

DEVELOPMENT OF A WASTE TREATMENT PROCESS TO DEACTIVATE REACTIVE URANIUM METAL AND PRODUCE A STABLE WASTE FORM

Dianne D. Gates-Anderson, Carola A. Laue, and Thomas E. Fitch
Lawrence Livermore National Laboratory
7000 East Ave., Livermore, CA 94551

ABSTRACT

This paper highlights the results of initial investigations conducted to support the development of an integrated treatment process to convert pyrophoric metallic uranium wastes to a non-pyrophoric waste that is acceptable for land disposal. Several dissolution systems were evaluated to determine their suitability to dissolve uranium metal and that yield a final waste form containing uranium specie(s) amenable to precipitation, stabilization, adsorption, or ion exchange.

During initial studies, one gram aliquots of uranium metal or the uranium alloy U-2%Mo were treated with 5 to 60 mL of selected reagents. Treatment systems screened included acids, acid mixtures, and bases with and without addition of oxidants. Reagents used included hydrochloric, sulfuric, nitric, and phosphoric acids, sodium hypochlorite, sodium hydroxide and hydrogen peroxide. Complete dissolution of the uranium turnings was achieved with the H₃PO₄/HCl system at room temperature within minutes. The sodium hydroxide/hydrogen peroxide, and sodium hypochlorite systems achieved complete dissolution but required elevated temperatures and longer reaction times. A ranking system based on criteria, such as corrosiveness, temperature, dissolution time, off-gas type and amount, and liquid to solid ratio, was designed to determine the treatment systems that should be developed further for a full-scale process. The highest-ranking systems, nitric acid/sulfuric acid and hydrochloric acid/phosphoric acid, were given priority in our follow-on investigations.

INTRODUCTION

Lawrence Livermore National Laboratory (LLNL) has an inventory of at least 11,700 kg (33 m³) of pyrophoric depleted uranium metal waste that requires treatment prior to disposal. Approximately 12 m³ of this waste is classified as mixed waste and must be treated in order for LLNL to remain in compliance with commitments made to state regulatory agencies. In addition, across the DOE complex an inventory of more than 40,000 kg of pyrophoric depleted uranium waste exists that also requires treatment. Developing a technology to treat the uranium metal waste is essential for DOE sites to remain in compliance with regulatory agreements. Furthermore, if a non-thermal process can be developed to treat both mixed pyrophoric uranium wastes and low-level pyrophoric uranium wastes, potential significant cost savings may arise.

Presently, LLNL has two options for disposing of radioactive waste: Envirocare, a commercial facility in Utah, and the Nevada Test Site (NTS). Both, however, do not accept metallic uranium wastes due to its pyrophoric nature. Key to shipping waste to

either disposal site is to remove the pyrophoric character of the uranium waste. Currently, no viable commercial treatment technologies for pyrophoric uranium mixed wastes are in place, and technologies available to treat low-level pyrophoric uranium wastes are very expensive.

Depleted uranium (Dep-U) wastes at LLNL are stored above ground in 30- and 55-gallon drums in a permitted waste treatment, storage, and disposal facility. The Dep-U waste consists of several forms: sludges, turnings, chips, chunks, and large sections. Most of the Dep-U stored is submerged in storage solutions to minimize contact with air. Storage solutions found are: mineral oil, coolant solution, water, or a combination of these. Many of these wastes have been in storage for several years and drums may not be fully characterized. Therefore, when treating a drum of this waste the composition of the Dep-U (pure metal or alloy), the size and shape of the waste, and the nature of the storage solution may not be known. The objective of the current project is to develop a versatile treatment process to treat the range of Dep-U wastes stored at LLNL and potentially to extend the treatment process to existing waste stream of Dep-U within the DOE complex.

Current efforts at LLNL are focused on developing a three-stage process (Fig 1) for the deactivation, treatment and stabilization of Dep-U waste. As currently proposed, treatment will be conducted in batch mode, in a series of tank reactors. The first step, cleaning the metal from the residues of storage solution, is followed by the dissolution in an appropriate reagent system. The third step of the process will be the solidification or stabilization of the residuals from stage 2.

