (H_2O_2) has the potential to meet this need. It has been reported that 10 gram samples of uranium metal and some uranium alloys react at a moderate rate with 50 mL of 1M sodium hydroxide-5M hydrogen peroxide mixtures in less than one hour to form the uranyl peroxide complex (6). The advantage of this method is the solution containing dissolved uranium can be quickly converted to the soluble uranyl nitrate complex with the addition of nitric acid and subsequent precipitation of pure uranyl peroxide by adding additional hydrogen peroxide.

SULFURIC ACID

Uranium and most alloys in which uranium is the bulk constituent do not react with sulfuric acid at moderate concentrations and temperatures. However, Larsen (6) has reported that dilute sulfuric acid (H_2SO_4) removed iron, magnesium, aluminum and other metals which have been bonded to, or mixed with, bulk uranium metal. Mixtures of sulfuric acid and hydrogen peroxide attack uranium slowly at 75 °C. The addition of chloride in catalytic amounts increases the rate of dissolution markedly. It has been reported that 10 grams of bulk uranium can be dissolved in less than 30 minutes in 100 mL of 6M sulfuric acid-1M hydrogen peroxide-0.01M hydrochloric acid. Uranium (IV) has a strong tendency to form soluble uranyl sulfate anionic chelates. The complexes $[UO_2(SO_4)_2]^{-2}$, and $[UO_2(SO_4)_3]^{-4}$, can be recovered by ion exchange to yield a product of very high purity.

HYDROGEN CHLORIDE-ETHYL ACETATE)

Hydrogen chloride (HCl) solutions in ethyl acetate (EtOAc) react with uranium at a moderate rate to form soluble uranium (IV) tetrachloride solutions. In a 3M solution, which is close to saturation, a 10 gram bulk uranium sample was reported to dissolve in a minimum of 10 hours (6). The hydrogen chloride-ethyl acetate dissolution of uranium is unique in that uranium metal is dissolved completely in a relatively mild reagent. This procedure has been used to selectively dissolve the uranium metal in metal oxide mixtures and separate certain intermetallic compounds by only dissolving the uranium matrix.

CHELATE ADDITION

Uranium forms stable complexes with liquid extractants and gel resins containing di (2-ethylhexyl) phosphoric acid (D2EHPA). The addition of chelates to selective solvents should promote the complexation of uranium ions and accelerate the rate of uranium dissolution (4). Chelating agents with high stability constants, the most desirable for our intended use, are those whose donor atoms, such as fluorine and oxygen, are the most electronegative (7). The best known extractants that meet this criterion is the synergistic mixture of Di-2-ethylhexyl phosphoric acid (HDEHP) and trioctyl phosphine oxide (TOPO). However, higher partition coefficients for uranium results if TOPO is replaced by phosphine oxides containing an ether oxygen at the beta position of the phosphorous atom. Examples are di-n-hexyl-2-oxa-decyl phosphine oxide [D(H)2-ODPO] and dibutyl(butyl-phosphonate) [DB(BP)]. In addition, the replacement of HDEHP by dialkyl phosphoric acids with ether chains may also synergistically improve the uranium/iron separation coefficients. Di (3-oxa-heptyl) phosphoric acid (HD3-OHP) is such an example (7).

The introduction of the ether oxygen in the above mentioned ligands make the phosphoryl oxygens less basic by reducing electron density (7). Consequently, the H^+-metal exchange is favored, and, given the acidity of the potential solvents should lead to an increase in partition coefficients.

When the ligand forming extractants are added to a compatible solvent like phosphoric acid, the ligand displaces the solvent molecules coordinated to the uranium metal. This reaction forms a chelate complex from the solvated uranium ion at the metal surface, exposing a fresh site on the target for the solvent to act on. For selective complexation of the depleted uranium ions in the presence of the metal target ions, chelating agents with high stability constants relative to those of the different solvated target ions are required. This will keep the equilibrium constant large enough to favor the sequestration of the uranium ion. The feasibility of improving uranium dissolution was evaluated using a synergistic mixture of HDEHP and TOPO.

SECTION III

DECONTAMINATION

The decontamination of impacted armor plates was conducted in three phases:

1. The dissolution characteristics of candidate solvents identified in the previous section were evaluated by measuring the percent dissolution of weapon grade DU-0.75 percent Ti pellets.

2. Selectivity of the two best solvents in (1) for DU-0.75 percent Ti was determined from simulated tests targets.

3. The best solvent from (2) was tested against an actual DU contaminated penetrated target to determine what degree the radioactivity associated with the penetrator hole could be reduced.

TARGET MATERIAL DESCRIPTION

DU-0.75 Percent Ti Pellets

The pellets used to screen candidate solvents were provided by Nuclear Metals, Inc. (Concord, MA) and are the same source material used in the production of high density armor piercing ammunition. Each pellet weighed between 16 and 20 grams with approximate dimensions of 1.2 cm x 0.75 cm.

Simulated Target Material

Simulated target plates consisted of 6 in. x 4 in. x 1 in. (15.2 cm x 10.2 cm x 2.54 cm) ASTM A36 structural steel and weighed approximately 3 kg. The specifications for the actual target material for wrought-steel follows the military specification (MIL-A-12560G(MR)) homogeneous armor plate.

The chemical compositions of the simulated and actual target materials are shown in Table 2.

TABLE 2. Target Material Chemical Composition.

Element	ASTM A36 (percent)	MIL-A-12560G(MR) (percent)
Carbon	0.17	0.10
Manganese	0.86	0.40
Phosphorous	0.011	0.025[a]
Sulfur	0.003	0.025[a]
Silicon	0.016	0.40
Nickel		0.50
Chromium		0.40
Molybdenum		0.15

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[a] Combined phosphorous and sulfur content does not exceed 0.04 percent.

Penetrated Targets

Pieces of impacted targets were obtained from the U.S. Army Ballistic Research Laboratory (Aberdeen Proving Ground, MD). The pieces measured approximately 5 in. x 5 in. x 1 in. (12.7 cm x 12.7 cm x 2.54 cm) and were torch-cut from impacted targets. Each piece contained a hole caused by a penetrator round. In the penetrations, the contamination is mainly fused uranium metal tightly bonded to the target material. The contamination on the surface was in the form of imbedded or fused fragments. Iron oxide, which formed with time on the metal targets, was contaminated from radioactive dust that became incorporated into the oxide.

A description of each sample is listed in Table 3.

SELECTIVE SOLVENTS

All selective solvents and other solutions or additives used in this project were prepared from reagent grade chemicals.

TABLE 3. Penetrated Target Characterization.

Sample	Plate (cm)	Hole (cm)	Average Contamination (cpm)
A	2.5 x 13.0 x 14.0	9.0 x 8.4	48,000
B	2.5 x 14.0 x 15.0	4.0 x 4.5	1,100

ANALYTICAL PROTOCOL

Radioactivity measurements were made using a Geiger-Mueller (GM) counter equipped with a pancake tube having a 0.2 millirem/hr window. All measurements were recorded in total counts per minute (cpm). No corrections for geometry were made.

