

START-UP OF DEPLETED URANIUM TREATMENT AT LLNL

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ABSTRACT

Engineers and waste treatment technicians in the Radioactive and Hazardous Waste Management division of Lawrence Livermore National Laboratory (LLNL) have recently started up a depleted uranium treatment process in the newly operational Decontamination and Waste Treatment Facility (DWTF) at LLNL. The novel 3-stage process converts pyrophoric depleted uranium metal turnings and sludges into a solidified final product that can be transported to and buried at a permitted land disposal site. The three process stages are: 1) pretreatment, 2) dissolution and 3) solidification.

INTRODUCTION

Because of the considerable hazards associated with depleted uranium, the storage, treatment, and disposal of uranium wastes are strictly regulated by the Department of Energy to ensure that human health and environmental integrity are protected. In addition the U.S. Department of Transportation strictly controls the transport of pyrophoric materials such as depleted uranium.

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 to render it suitable for disposal. Waste depleted uranium metal can be found in many physical forms including chips, turnings, chunks, sludges, and large fragments. Typically pyrophoric uranium wastes are placed in steel drums and covered with liquid (either coolant, mineral oil, or water) prior to storage. Depleted uranium waste is problematic for several reasons including its toxicity, radioactivity, and pyrophoricity. Of depleted uranium's three primary hazardous characteristics, its pyrophoricity is the one that provides the greatest impediment to disposal. With mixed (low level and hazardous) Dep-U waste, the hazardous constituents in the waste must be treated to meet RCRA disposal requirements in addition to processing the waste to remove the pyrophoric characteristic of the waste.

Waste treatment engineers at LLNL have developed a three-stage treatment process to convert pyrophoric depleted uranium waste into a stable solidified waste form that can be transported and disposed of at an off-site low-level waste disposal site. This proceeding will review the development of this process and the scale-up and installation of a full-scale treatment unit.

DEVELOPMENT OF DISSOLUTION TREATMENT PROCESS

In FY01 a 3 year LLNL Laboratory Research and Development (LDRD) Project was initiated to develop a Dep-U treatment process that would be applicable to LLNL's Dep-U waste stream. The following criteria were established as being essential for a waste Dep-U dissolution system:

- Operating conditions: The reagent system selected must proceed at an acceptable dissolution rate at ambient temperature and pressure. It was our desire to avoid the energy costs and potential hazards associated with heating treatment reagents, prior to Dep-U treatment.
- Treatment time: The reagent system selected must be capable of completely dissolving uranium in a reasonable time period. The dissolution time must be less than 6 hours to allow a batch of waste to be dissolved during 1 work day.
- Applicability: The reagent system selected must meet the above 2 criteria for both pure uranium metals and uranium alloys. The reagent system must also be applicable to turnings, sludges and chips.

The dissolution processes that met the essential treatment criteria listed above were then further compared using the following criteria, listed in descending order of significance, to facilitate the selection of the system most suitable for full-scale implementation:

- Hazardous by-products: The generation of hazardous reaction products that would compromise worker safety or require further treatment must be avoided.
- Temperature increase: All dissolution reactions evaluated were exothermic. It was our desire to select an effective dissolution system that had acceptable reaction rates with the least increase in temperature.
- Off-gas: Many of the dissolutions systems evaluated generated an off-gas during dissolution. Processes with no or minimal off-gases were preferred over those that generated a larger volume of off-gas.
- Corrosiveness: The least aggressive reagent solution that met the essential criteria was desired in order to minimize worker hazard and equipment cost. Some of the more aggressive reagent systems may require equipment constructed of costly materials.
- Complexity: The least complex dissolution system with the fewest required treatment steps was desired.
- Final waste volume: Because offsite disposal costs are based on the volume of waste, reagent systems that generated lower volumes of residuals were preferred over those that generated larger volumes.

In summary, it was our desire to select a uranium dissolution reagent system that could safely and completely dissolve depleted uranium metal and alloys at ambient conditions in one work shift with out the generation of hazardous byproducts and with the least production off-gases and residuals requiring solidification and disposal.

It was decided that the preceding objective could be best met with a three-stage process. The three process stages are: 1) pretreatment 2) dissolution and 3) solidification. Each stage was developed following extensive experimentation.