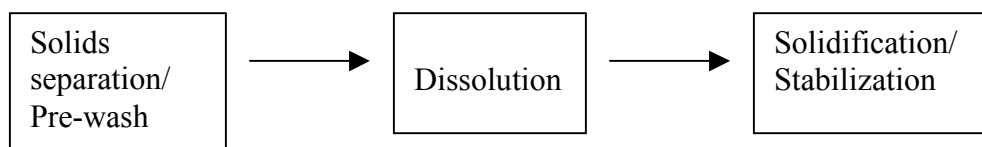


Fig. 1. Schematic of proposed three stages of depleted uranium deactivation process.

Our experimental studies began with the second stage of the proposed process, because the development of the other two stages depends on which dissolution system is selected. Uranium dissolution was studied using small size batches first. The smaller (1 gram) scale studies were designed to allow the maximum number of systems to be studied while minimizing the amount of waste generated. Follow-on studies are in progress to determine the reaction kinetics and thermodynamic characteristics of selected systems.

This paper focuses on the description and the results of the initial experimental small-scale Dep-U investigations that lead to a ranking of the treatment systems. We will describe the chemical reagent systems that most successfully removed the pyrophoric character of the Dep-U waste without generating an excessive volume of residuals.

Uranium Dissolution

The production of uranium metal by leaching or dissolving uranium-bearing ores with acids is a well-documented process [1, 2]. The dissolution of the metal produced was not, until recently, considered desirable. Dissolution of minute amounts of uranium metal or alloys to determine the purity of the metal or the uranium content in an alloy are described in the literature. The basic thermodynamic, kinetic, speciation, complexation, and reaction behavior of uranium's most prevalent oxidation states (IV, V, and VI) has been thoroughly studied [1-5] as has its metallurgical properties [3]. However, in our literature search we found limited data pertaining to the dissolution of uranium metal that would be applicable to waste treatment. The dissolution systems that were described in the literature, provide primarily qualitative information. Detailed experimental findings which included thermodynamic and kinetic data or mechanistic explanations were rarely found. One of the basic science research goals of this project is to establish the reaction mechanism of the dissolution system(s) that are found to be most suitable for Dep-U treatment.

MATERIALS AND METHODS

Depleted uranium turnings for this study were obtained from the Manufacturing and Materials Engineering Division of LLNL. This source was selected because the turnings were characterized by composition and size and were stored in air as opposed to being stored in mineral oil or coolant solution. Turnings of pure depleted uranium and the uranium alloy U-2%Mo were collected in three different sizes; 4, 8 and 16 mil.

All reagents were ACS reagent grade chemicals. The acidic solutions, as listed below in Table I, were prepared by mixing and/or dilution of the concentrated acids (sulfuric 18M, hydrochloric 12M, phosphoric 15M, and nitric 15M). Hydrogen peroxide, 30%, was used in our studies. The sodium hypochlorite (6%) was obtained fresh before our experiments and used as is.

Experiments were conducted in 65 mL glass test tubes into which the desired volume of dissolution solution and 1 g of turnings were placed. The dissolution solutions were heated to the desired temperature, prior to the addition of the depleted uranium turnings. Heating was accomplished by placing the test tubes in an aluminum heating block preheated to the desired temperature. Mixing was accomplished using a vortex mixer with a test tube adapter for several of the experiments. After the depleted uranium was added to the dissolution solution, the time required for complete dissolution was recorded. The amount, if any, of off-gas generated was observed and recorded. In some cases, the increase in temperature was also recorded. The range of dissolution solutions and treatment conditions evaluated in the phase one studies is given in Table I.

Table I. Summary of reagent systems and conditions used in initial studies to evaluate the deactivation of one gram of pyrophoric uranium metal