Total iron in the acid solvent was determined by atomic absorption spectrometry. Measurments were made on a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer at a wavelength of 248.3 nm.

Uranium analysis was made in contaminated solvent samples using an EG&G Model 264A Polarographic Analyzer/Stripping Voltammeter in conjunction with an EG&G Model 303A Static Mercury Dropping Electrode. Samples were prepared in a 1M sulfuric acid electrolyte. Measurements were made while screening at 10 mV/sec between the potential range of +0.03 mV through -0.50 mV.

LABORATORY PROCEDURES

All the screening and dissolution studies were conducted in an immersion test apparatus. The test apparatus employed a 3.0 L Pyrex reaction kettle (Figure 1). The reaction kettle was sealed with a Teflon O-ring and capped with four neck cover secured with a McCartier clamp. A DU-0.75 percent Ti pellet or target plate was placed into the reaction kettle and reacted with 300 mL of solvent, the amount required to completely immerse the pellet or enough solvent to cover the target plate. The solvent was dispensed by

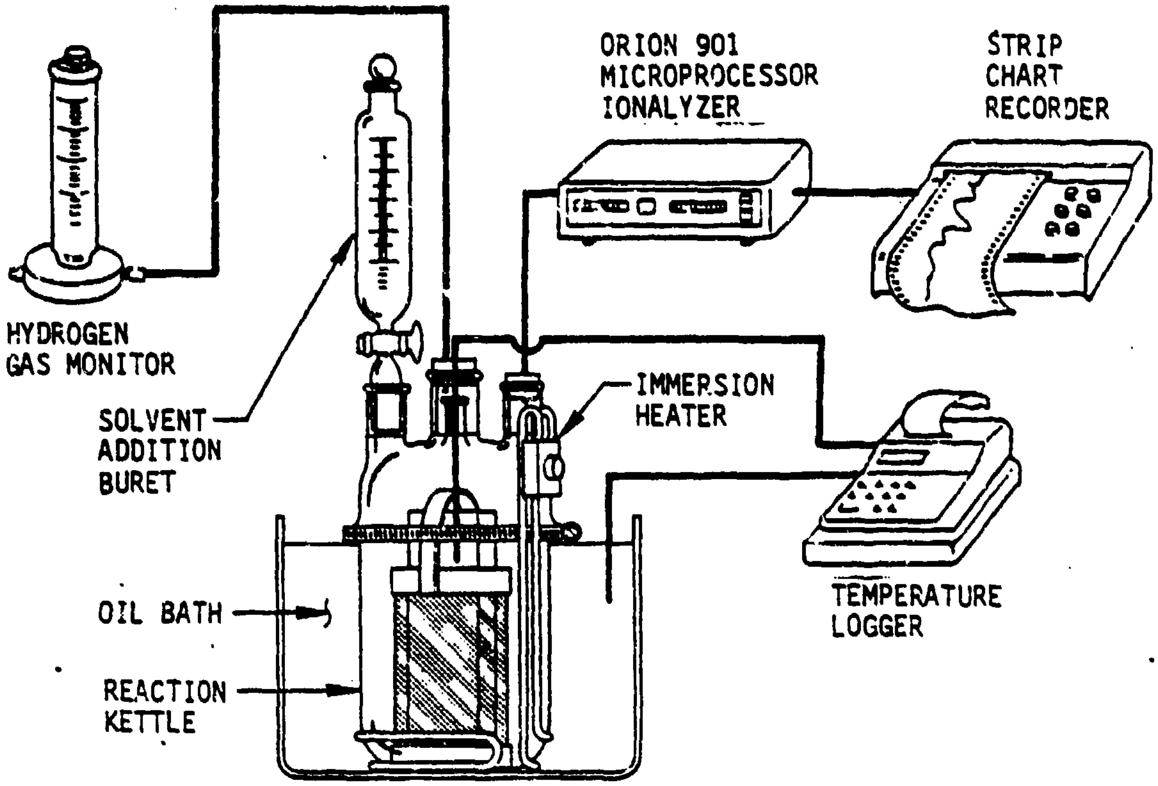


Figure 1. Reaction Kettle.

opening the stopcock of a 500 mL separating funnel mounted on the reaction kettle cover. The solvent temperature was adjusted and maintained to the desired study temperature using a thermostated water bath. To allow intermittent inspection of the pellet/target during testing, the test sample was lowered and raised into the reaction kettle in polypropylene dipping baskets.

The temperature and pH of the solvent were monitored by probes immersed into the reaction bottle through the four-neck kettle cover. Qualitative observations regarding color changes of the solvent and gas evolution were recorded during testing.

In the first phase of laboratory testing the dissolution characteristics of candidate solvents identified in Section 2 were measured as a function of the percent weight loss of the DU-0.75 Ti pellet. The pellets were rinsed, dried, and weighed at the completion of each screening test.

In the second phase of testing, the selectivity characteristics of the two best solvent compositions were evaluated using DU-0.75 percent Ti pellets lodged into bore holes that were drilled into simulated target plates. This represents a large impacted depleted uranium fragment that may be found in actual penetrated armor targets. The dimensions and weights of the steel plate and depleted uranium pellet were taken prior to and immediately after testing. The steel plate containing the depleted uranium pellet was placed into the 3 liter reaction kettle and reacted with one liter of acid solvent. The plate was reacted at temperatures between 80 and 85 °C for up to 75 minutes. The target plate was inspected every 10 minutes to determine the minimum reaction time needed to completely dissolve the embedded DU pellet. The test was terminated after the pellet was completely dissolved or 75 minutes. After the test, the target plate and the DU pellet, if any existed, were weighed and the percent metal weight loss was calculated for both the uranium pellet and target plate.

In the third phase of the decontamination studies, the best solvent determined from the previous test was evaluated against a contaminated penetrated target. The most contaminated plate (Sample A, see Table 4), determined as the plate with the highest cpm value, was decontaminated with the best solvent using the procedure followed for selectivity testing. The contaminated plate was immersed into the 3 liter reaction kettle containing approximately 2 liters of solvent heated to 84 °C. Periodically, the plate was raised from the kettle reactor, rinsed with deionized water and the average contamination (cpm) measured. This procedure was repeated until the cpm value was reduced by at least 95 percent.

RESULTS

DU-0.75 Percent Ti Pellets

In general, solvents that contain at least 4M hydrochloric acid (HCl) react very rapidly and completely with DU-0.75 percent Ti alloy to form uranium (IV) chloride (Table 4). When 4M HCl is reacted with the DU-0.75 percent Ti pellet, there is a short quiescent period before the rapid evolution of hydrogen begins. Dissolution of the pellets with only HCl forms a black precipitate

TABLE 4. DU-0.75 Percent Ti Pellet Dissolution Summary.