Pretreatment

Waste depleted uranium is typically stored in 30- and 55-gal drums immersed in a storage solution such as coolant, mineral oil or water in order to minimize contact with air. Many of the Dep-U storage solutions have a high concentration of organic compounds that are incompatible with the acids selected for dissolution. Also, in some of the mixed waste depleted uranium, the hazardous constituents are dissolved in the storage solution. Therefore, pretreatment is required to remove all traces of storage solution from the Dep-U solids. An additional goal of pretreatment is to obtain a defined and reproducible starting condition for the subsequent acid dissolution treatment process. Pretreatment includes separating the turnings from the storage solution, removing non-metal item from the waste (PPE, trash etc.) and washing the turnings to remove traces of storage solution from the depleted uranium solids

A pretreatment study was completed to determine the most effective method to prepare the depleted uranium waste for acid dissolution treatment. The independent variables were wash solution type, concentration and volume; number of wash/rinse cycles; and method of agitation. We used a factorial screening design treating all six variables as noncontinuous, to reduce the number of experiments. There were four different wash solutions, three types of turnings, and two settings each for the other four variables. The wash solutions evaluated included 1) tap water, 2) mild acid (0.1 M HNO₃), 3) a commercial coolant wash solution, and 4) a commercially available metal washing solvent typically used with vapor degreasing systems. Agitation was provided by either an orbital shaker or an ultrasonic bath. The dependent factor in the pretreatment study was the percentage of TOC removed from the turnings.

The type of storage solution and the age of the turnings both influenced the treatment efficiencies observed in the pretreatment study. Turnings stored in mineral oil achieved higher cleaning efficiencies than turnings stored in an organic based coolant solution. Our desire was to select a washing regime that would be applicable to all of the turnings, independent of the type of turning or storage solution. The most effective washing for the various DU turnings was accomplished using a concentrated, surfactant based wash solution, an ultrasonic bath and a total of 2 wash/rinse cycles.

Dissolution

Although uranium dissolution is discussed extensively in the literature, information that is pertinent to the use of chemical dissolution as a treatment process is lacking [1]. Our desire was to develop and design a treatment process that could treat up to 80 kg of Dep-U a day. At this larger scale, more attention would need to be paid to the hazards associated with the dissolution of uranium with the different reagents. It is essential that the dissolution process developed for Dep-U treatment remain under the operator's control for the entire duration of treatment. Uranium dissolution reagents that result in rapid and significant heat generation at an analytical scale may be uncontrollable at this larger scale. During FY01-02 comprehensive screening studies were completed. During these studies several reagent systems were evaluated including

sulfuric, phosphoric, nitric, and hydrochloric acid, hydrogen peroxide, sodium hypochlorite, and sodium hydroxide used either individually or in combination [2].

One of the reagent systems that was selected for further study following the completion of the screening studies was phosphoric and hydrochloric acid mixtures. Czupryna et al. [3] reported that adding phosphoric acid to hydrochloric acid solutions resulted in a total dissolution of the U-Ti alloy. A 16 g piece of the U-Ti alloy dissolved in 4 mol/L HCl / 7 mol/L H₃PO₄ acid mixture at 85°C in 1 hr. Larsen [4] reported that a 5 gram sample of bulk uranium metal can be completely dissolved in 30 minutes in 4M HCl / 7M H₃PO₄ (temperature not specified). Phosphate is a strong uranium complexing agent and prevents the precipitation of pyrophoric uranium oxide. Concentrated, boiling phosphoric acid attacks uranium metal, and as water is driven off, a point is reached where an exothermic reaction occurs, yielding a clear uranium-(IV)-phosphate solution. If oxidizing agents are added, a uranyl phosphate solution can be obtained. Prolonged heating, however, can result in polymerization of the solution and the formation of a glassy material that is extremely resistant to chemicals.