Reagent or Mixture	Reagent volume added [mL]	Temperature studied [°C]
NaOCl	5, 10, 15, 20, 25	25, 40, 50, 60
10 M H ₂ SO ₄ , 1 M H ₂ O ₂ , 0.1 M HCl	10, 20	25, 35, 45, 55, 65
1.67 M NaOH, 30% H ₂ O ₂	25, 50	40, 65
7 M H ₃ PO ₄ , 4 M HCl	5, 10, 15, 20, 25	25, 35, 45, 55, 65
H ₃ PO ₄ /HCl [M/M] 7/3, 7/2, 7/1, 7/1.5, 6/4, 4/4, 4/2, 2/4	10	25
3 M HCl, 0.2 M Fe ₂ (SO ₄) ₃	50	25
3M HCl, 0.2M FeCl ₃	50	25
6M H ₂ SO ₄ , 1 M H ₂ O ₂ , 0.2 M FeCl ₃ , 3M HCl	60	25
12 M HNO ₃	25	25, 65
HNO ₃ /H ₂ SO ₄ [M/M] 12/0.1, 12/0.2, 12/0.6	25	25, 40
HNO ₃ /H ₃ PO ₄ [M/M] 12/0.1, 12/0.2, 12/0.5	25	25, 40

RESULTS AND DISCUSSION

Several of the dissolution systems evaluated required either excessive amounts of time to reach complete dissolution (more than 24 hrs or if reached at all) or excessive amounts of reagents (>25 mL per 1 gram). Dissolution systems of the latter category include dilute HNO₃, NaOH + H₂O₂, HCl + FeCl₃ and HCl + Fe₂(SO₄)₃. These systems were deemed unsuitable for depleted uranium treatment and will not be discussed in detail.

Hydrochloric and Phosphoric Acid

The H₃PO₄/HCl system completely dissolved uranium turnings under most of the conditions evaluated. Both the D38 and the U-2%Mo alloy were completely dissolved within 1 minute after their addition to 25 mL of a 7 M H₃PO₄, 4 M HCl solution at 65°C. Vigorous evolution of gas was observed during dissolution. Following this initial experiment, the concentration, volume, and temperature of the H₃PO₄/HCl system were varied to determine if the dissolution reaction would be complete under more suitable

conditions such as lower initial temperature and less gas generation. Holding the H_3PO_4 and HCl concentration constant at 7 and 4 molar, respectively, we achieved complete dissolution in less than 5 minutes at temperatures as low as room temperature and liquid to solid ratio (L:S) as low as 5 mL/g (Figure 2).



Fig. 2. Dissolution of one gram of both types of Dep-U studied with 7M H_3PO_4 is complete within 1 min at 45°C.

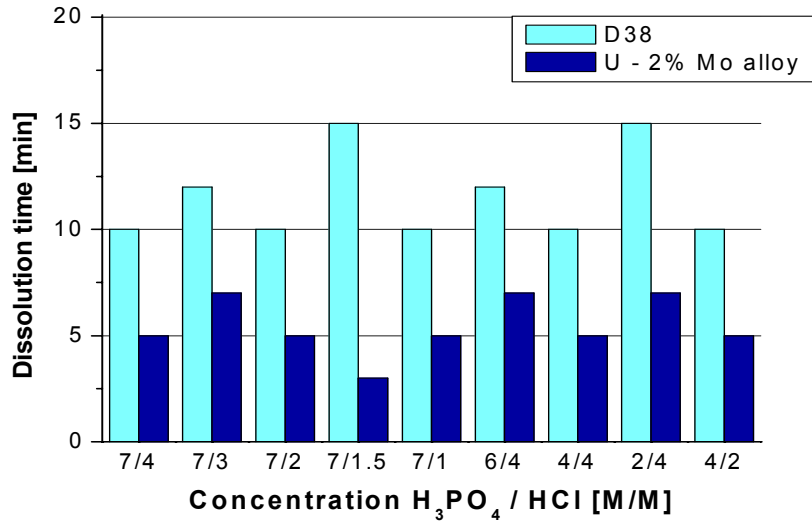


Fig. 3. Dissolution times for the different H_3PO_4 /HCl systems studied at 25°C and L:S = 10 mL/1 g.

Variation of the individual concentrations of the phosphoric and hydrochloric acid in the mixture yielded non-systematic variations in the dissolution times. With a L:S ratio of 10 mL/g at room temperature, mixtures of H_3PO_4 /HCl with concentrations of 7M/3M, 7M/2M, and 6M/4M were found to completely dissolve turnings in 30 minutes or less (Figure 3). Furthermore, with a L:S ratio of 10 mL/g at room temperature, mixtures of H_3PO_4 /HCl with concentrations of 7M/1M, 7M/1.5M, 4M/4M, 4M/2M,

2M/4M resulted in the dissolution of the uranium turnings and generated a “waxy, glassy” solid or sludge. Only minute amounts of free liquid remained after the precipitates were formed. Gas evolution was moderate in the $\text{H}_3\text{PO}_4/\text{HCl}$ systems in which a solid was formed. Further studies will be completed to determine the speciation of the post-treatment liquids and solids and to establish the reaction mechanism.