Solvent	Pellet Wt (g)	Percent Dissolved	Comments
12M HCl	18.345	100	-Rapid dissolution rate -Black precipitate -Forms uranium tetrachloride
4M HCl	19.143	100	Same as 12M HCl
3M HCl:1M H_3PO_4: ethyl acetate	20.375	93.5	-Moderate dissolution rate -Forms uranium tetrachloride -No black precipitation
4M HCl:7M H_3PO_4	15.952	100	-Rapid dissolution rate -Forms U(IV) chloride and sulfate complexes -No precipitate formation
7M H_3PO_4	17.206	0	-Non-reactive
4:1 - HCl:HNO_3	16.953	100	-Uranium IV chloro and nitrate complexes
1M NaOH:5M H_2O_2	18.869	2.2	-Slow dissolution rate -Uranyl peroxide complex
6M H_2SO_4:0.01 HCl: 1M H_2O_2	17.772	1.4	-Slow dissolution rate -Uranyl sulfate complex
4M HCl: 7M H_3PO_4 with 0.5M D2EHPA and 0.125M TOPO	17.676	100	-Rapid dissolution rate -Tetravalent uranium complexes -Organic complexes
6M H_2SO_4:0.01M HCl: 1M H_2O_2 with 0.5M D2EHPA and 0.125M TOPO	17.992	1.7	-Uranyl sulfate complex -Organic chelate does not significantly enhance rate

that is characterized as a pyrophoric and potentially explosive hydrated (III-IV) oxide. No amount of heating in the acid could solubilize the precipitate completely. In 4M HCl at 85 °C, a 19 gram sample pellet was 100 percent consumed in one hour; in 12M HCl, the evolution of hydrogen was explosively rapid. The pellet, when removed from the reactor kettle after partial dissolution, was covered with a heavy black coating. Most of this was easily scraped away, but next to the bulk metal it was very adherent. This coating is very reactive when dried, glowing red hot from sudden air oxidation.

Two reagents, phosphoric acid and ethyl acetate, when added to the hydrochloric acid dissolutions of the DU-0.75 percent Ti pellet, prevented the formation of the heavy black residue. Both are strong complexants of uranium. Phosphoric acid in high concentrations (7M) prevented the formation of the black residue associated with HCl uranium dissolution. A 16 gram sample of bulk DU-0.75 percent Ti was completely dissolved in one hour in a 4M HCl-7M H_3PO_4 acid solvent.

Hydrochloric acid solutions in ethyl acetate reacted with a DU-0.75 percent Ti pellet at a moderate rate to form a uranium tetrachloride solution. In a 3M HCl solution, which is close to saturation, a 20 gram sample pellet was 93.5 percent dissolved in one hour, but formed some residue. The addition of 1M H_3PO_4 resulted in a residue free dissolution.

Soon after the introduction of the pellet in the solvent, hydrogen evolution begins and the solution takes on the characteristic green color of quadrivalent uranium. The ethyl acetate-hydrochloric acid dissolution of depleted uranium is unique in that the metal can be dissolved completely in a relatively mild reagent. Its action is similar to hydrochloric acid but does not lead to the insoluble hydrated oxides.

Aqua regia (4:1 - $HCl:HNO_3$) was very effective in completely dissolving a DU-0.75 percent Ti pellet. A 17 gram sample pellet was 100 percent dissolved in one hour at 80 °C. The dissolution resulted in the formation of uranium IV chloro- and nitro- complexes.

The dissolution of DU-0.75 percent Ti pellet in a sodium hydroxide-hydrogen peroxide mixture was tested to evaluate the effect of a basic medium. The literature (6) reports that uranium metal reacts at a moderate rate with 1M sodium hydroxide-5M hydrogen peroxide mixture to form a colored uranyl peroxide complex. However, a 19 gram DU-0.75 percent Ti pellet was only partially dissolved (2.2 percent) in one hour at 85 °C.

Solvents containing sulfuric acid (H_2SO_4) do not significantly react with DU-0.75 percent Ti at moderate concentrations. Only 1.4 percent of an 18 gram pellet was dissolved in one hour at 75 °C in 300 mL of a 6M sulfuric acid-1M hydrogen peroxide-0.01M hydrochloric acid mixture. The addition of HCl and H_2O_2 in catalytic amounts was intended to increase the rate of dissolution, but proved ineffective. There was an initial effervescence at the pellet surface, indicating the evolution of hydrogen gas and uranium dissolution, but all visible reaction ceased after 10 minutes. There was a visible darkening of the metal surface, which could be responsible for protecting the pellet from further attack. This is somewhat surprising because uranium (IV) is strongly complexed by sulfate, and uranium (IV) sulfates are soluble. The addition of the chelate 0.5M D2EHPA-0.125M TOPO did not have any significant effect on the rate of dissolution.

Based on the dissolution properties of the solvents for DU, two solvents were selected for further laboratory evaluation. The solvent systems:

- 4M HCl:7M H_3PO_4
- 3M HCl:1M H_3PO_4:ethyl acetate

were judged most practical.

Simulated Target Material

A summary of the test conditions and results conducted on the simulated target are summarized in Table 5. The results indicate that 4M HCl:7M H_3PO_4 is an excellent solvent for selectively dissolving DU-0.75 percent Ti fragments from simulated target plates. In 55 minutes, a 17.36 g DU-0.75 percent Ti

TABLE 5. Simulated Target Summary.

Experimental Conditions

Solvent Composition	4M HCl:7M H_3PO_4	4M HCl:1M H_3PO_4:EtOAc
Solvent Temperature (°C)	85	77
Solvent Volume (mL)	1000	1000
Test Duration (min)	55	75
Target Plate Dimensions (cm)	2.54 x 10.2 x 15.2	2.54 x 10.2 x 15.2
Bore Hole Dimensions (cm)	1.3 x 0.77	1.3 x 0.77
Target Plate Weight (g)	3117	3108
DU Pellet[a] Dimensions (cm)	1.2 x 0.77	1.2 x 0.77
Pellet Weight (g)	17.3604	18.6969

Test Results

Target Plate Dissolution (%)	0.69	0.43
DU Pellet Dissolution (%)	100	Approx 50
Gas Evolution	Rapid	Moderate
Comments	Forms clear green U(IV) chloride and phosphate complexes. No residue.	Partial dissolution. Pellet fused to target.

---

[a] Pellet consists of DU-0.75 percent Ti.

pellet was completely dissolved in a pre-drilled bore hole. The dissolution is rapid and selective. The target plate remained intact with only 0.69 percent of its total weight dissolved. Vigorous gas evolution around the area of the pellet demonstrates the solvent's preference for DU-0.75 percent Ti over the target composition.