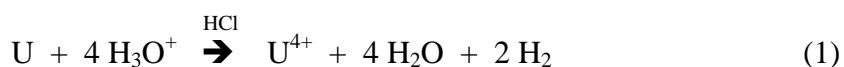
The conditions for our initial experiments with HCl and H₃PO₄ were selected based on the findings of Czupryna et al. Dep-U and 2%Mo-U alloy turnings were treated with 25 mL of a 7 M H₃PO₄ / 4 M HCl solution at 85°C. Both sets of 1 g metal turnings were completely dissolved in less than 1 minute. The reaction was accompanied by the vigorous generation of a colorless gas. During our follow-on studies to further evaluate the HCl/H₃PO₄ system for the dissolution of uranium turnings, the following parameters were varied: acid concentration, liquid to solid ratio, and temperature. Initially our primary goal was to decrease the reaction rate to the extent that treatment at a larger scale could be safely controlled. Neither decreasing the temperature nor decreasing the liquid to solid ratio affected the dissolution rate with 7 M H₃PO₄ / 4 M HCl solution. Even when using only 5 mL of the 7 M H₃PO₄ - 4 M HCl solution at ambient temperature, 1 g of Dep-U turnings were dissolved in less than 5 minutes. Subsequently, the acid concentrations in the mixture were incrementally lowered to determine the optimum conditions for the uranium dissolution (see Table I).

Table I. Results of the Phosphoric – hydrochloric acid dissolution systems (H_3PO_4 -HCl) investigated to evaluate the dissolution of uranium turnings (1 g Dep-U turnings per experiment)

H_3PO_4 [mol/L]	HCl [mol/L]	Volume [mL]	Temperature [°C]	Dissolution Time	Remarks
7	4	5, 10, 15, 20, 25	25, 35, 45, 55, 85	< 5 min	independent of temperature or volume
7	3 2 1.5 1	10	25	6 min 10 min 30 min ~ 24 hrs	sludge-like solid forms after 2 days
6	4	10	25	4 min	
4	4 2 1	10	25	8 min 1.5 hrs 1.5 hrs	sludge-like solid forms
2	4 2 1	10	25	~ 20 min 1.5 hrs 1.5 hrs	sludge-like solid forms
1	4	10	25	~25 min	sludge-like solid forms

We observed that the reaction of the HCl/ H_3PO_4 acid mixture with the uranium metal changed from complete dissolution to complete conversion as the acid concentrations were decreased. The conversion results in the direct formation of the hygroscopic sludge-like solid. No metallic residues were observed. The change from complete dissolution to complete metal conversion occurs if the phosphoric acid concentration was equal to or below 4 mol/L or if the hydrochloric acid concentration was below 2 mol/L (Table I). At a solid to liquid ratio of 1g metal in 10 mL of reagent mixture, very small amounts of free liquid (less than 0.1%) remain after the solid forms and only moderate gas evolution is observed. Increasing the reagent volume did not affect the dissolution rate but increased the amount of free liquid remaining, although not proportionally. The excess liquid can easily be separated from the solid by mechanical means, such as pressing, centrifugation, or drying if desired. Uranium analysis by gross alpha-beta counting determined that the excess free liquid did not contain any uranium. The uranium concentration in the liquids was below the methods minimum detectable limits of 0.6 mg/L (20 pCi/L) assuming U-238 is the sole alpha-emitter. The solids formed are greenish-gray in color, indicating the formation of a solid containing uranium in its tetravalent oxidation state. Examining the solids under a scanning electron microscope revealed a fibrous structure (Figure 1), which explains the solid's extreme hygroscopic nature resulting in the ability to absorb large quantities of free liquids.

The dissolution time per gram uranium does not appear to be proportional to the surface area, which indicates that the uranium metal dissolution reaction is controlled by the chemical elementary reactions involved rather than by any of the physical processes that often dominate heterogeneous reaction, such as diffusion, sorption and desorption processes. This observation is typically made for metal dissolutions in oxygen containing acids. Such dissolutions are generally characterized by consecutive reaction, e.g., oxidation of the metal to a cation followed by complexation mediated dissolution. We hypothesize that the hydrochloric acid in the reagent mixture oxidizes the uranium metal to U^{4+} . Phosphoric acid is a strong uranium ion complexing agent and the uranium-IV-ions formed are immediately complexed by the phosphate ions, making the conversion from metal into the phosphate solid instantaneous. This immediate complexation prevents the formation of the finely divided black UO_2 precipitate usually observed during the dissolution of uranium in solutions with hydrochloric acid only. The conversion of the metal to the phosphate solid (eq. 1 and 2) results in an irreversible removal of the uranium and hydrogen phosphate ions from the reagent mixture, favoring this reaction just as much as the uranium dissolution due to the action of the hydrochloric acid.