Sulfuric Acid with traces of Hydrogen Peroxide and Hydrochloric Acid

Initially, 1 g of turnings (4 mil samples of D38 and U-2%Mo alloy) were subjected to 9 mL of a mixture of 7.4M H_2SO_4 , 0.2M HCl and 0.1M H_2O_2 at 65°C. Under these conditions, the turnings of both metals were partially dissolved after 4.5 h. A second addition of 1 mL 30% H_2O_2 at that time resulted in complete dissolution of both metals 6 hours after the initiation of treatment. Several studies were performed to determine if the system would also dissolve the metals at lower temperatures. We found that a treatment at room temperature would be feasible for the U-2%Mo alloy but not for D38. The dissolution times observed for the above described system at room temperature were 2.5 and 24 h for U-2%Mo-alloy and D-38, respectively. We concluded that treatment temperatures of at least 45°C and repeated additions of H_2O_2 are needed in order to achieve the dissolution of a waste with undetermined uranium composition with a solution of H_2SO_4 , HCl and H_2O_2 in a reasonable amount of time.

Sodium Hypochlorite

Treatment with sodium hypochloride, NaOCl, was evaluated at temperatures ranging from 25 to 60°C and L:S ratios in the range of 5 to 25 mL NaOCl per gram uranium. Our experimental results show that a treatment temperature of at least 40°C and a L:S ratio of at least 10:1 mL/g are required to achieve dissolution of both D38 and U-2%Mo alloy.

Nitric Acid without and with Phosphoric or Sulfuric Acid

Our first attempts to dissolve uranium turnings in 2 and 4 N HNO_3 at room temperature resulted in dissolution times in excess of 24 hours. The resistance of the uranium metal and the alloy to dilute nitric acid prompted us to increase the acid strength and temperature. Next, the D38 and U-2%Mo turnings were reacted with 12 M HNO_3 at 65°C. Under these conditions, the U-2%Mo dissolved very quickly and the D38 required more than 18 hours to fully dissolve. Further studies showed that the addition of small amounts of H_3PO_4 , or H_2SO_4 to 12 M HNO_3 at temperatures of 25 and 40°C increased dissolution rates for D38. With the addition of these acids, D-38 was completely dissolved in less than 4 hours at 25°C and less than 2 hours at 40°C.

COMPARISON OF THE DISSOLUTION SYSTEMS AND CONCLUSIONS

After the screening study was completed, we compared the findings using a ranking system to select the most suitable systems for further development. The ranking criteria (Table II) were established after consulting with LLNL Waste Treatment Group

engineers and technicians. The Resource Conservation and Recovery Act (RCRA) interim status permit for LLNL's treatment, storage and disposal facility was also reviewed to insure that the process developed would comply with regulatory requirements since it was desired to develop a treatment process that would not require any permit modifications.

Table II. Ranking system of evaluated uranium metal dissolution systems, criteria and selected examples.

Ranking criteria	Levels and weight	7M H ₂ SO ₄ / 6% H ₂ O ₂ 0.1M HCl	7M H ₃ PO ₄ / 3M HCl	4M H ₃ PO ₄ / 2M HCl	12M HNO ₃ / 0.2M H ₂ SO ₄
Temperature (starting)	< 40°C = 0 > 40°C = 1	1	0	0	0
Temperature (maximum reached)	< 80°C = 0 > 80°C = 1	0	0	0	0
Dissolution time	< 5 hr = 0 > 5 hr = 1	0	0	0	0
Corrosiveness	No HCl = 0 With HCl = 1	1	1	1	0
Off-gas	None = 0 Moderate = 1 Profuse = 2	2	1	0	1
Liquid:solid ratio (mL/g)	< 10:1 = 0 > 25:1 = 1 > 50:1 = 2	1	1	0	1
Dissolution final product	Liquid or solid = 0 Mixture = 1	0	0	0	0
Score of given examples		5	3	1	2

The most important factors for ranking the potential treatment systems were temperature, dissolution time, corrosiveness, L:S ratio, and off-gas quantity. The nature of the dissolution product (liquid or solid) was also considered when ranking the treatments. Corrosiveness was seen as one of the most important criteria because the choice of the materials for the construction of the treatment tanks and the long-term integrity of the disposal container are impacted by the corrosiveness of the reagents used. Systems containing chloride are most corrosive and would require more costly equipment than any other system. A treatment time of less than 5 hours was desired able so the dissolution step could be completed during an 8-hour work shift.