During decontamination, the acid solvent turned green in color, indicative of quadrivalent uranium chloride and phosphate complexes. No potentially hazardous precipitates were formed. The bore hole was inspected for residue and tested for radioactive contamination with a Geiger counter. No residue was found and only background radioactivity was detected.

The 3M HCl:1M H_3PO_4:ethyl acetate solvent performed reasonably well. This solvent is less vigorous than the former, as indicated by the dissolution of approximately 50 percent of the uranium pellet in 75 minutes. Although this solvent is effective over time and produces no dangerous precipitate, its volatility precludes its use as a safe and economical decontamination solvent. Since this solvent offers no apparent advantages relative to the 4M HCl: 7M H_3PO_4 acid solvent, no further testing was conducted.

Penetrated Targets

The 4M HCl:7M H_3PO_4 acid solvent was tested to evaluate the decontamination kinetics on penetrated targets. The target was decontaminated in the reaction kettle at 84 °C. The target was periodically removed, rinsed in deionized water, surveyed to determine the residual contamination levels, and then reinserted into the reaction kettle. The results of this test are presented in Figure 2. The 4M HCl:7M H_3PO_4 formulation turned dark green during decontamination.

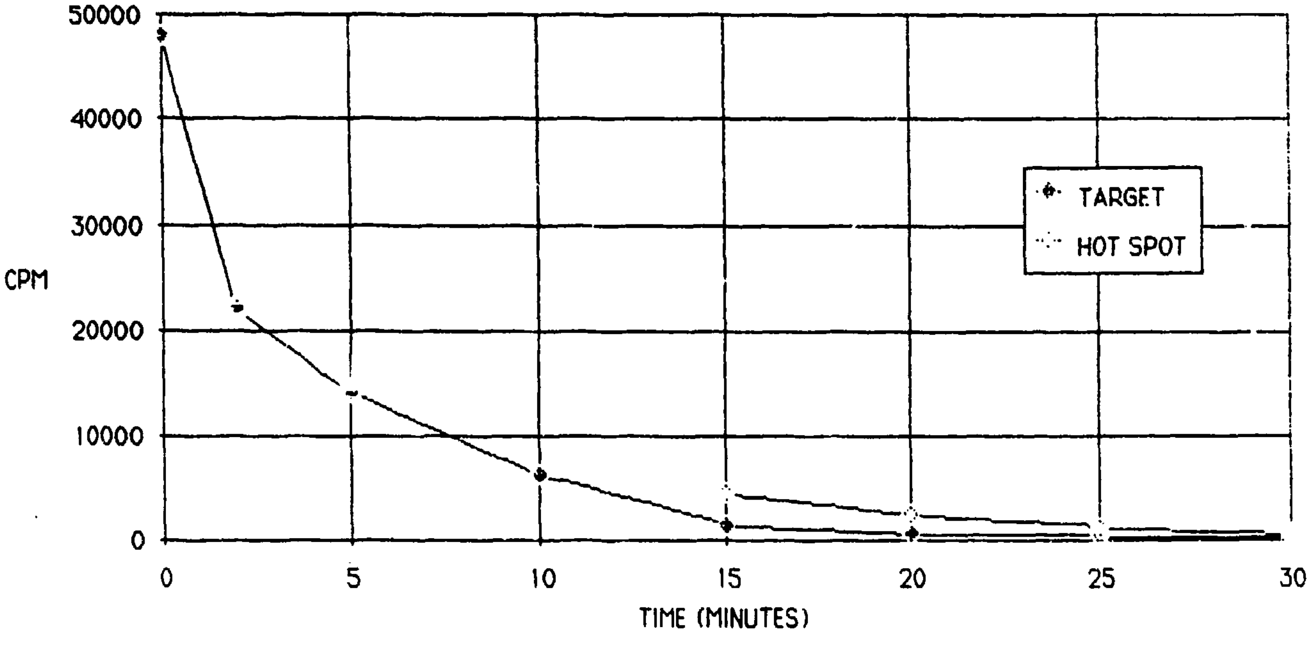


Figure 2. Decontamination of a Penetrated Target Using a HCl/H_3PO_4 Selective Acid Solvent.

A hot spot was identified during a 15 minute immersion inspection of the plate with a GM counter. The hot spot was located in a crevice located at the perimeter of the hole. The average decontamination of the hot spot was recorded at 4,400 cpm and was monitored at subsequent inspections. It is unclear as to why the hot spot wasn't detected during initial characterization of the plate. A possible explanation is the uranium fragment was shielded by target material and was detected after a portion of the target was dissolved.

The 4M HCl:7M H_3PO_4 acid solvent effectively removed fixed uranium contamination from the penetrated area of the target including the hot spot. The average contamination of the hot spot was 4,400 cpm when it was detected and was reduced to 600 cpm (86 percent reduction) in the time required to decontaminate the rest of the plate to 200 cpm (99.5 percent reduction). This suggests that regions which are contaminated with bulk uranium will require longer immersion times to reach the same level of decontamination as the rest of the target.

The acid solvent also removed rust from the surface of the target resulting in a dull gray appearance characteristic of the bare metal. The H_3PO_4 in the solvent inhibited excessive corrosion of the target plate, resulting in a 1.1 percent total weight loss. Target weight loss measurements are summarized in Table 6.

TABLE 6. Contaminated Target Dissolution.

Solvent	Time (min)	Temp (°C)	Pre-Weight (g)	Post-Weight (g)	Weight Loss (percent)
4M HCl:7M H_3PO_4	30	84	3122	3089	1.1

DISCUSSION

The test results indicated both the DU-0.75 percent Ti pellet from the simulated target plate and the metallic radwaste from the actual penetrated target could be greatly reduced an 4M HCl:7M H_3PO_4 acid solvent. A synergistic effect occurred when the HCl and H_3PO_4 were combined for target decontamination. This formulation removed rust and scale containing entrained uranium from the metal surface in addition to solubilizing uranium "hot spot" contamination. The decontamination solvent was selective and inhibited excessive attack of the steel target. The ferric iron that did result from partial target dissolution acted as an oxidant to facilitate uranium dissolution from the steel specimens.

SECTION IV

SOLVENT RECYCLE/WASTE REDUCTION

The feasibility of recycling (and reusing) the acid solvent back to the decontamination process was demonstrated using ion exchange, solvent extraction and precipitation technologies. Recycling the solvent improves the efficiency of the decontamination process by maintaining a constant, but low level of contaminant concentration in the bath, minimizes operating cost, and decreases the volume of secondary waste. In addition, the DU is concentrated during the recovery process and is reduced to the smallest possible volume for disposal or purification/recovery.

ION EXCHANGE

Uranium normally forms cationic phosphate and chloride complexes in the IV and VI oxidation states in acidic phosphate and chloride solutions. However in the presence of Fe(II+), due to the partial dissolution of the target, U(VI) is reduced to U(IV). Excess phosphate in the solvent displaces the equilibrium towards the larger and more stable phosphate complexes, e.g., $UO_2(H_2PO_4)_2.H_3PO_4$.