Although chloride containing reagent systems pose engineering challenges, the direct formation of a stable solid that is potentially suitable for direct disposal is extremely appealing. The most efficient conditions for the uranium metal conversion by the hydrochloric – phosphoric acid mixture are 10 mL of a solution of 3 mol/L in hydrochloric acid and 1 mol/L in phosphoric acid per gram uranium metal at ambient temperature.



Fig. 1. SEM photograph of the sludge like solid form in the reaction of phosphoric-hydrochloric acid with uranium metal

Solidification

The third and final stage of the depleted uranium deactivation process is solidification of the residuals from the dissolution stage. Laboratory studies were completed to evaluate solidification. At DWTF, waste solidification with clay-based materials is an established, permitted treatment process. Once it was determined that the depleted uranium dissolution residuals could be solidified with commercially available clay additives, the evaluation of alternative stabilization agents was discontinued. We were able to demonstrate that following neutralization with NaOH, the residuals from the treatment of depleted uranium with HCl/H₃PO₄ could be solidified to a final product that is suitable for land disposal.

FULL-SCALE IMPLEMENTATION OF PROCESS

Once the experimental studies were completed our efforts were focused on designing and installing a full-scale depleted uranium treatment unit. The RCRA permit limits the batch size for mixed depleted uranium waste to 80 kg, so we used this as our design amount. Our investigations determined that an acid solution of 3 mol/L in hydrochloric and 1 mol/L phosphoric acid, is a viable acid mixture for the dissolution treatment of metallic uranium at ambient temperature. In the laboratory studies one gram of uranium metal turnings can be converted in less than 4 hours with 10 mL of this solution. Increasing the volume of acid solution used above this volume does not improve the dissolution process, but rather contributes to an increase in generation of secondary waste that requires further treatment and disposal.

Thus for an 80 kg batch of depleted uranium 211 gallons of acid mixture are required. Following the acid dissolution, 64 gallons of 50% NaOH are required to neutralize the dissolution residuals. Each 80 kg batch of depleted uranium treated generates approximately 275 gallons of slurry to be solidified and subsequently land disposed.

The full-scale depleted uranium deactivation process is located inside the LLNL Decontamination and Waste Treatment Facility. The equipment used in the process includes 1)a stainless steel waste sorting table for stage 1 sorting and washing, 2)a Hastalloy-C reaction vessel, and 3)a double planetary mixer for stage three solidification (See Figure 2).