The ranking criteria were used to calculate a score for each dissolution system at the treatment conditions evaluated. Each ranking factor was equally weighted in determining the score. The ranking criteria and some examples of systems ranked are provided in Table II. The uranium dissolution treatments with the highest ranking (lowest scores), $\text{H}_3\text{PO}_4/\text{HCl}$ and $\text{HNO}_3/\text{H}_2\text{SO}_4$, were selected for further investigations. There are two reasons why $\text{H}_3\text{PO}_4/\text{HCl}$ was selected even though it was one of the more corrosive systems evaluated. First, $\text{H}_3\text{PO}_4/\text{HCl}$ is capable of dissolving large amounts of uranium in a small volume of liquid, at room temperature very quickly. Therefore, the amount of uranium-containing solution generated that will require solidification or stabilization is minimized reducing treatment and disposal cost. Secondly, many of the $\text{H}_3\text{PO}_4/\text{HCl}$ systems evaluated produced following dissolution a stiff, waxy solid (Figures 4 and 5). It may be possible to treat Dep-U waste using $\text{H}_3\text{PO}_4/\text{HCl}$ and minimize the amount of waste handling and the number of treatment stages, if a solid product can be generated in a lined disposal container. The feasibility of this approach has not been fully established, but it was felt that the potential advantages of such a process warranted further exploration.



Fig. 4. Tube containing uranium precipitate formed following dissolution with $\text{H}_3\text{PO}_4/\text{HCl}$. (10 mL/1 g, T= 25, dissolution time = 15 min)



Fig. 5. The solid from test tube in Fig.4 was removed from the tube. No free liquid was noted.

FUTURE WORK

Each stage of the proposed treatment process (Figure 2) will be experimentally investigated during the current project. Solids separation studies will be conducted to determine the most efficient separation process for uranium sludges and turnings submerged in storage solution. Gravity, vacuum assisted, and centrifuge separation will all be considered. Pre-wash detergent and solvent solutions will be investigated, if a water-only wash is found to be insufficient to meet feed requirements for the dissolution stage. Further investigations of both the thermodynamics and kinetics of uranium dissolution will be essential for the scale-up of the proposed process to a technologically feasible operation. The final phase of this project will be to evaluate the stabilization

and/or solidification of the uranium dissolution residues. Solidification with clays, cement, and polymers will be considered as well as ion exchange and adsorption. It must be demonstrated that the final product meets all disposal requirements for this waste type.

REFERENCES

- [1] Gindler, J.E., "The Radiochemistry of Uranium", NAS-NS 3050, 1962.
- [2] Katz, J.J., Rabinowitch, E., "The Chemistry of Uranium", National Nuclear Energy Series, Manhattan Project Technical Section Division VIII—Volume 5, McGraw-Hill Book Company, Inc., New York, 1951.
- [3] Gittus, J.H., "Uranium—Metallurgy of the rarer Metals", Vol. 8, Butterworths, London, 1963.
- [4] Warf, J.C., in "Chemistry of Uranium—Collected Papers", ed. Katz, J.J. and Rabinowitch, E., Book 1, pg 29, ORNL-TID, 1958.
- [5] Gmelins Handbuch der Anorganischen Chemie, System No. 55, "Uranium", Suppl. Vol. B5, Springer Verlag, Berlin 1997.
- [6] Larsen, R.P., "Dissolution of Uranium Metal and Its Alloys", Anal. Chem. 31 (1959) 545-549.

ACKNOWLEDGMENTS

The authors would like to acknowledge the assistance of Harold Rogers and Corry Painter during the experimental studies. The assistance and input from John Bowers, Scott Kidd, Gary Striker, and Chris Rasmussen were also greatly appreciated.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.