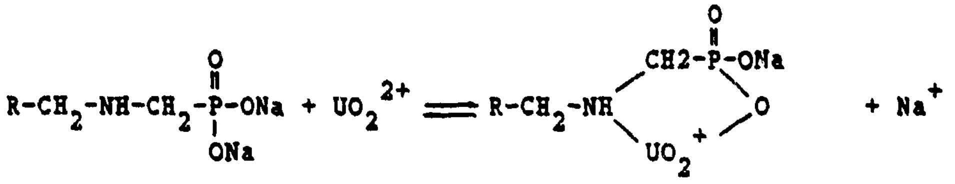
Resin Properties

The extraction of uranium from the 4M HCl:7M H_3PO_4 acid solvent was successfully demonstrated with the ion exchange resin, Duolite ES 467. Although not required as part of the Phase I program, FMI successfully demonstrated that the extracted uranium can be recovered from the resin as ammonium uranyl tricarbonate. Duolite ES 467, is a chelating resin that is commercially available from Rohm and Haas (Philadelphia, PA). The resin has a macroporous structure and its polystyrene matrix, which is cross-linked with divinyl benzene, contains aminophosphonic acid groups. Duolite ES 467 forms complexes with metallic ions and extracts uranium in the IV and VI valency states. Duolite ES 467 may be distinguished from the more standard aminodiacetic resins by its wider variation in stability in the presence of various cations and by the greater stability of the complexes formed with metallic cations of low atomic mass. A description of the chemical and physical properties of Duolite ES 467 is given in Table 7 (8).

TABLE 7. Properties of Duolite ES 467.

Matrix	Macroporous polystyrene
Functional Groups	$-NH-CH_2-PO_3Na_2$
Physical Form	Beige-colored beads
Bulk Density	About 0.75
Specific Gravity	About 1.12 (in Na form)
Particle Size (mm)	0.3 - 1.2
Moisture Content (percent)	60-65
Ionic Form (shipped)	Na
Minimum Total Exchange Capacity (g Cu/L)	45 (at pH 6)
Operating Temperature Limit (°C)	65
Maximum Reversible Swelling (percent)	About 50 (H to Na form)
Solubility	Insoluble in water, dilute acids and bases, and common solvents

The characteristic reaction of uranyl species with the amino-phosphonic functional group of Duolite ES 467 is as follows:



Test Procedures

An ion exchange column was prepared to remove dissolved uranium contaminants (cationic complexes of phosphate and chlorides) from the acid solvent. The column was charged with 122 mL of Duolite ES 467 in the Na form.

The resin column was backwashed with 5 bed volumes (BV) of fresh solvent to remove any water that could cause uranium to precipitate from the acid solvent. The acid solvent containing depleted uranium at a temperature of 60 °C was then permitted to flow through the column at an extraction flow rate of 8 BV/hr, or approximately 1 gpm/ft^3 resin. Flow was provided by a peristaltic pump head driven by a variable speed drive.

As the acid solvent was treated, the exhaustion of the exchange resin was followed by noting the color change taking place in the resin bed. As the uranium complexes and the ferric chloride complex, which is present due to partial target dissolution, is adsorbed, the Duolite ES 467 darkens. Regeneration of the resin was accomplished by washing the column with 5 BV of deionized water followed by 4.5 BV of 1M ammonium carbonate [$(NH4)_2CO_3$] (8,9). The course of the regeneration can be followed by noting the color, as the resin becomes lighter. The flow rate for the regeneration cycle was 4 BV/hr, or approximately 0.5 gpm/ft^3 resin.

The temperature of the eluant was maintained at about 20 °C to increase the kinetics of elution and the efficiency of the ion exchange column. Aliquots of the effluent and eluant were sampled at regularly timed intervals and analyzed for uranium and iron content.

Results

The Duolite ES 467 chelating resin gave very good sorption of uranium from the 4M HCl:7M H_3PO_4 acid solvent. Extraction data for the ion exchange resin is shown in Figure 3. In a parallel study, the equilibrium capacity of the resin was determined to be 0.33 equivalents (eq)/L. Because of the high acidity of the acid solvent, the efficiency of uranium removal is low and therefore the resin has to be regenerated often. Impurities in the acid, such as Fe (II+) and Fe(III+), have some effect on uranium uptake (9). The presence of Fe (II+). which reduces uranium to the tetravalent oxidation state, is also sorbed by Duolite ES 467. However, Duolite ES 467, is a powerful chelating resin in the strong acid solvent and selectively sorbs uranium over Fe (II+). The Duolite ES 467 aminophosphonic acid resin is readily eluted with an ammonium carbonate solution (Figure 4). About 90 percent of uranium is eluted at 20 °C using 1M $(NH_4)_2CO_3$. Sorbed ion chloride complexes are selectively eluted with water prior to ammonium carbonate elution. This affords many advantages since it is possible to extract uranium from the acid solvent and recover the pure concentrate in the carbonate solution.

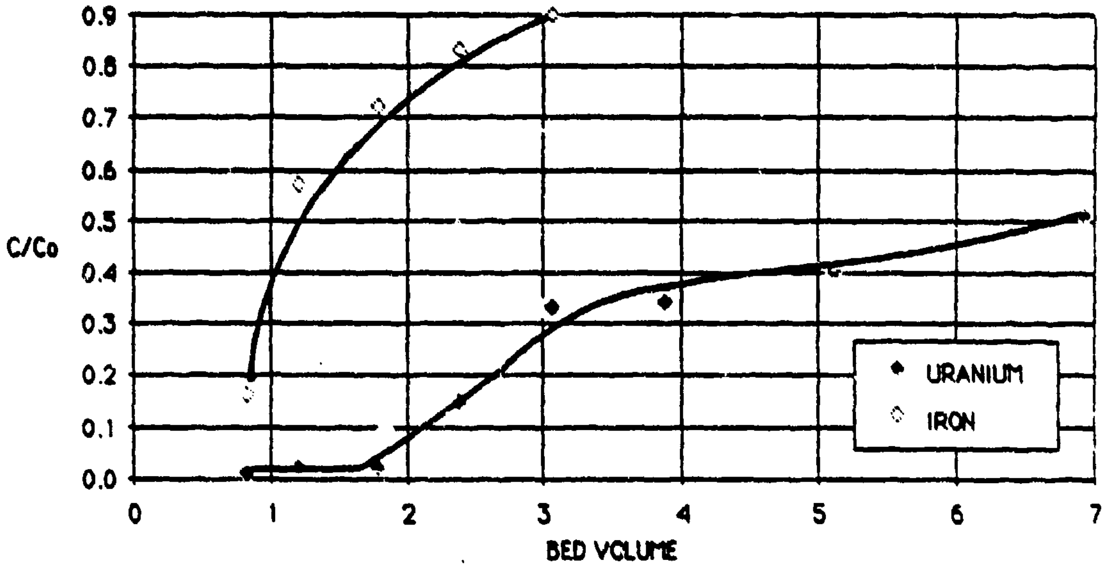


Figure 3. Extraction of Uranium Metal Complexes by Duolite ES 467.