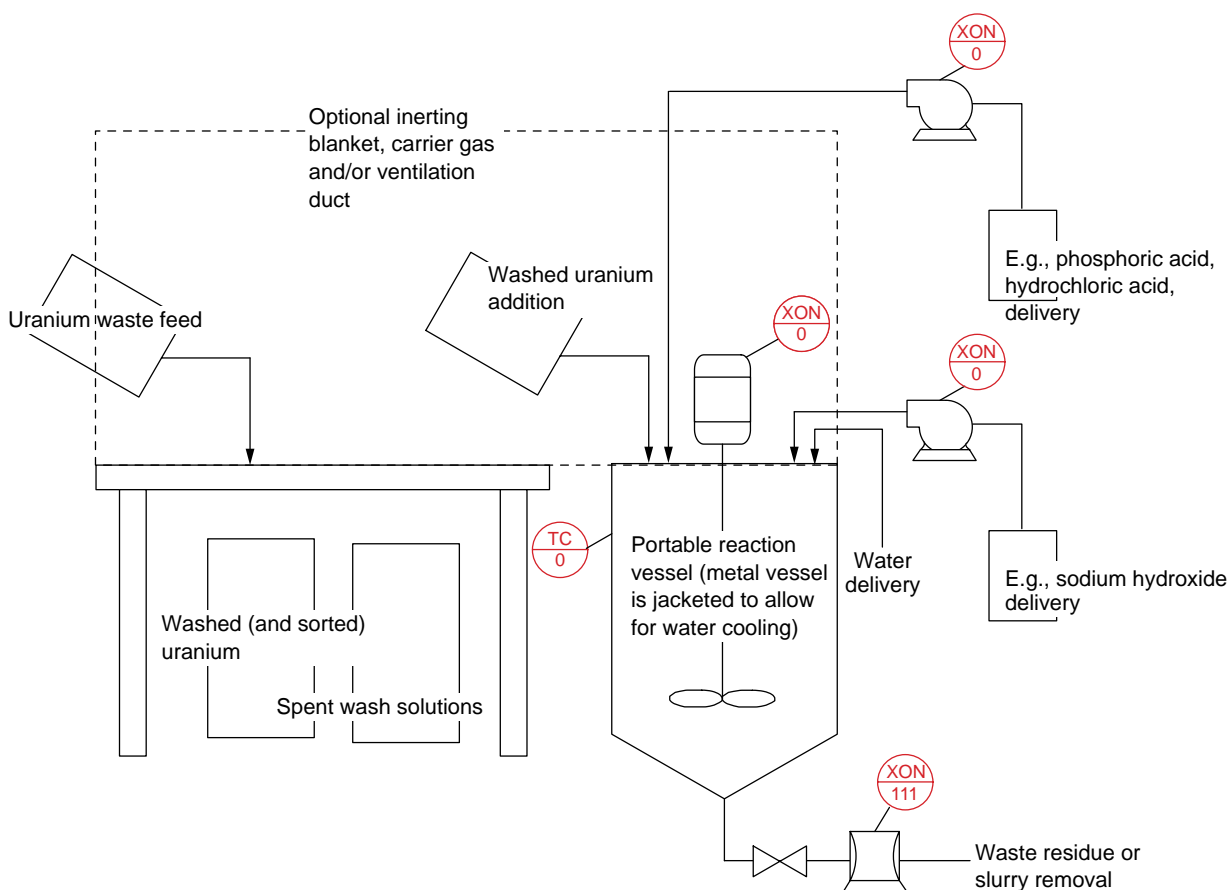


Fig. 2. A Schematic of the Full-scale Depleted Uranium Deactivation Process at LLNL.

Most equipment is considered portable and will be mounted to allow for movement in and out of the area using a forklift. The sorting table was fabricated with stainless steel and will be used to both sort and wash the uranium to prepare it for delivery to the reaction vessel. The sorting table is elevated to allow the placement of 30 or 55-gallon drums under the table to collect the washed and sorted uranium and spent wash solutions. The 1200-liter reactor was fabricated with Hastalloy-C and includes a cooling jacket that allows the use of house low conductivity-water to cool the reaction fluid as the reaction progresses. This reactor is secured to a skid-mounted

platform with forklift pockets to allow the system to be easily transported. Electric power, process water, and air supplies are from the Building 695 utility system. The skid anchoring and other structural supports are designed to meet seismic requirement. The uranium dissolution skid also includes reagent feed pumps to transfer the acids (phosphoric and hydrochloric acids) and sodium hydroxide from their respective containers, water delivery from a hose bib or pumping system, and a crane to facilitate waste loading into the reaction vessel.

As previously discussed the uranium waste must first be separated from the storage solution before it can be deactivated. Containers are processed individually. As shown in Figure 2, the container is opened, and its contents are emptied onto a draining table either manually or with the aid of a forklift. Process water and/or detergent specific for residues are added to the system to remove organic residues from the uranium waste. This is done using hand tools, hoses, and spray nozzles. The acids are premixed in the reaction vessel prior to uranium addition from working stock of 12% hydrochloric acid and 85% phosphoric acid. Once the acids are mixed, the washed uranium is added using a manually operated davit crane. The rate of waste loading is carefully controlled to limit the reaction rate and controls the temperature. An overhead mixer may be used to enhance the process. The temperature of the reaction vessel is continuously monitored and additional uranium is added only if the temperature is sufficiently low or is stabilized. When the dissolution process is completed, the wet amorphous solids are neutralized with sodium hydroxide (NaOH) solution. An operator then transfers the neutralized slurry from the reactor. The slurry may be placed directly in 55-gallon drums or consolidated in larger portable poly-tanks. The neutralized slurry is solidified in 55-gallon drums using a double planetary mixer.

FUTURE PLANS

To date a successful 5 kg trial has been completed using the full-scale depleted uranium deactivation process. Our plans are to proceed with 15, 30 kg trials, prior to deploying the process on a routine basis.

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