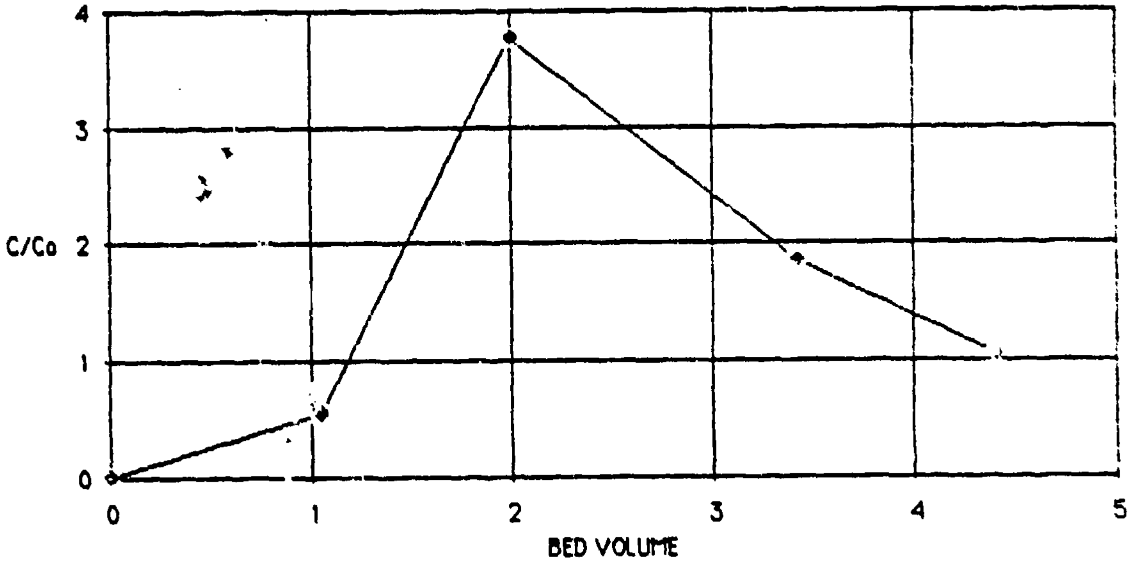


Figure 4. Elution of Uranium Metal Complexes from Duolite ES 467.

Discussion

A conceptual flow sheet for recovering uranium using Duolite ES 467 is illustrated in Figure 5. The contaminant U (IV) in the 4M HCl:7M H_3PO_4 acid solvent can be sorbed in the extraction contactor at 60 °C. After the sorption step (1), the resin is eluted with ammonium carbonate solution (2). The eluted resin is regenerated with a dilute NaOH solution (3). The ammonium uranyl tricarbonate eluant can be precipitated (4) directly with excess NH_3 and CO_2. The precipitate is filtered (5) and calcined (6) at 300 °C to yield U_3O_8 "yellow cake" (8,9).

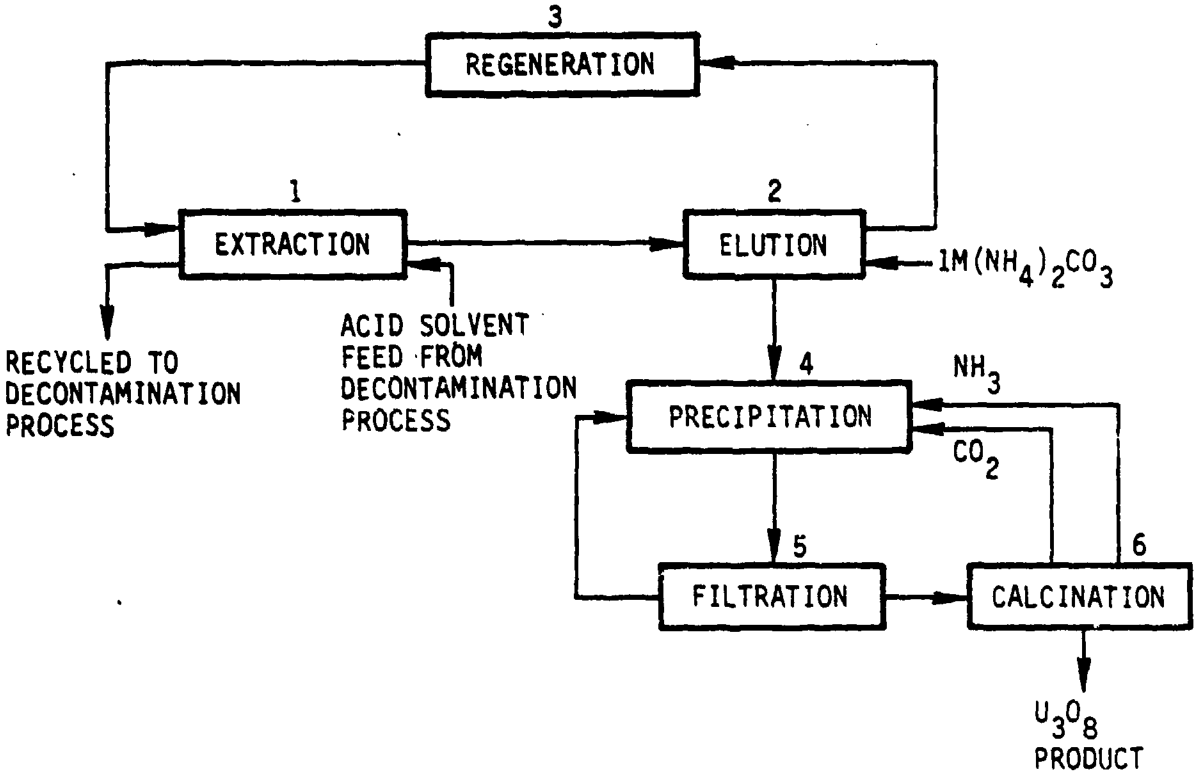


Figure 5. Flow Sheet for Uranium Extraction and Recovery by Ion Exchange.

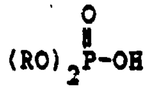
This process route is simple and reduces the contaminated waste to the smallest volume possible. The recovery of uranium from the acid solvent allows the solvent to be recycled back to the decontamination process.

SOLVENT EXTRACTION

Extractant Properties

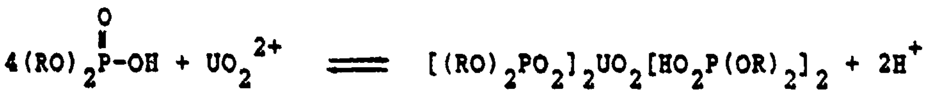
The potential of solvent extraction is well documented by the wide variety of solutions containing uranium which are amenable to recovery, purification, and concentration by liquid ion exchange. The extractants tri-n-octylphosphine oxide (TOPO) and di-2-ethylhexyl-phosphoric acid (D2EHPA), when used together in synergistic combinations and dissolved in an aliphatic solvent, exhibit very high uranium loading from sulfate leach liquors. Successful uranium recovery has also been demonstrated in acid chloride and phosphate solutions (10).

TOPO is basic in nature in that it coordinates to the uranium in a neutral metal complex, thereby causing the resulting organo-uranium complex to be organic soluble. The chemistry of D2EHPA resembles the chelate extractants and also show some similarity to neutral or solvating types of extractants. The chemical structure of D2EHPA is represented as follows:



$$(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}\text{-}OH$$

where R = C_8H_{17}. The following equation shows the behavioral characteristics of the two extractants when used together:



$$4(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}\text{-}OH + UO_2^{2+} \rightleftharpoons [(RO)_2PO_2]_2UO_2[HO_2P(OR)_2]_2 + 2H^+$$

In the above formulation, two of the D2EHPA molecules lose a proton, much like a chelate extractant, while two other D2EHPA molecules solvate the uranium, similar to solvating-type extractants.

The feasibility of using a synergistic mixture of TOPO and D2EHPA for the recovery of uranium from the acid solvent was demonstrated.

Test Procedures

The contaminated 4M HCl:7M H_3PO_4 acid solvent used to treat the actual impacted target plate contained 0.234 g U/L and 5.7 g Fe(total)/L. The uranium was extracted from the acid solvent with 0.5M D2EHPA:0.125M TOPO dissolved in reagent grade kerosine. The ratio of organic/aqueous was unity, which permitted good separation of the two phases. The two phases were contacted in a 100 mL Erlenmeyer flask. Mixing was accomplished with a magnetic stirrer. It was experimentally determined that equilibrium was established in less than 5 minutes, but for convenience 30 minutes was selected. Separation of the aqueous and organic phases was carried out in a 100 mL separation funnel. After complete separation of the two phases, samples of the extracted acid solvent were taken for uranium and iron analysis.

Results

In a simple experiment on uranium removal in a contaminated selective acid solvent, the effect of the D2EHPA and TOPO synergistic mixture is shown in Table 8.

TABLE 8. Results of Uranium Removal by Solvent Extraction.

	Acid Solvent Concentration (g/L)		Removal	Distribution
Element	Before Extraction	After Extraction	(percent)	Coefficient[a]
U	0.234	0.062	73.5	2.78
Fe(total)	5.70	2.30	59.6	1.49

---

[a] Molar ratio of the element in the organic and aqueous phases at equilibrium.

The distribution coefficient, D, is defined as the molar ratio of the element in the organic and aqueous phases at equilibrium. The relative selectivity of the solvent for uranium relative to iron is measured by the separation factor; the larger the separation factor the more selective the solvent is for uranium. The separation factor, S, which is defined as the ratio of the distribution coefficients for uranium and iron, was found to be S = 1.87 for the experiment.

Discussion

Extraction of the uranium is very rapid. The uranium distribution coefficient, $D_U = 2.78$, obtained using the TOPO/D2EHPA extractant, was higher than the distribution coefficient for iron, $D_{Fe} = 1.49$, emphasizing the selectivity of the extractant for uranium. The percent removal of uranium is dependent on the D2EHPA concentration (with a constant TOPO:D2EHPA ratio). Consequently, the extraction efficiency of 73.5 percent can be increased by increasing the extractant concentration. Although not demonstrated in these experiments, the uranium is effectively stripped from the TOPO:D2EHPA extractant by contacting with ammonium carbonate solutions (10,11) . The stripped solution can be precipitated and calcined to yield U_3O_8, as described previously for ion exchange.

Some of the major drawbacks of a solvent extraction process for decontaminating impacted targets include the possible buildup of solids at the aqueous/organic interface, the entrainment of organic solvent in the acid solvent solution, and the high cost of TOPO.

In conclusion, the method based on solid ion exchange using Duolite ES 467 resin will offer several advantages over the liquid extractant system, the major ones being the ease of separating the reactants from the products and the ease of recycling the extractant and the 4M HCl:7M H_3PO_4 acid solvent.

PRECIPITATION

The recovery of uranium from the contaminated 4M HCl:7M H_3PO_4 solvent is based on the formation of sparingly soluble compounds. A list of sparingly soluble uranium compounds is given in Table 9. The separation of a pure product from a contaminated 4M HCl:7M H_3PO_4 acid solvent cannot be achieved because the precipitate often contains considerable amounts of the precipitant itself, or co-precipitation of interfering elements, like iron. However, precipitation is often very effective in removing up to 97 percent of the solution uranium content.

TABLE 9. Solubility of Sparingly Soluble Uranium Compounds.

Compound	Solubility Product	Solubility
$UO_2NH_4PO_4$	$4.36\text{x}10^{-27}$	-
$(UO_2)_3(PO_4)_2$	$4.73\text{x}10^{-47}$	-
UO_2KPO_4	$7.76\text{x}10^{-24}$	-
UO_2HPO_4	$2.14\text{x}10^{-11}$	-
UO_2SO_3	$2.56\text{x}10^{-9}$	-
$UO_2NH_4AsO_4$	$1.71\text{x}10^{-24}$	-
UO_2KAsO_4	$2.52\text{x}10^{-23}$	-
UO_2NaAsO_4	$1.35\text{x}10^{-22}$	-
UF_4	-	10^{-4} mole/L(25 °C)
$U(OH)_4$	$(1.1\pm0.7)\text{x}10^{-52}$	-
$UO_2(C_6H_5N_2O_2)_2 \cdot NH_4C_6H_5N_2O_2$[a]	$(5.8\pm2.5)\text{x}10^{-10}$	-
UO_2HAsO_4	$3.17\text{x}10^{-11}$	-
$UO_4 \cdot 2H_2O$	-	$7.78\text{x}10^{-10}$ mole/L
$U(C_2O_4)_2 \cdot 6H_2O$	$4.3\pm0.4)\text{x}10^{-22}$	$5\text{x}10^{-2}$ g/L(25 °C)
$U(HPO_4)_2$	$3.1\ \text{x}10^{-18}$	-
$NH_4[UO_2(OH)_2VO_3]$	$1.7\ \text{x}10^{-13}$	-
$NH_4[UO_2(OH)(VO_3)_2] \cdot 1.5H_2O$	$2.9\ \text{x}10^{-14}$	-
$NH_4[UO_2(VO_3)_3] \cdot 3.5H_2O$	$9.6\ \text{x}10^{-15}$	-

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[a] Uranyl ammonium cupferronate

Test Procedure

The contaminated 4M HCl:7M H_3PO_4 solvent solution resulting in the decontamination of the impacted target was precipitated with sodium hydroxide (NaOH) and ammonium phosphate $[(NH_4)_2HPO_4]$ solutions. Each solution, at a concentration of 2M (molar) was titrated into the contaminated 4M HCl:7M H_3PO_4 solvent until the precipitation reaction was evident. Sufficient excess of precipitant was added to drive the precipitation reaction to completion. Constant stirring was maintained with a magnetic stirrer. The progress of the reaction was monitored by sampling aliquots of the acid solvent for analysis. The final pH value was recorded following the last addition of precipitant.

Results

The addition of sodium hydroxide and ammonium phosphate to the 4M HCl:7M H_3PO_4 acid solvent resulted in the precipitation of uranium as the insoluble uranyl ammonium phosphate, $UO_2NH_4PO_4$, and uranium hydroxide, $U(OH)_4$, with solubility products of (1.1 ± 0.72) x 10^{-52} and 4.36 x 10^{-27}, respectively. A summary of the final pH values and percent uranium removal are given in Table 10. Removal efficiencies of 97.6 percent for NaOH and 94.5 percent for $(NH_4)_2HPO_4$ demonstrate effective removal of uranium in the 4M HCl:7M H_3PO_4 contaminated solvent.

TABLE 10. Results of Uranium Removal by Precipitation.

		U Concentration (g/L)		
Precipitant	Final pH	Before Precipitation	After Precipitation	Removal (percent)
NaOH	10.9	215	5.2	97.6
$(NH_4)_2HPO_4$	6.5	215	11.9	94.5

Discussion

Precipitation has proven to be an effective technique for removing uranium and other contaminants from contaminated 4M HCl:7M H_3PO_4 acid solvents. Uranium compounds that precipitate out can be removed in a subsequent treatment step and disposal as a low level waste. The recovery of uranium from acid solvents is greatly dependent on pH. Increasing the pH of the acid solvent for uranium recovery, neutralizes the solvent and precludes any chance of recycling the solvent. However, precipitation remains a viable waste reduction method pending a cost analysis of the other recovery methods mentioned in this report.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

All of the objectives of the Phase I SBIR program have been achieved, namely:

- To develop a selective solvent that can decontaminate impacted armor targets containing depleted uranium for disposal or recycle.
- To identify and characterize technologies that can remove depleted uranium from the solvent for solvent recycle and uranium recovery for easier disposal.

This program has demonstrated the technical feasibility of using a 4M HCl:7M H_3PO_4 acid solvent to dissolve depleted uranium fragments from contaminated metal targets for disposal or recycle as non-radioactive material. Decontamination testing on targets characterized as containing residual entrained penetrator fragments is necessary to determine if all of the radioactivity associated with penetrator holes in the metal target material can be removed.

The HCl:H_3PO_4 acid solvent completely and very rapidly dissolved a DU alloy pellet inserted in a pre-drilled bore hole in a simulated metal target, while the target plate remained intact with less than 1 percent of its total weight dissolved. In less than 30 minutes, the acid solvent reduced the average contamination of a hot spot on a real penetrated target by 86 percent, while reducing the overall contamination of the rest of the plate by 99.5 percent; the phosphoric acid in the combined solvent inhibited excessive corrosion of the target plate resulting in about a one percent total weight loss.

The 4M HCl:7M H_3PO_4 decontamination acid solvent has many advantages over existing chemical decontamination methods. The most noteworthy are:

- Hydrochloric acid is one of the most active solvents for uranium alloy dissolution.

- Phosphoric acid is a powerful sequestrant that removes radioactive oxide scales and rust on the target and passifies the target surface with a film of iron phosphate.

These characteristics make the addition of expensive corrosion inhibitors (e.g., formaldehyde and gluconic acid) that may interfere with uranium recovery and solvent recycle unnecessary.

Removing the depleted uranium from the acid solvent results in recycling of the acid solvent and in concentration of the depleted uranium for easier disposal. Three technologies for removing the depleted uranium from the acid solvent were demonstrated experimentally, namely ion exchange, solvent extraction, and precipitation.

Ion exchange using an amino phosphonic acid chelating resin, Duolite ES 467, appeared to be the most feasible technically for removing and concentrating the depleted uranium from the 4M HCl:7M H_3PO_4 acid solvent. A conceptual flow sheet, based on preliminary test data, suggested that uranium could be extracted from the acid solvent while at the same time recycling the acid solvent. The resin could be eluted with ammonium carbonate solutions, ultimately recovering stable U_3O_8 ("yellow cake") for hazardous waste disposal. This technique can completely separate the depleted uranium from the target generating a small volume of contaminant for disposal as low level radioactive waste and the target can be disposed of as trash or salvage.

Organic extractants containing the synergistic mixture D2EHPA:TOPO was also evaluated for the recovery of uranium from a contaminated 4M HCl:7M H_3PO_4 acid solvent. About 75 percent of the uranium and 60 percent of total iron content was recovered from the acid solvent. However, the major drawbacks of a solvent extraction system involve the possible buildup of solids at the aqueous/organic interface, entrainment of the organic solvent in the acid solvent, and the high cost of the extractants.

Precipitation also presents an attractive method of recovering uranium from the acid solvent, since the uranium product is obtained directly with a consumption of reagent which is limited to the amount required to form the uranate salt and the stoichiometric equivalent of the other precipitated metals, namely Ti and Fe. Increasing the pH of the acid solvent for uranium recovery neutralizes the solvent and precludes any chance of recovering the solvent. If uranium is recovered from the contaminated acid solvent by simple hydrolytic precipitation, neutralization of the moderately high acid concentrations needed may involve a considerable chemical expense. Further testing and cost analysis are required to indicate the feasible limit of this procedure.

RECOMMENDATIONS

Since the major cost of the recovery process is that of the acid solvent, the economic success of the process depends on keeping the frequency of solvent replacement or acid make-up at a tolerable level. Although solvent recycle was demonstrated by removing uranium from the contaminated solvent in the laboratory by ion exchange, it will be necessary to demonstrate that the decontaminated 4M HCl:7M H_3PO_4 acid solvent is strong enough to decontaminate additional targets before solvent disposal is necessary. The effectiveness of this chemical decontamination process, measured by meeting the disposal criterion for DU contaminated materials and acid solvent recyclability, can be more accurately determined in a small pilot plant located at a plant site where the process can be run continuously. The results of this pilot scale test can be used to determine the working parameters, equipment, safety, cost and other factors that may be identified as pertinent for the design and operation of the target decontamination facility.

Treatment of metal targets containing large residual bulk penetrator material needs evaluation to determine if complete target decontamination can be achieved. Sufficient attention should be given to incorporating chelate ion exchange into the pilot plant testing to demonstrate continuous depleted uranium removal from the acid solvent for solvent recycling and to demonstrate depleted uranium recovery and concentration for easier hazardous waste disposal.

SECTION VI

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