MILD CHEMICAL OXIDATION OF REACTIVE URANIUM FOR DISPOSAL OR RECOVERY

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ABSTRACT

Large quantities (thousands of drums) of waste uranium metal or alloyed metals as scrap or chips and turnings are generated annually in the DOE complex. The high surface area of this waste renders it highly reactive with both air and moisture. Storage of the materials is hazardous and expensive, but most DOE sites are forced to store the waste, because no adequate treatment or recycle technology is available. Los Alamos National Laboratory (LANL) currently has over 200 55-gal drums of reactive uranium awaiting treatment or recovery.

To address this problem, LANL has developed a process for the low-temperature conversion of waste uranium metal to uranium oxide. The basis of our technology is a mild solution oxidation using sodium hypochlorite (bleach). Divided uranium metal or alloys are excellent candidates for this type of oxidation because of their high chemical reactivity. Uranium turnings react rapidly with dilute solutions of sodium hypochlorite to form an insoluble uranium (VI) oxide, $UO_2(OH)_2$, as a finely divided yellow powder. The resulting powder is suitable for disposal after solidification or for recycle. Designs for a suitable reactor system for this process have been completed in the Waste Management Group at LANL. The skid-mounted mobile unit will be capable of treating up to 100 kg of metal or alloy per batch.

This paper summarizes the details of the process, including formation and characterization of the uranium product, identification of process operating conditions, and reactor design. Included is a description of the steps for permitting the process.

INTRODUCTION

When uranium metal is machined for defense applications, the process produces small chips and turnings, which are considered a waste that must be properly treated and disposed of.

As with some other metals, the smaller the pieces of uranium or the greater the surface area of the turnings, the more likely they will oxidize in the presence of air, water, or both. This oxidation process is exothermic (that is, it gives off energy and heat) and is accelerated by heat. Under certain conditions, then, a mass of uranium chips could ignite spontaneously. If the mass of fine material is great enough, the reaction, once started, is self-sustaining, and temperatures can exceed 1000° C. Fine oxide particles can become airborne and would be hazardous if they were inhaled. If water is present, the reaction can produce hydrogen, a flammable and explosive gas.

Despite the hazard and expense of storage, most DOE sites must store this waste because no adequate treatment has been available. Los Alamos is no exception. To prevent the waste chips of depleted uranium from accidentally igniting in the presence of air or water, the Laboratory stores the chips, which are tangled and not easily compacted, under diesel fuel in 30-gal. stainless steel drums, which are in turn stored inside 55-gal. drums and surrounded by vermiculite. We currently have over 200 55-gal drums awaiting a treatment method for these wastes. These drums now occupy a significant portion of the limited waste storage space at the Laboratory. An additional 50-75 drums are generated each year.

However, storage is only a temporary measure. Because the drums contain diesel fuel and because the chips are reactive, we cannot dispose of them in the conventional ways--burying the drums in a landfill or incinerating the contents. The chips also have a tendency to oxidize when they are melted down, which also makes recycling difficult. The industrial applications for the chips of depleted uranium, primarily some small use as ballast and in armor-piercing shells, are limited.

For safe long-term storage and before disposal or recovery of the uranium for reprocessing, these metal wastes must be rendered unreactive. Environmentally sound methods to accomplish this have not been available until now.

Suggested Treatment Technologies

Several treatment technologies have been suggested for waste uranium scrap.

Roasting. Reactive uranium is traditionally oxidized by "burning" (roasting) the metal in air at a high temperature, 500-700°C. Some sites in the DOE complex have roasted their most common waste uranium at high temperature to oxidize their waste metal; however, roasting pyrophoric metals (metals that can ignite spontaneously) is difficult and dangerous because of the potential for uncontrolled oxidation and explosion.

Supercompaction. Supercompaction of the metal has also been suggested for depleted uranium wastes. This process is cumbersome and subject to safety concerns and requires large, expensive equipment. Compaction operations are inherently dangerous, especially when coupled with a radioactive, reactive material like uranium. Although compaction reduces waste volume, it does not eliminate it, nor does it recover the metal for reprocessing.

Ingot formation. Ingot formation, by remelting and casting the metal, has also been used to recover waste uranium scrap. This process also requires expensive processing equipment. It is labor intensive and must be done under carefully controlled, inert conditions.

Recovering Enriched Uranium Metal

In addition to a waste treatment process, a method for recovering enriched uranium metal is also needed. For sites at which large quantities of uranium are processed, reducing the amount of waste produced is necessary.

Investigating Several Oxidation Reactions

How then, can we treat this waste; protect the environment, the public, and our workers; and allow recycling or

reprocessing? We explored several reactions that would convert the metal to uranium oxide or halides. Reactions included the direct reaction of uranium chips with neat alcohol, which produces hydrogen and takes several weeks, during which the uranium turnings were not completely dissolved; dissolving the uranium in iodine or iodide, which is difficult to incinerate and expensive to use; reacting the uranium in bromine, a reaction that is less "clean" than the iodine oxidation because insoluble products remain; and bubbling chlorine gas into an alcohol solution, a reaction that produces heat and becomes quite vigorous if the chlorine flow is not stopped intermittently.

Treating Chips and Turnings with Bleach

We have developed and demonstrated a process for the low-temperature conversion of waste depleted uranium metal to uranium oxide. It avoids all the difficulties and hazards associated with high-temperature oxidation while using an environmentally benign oxidant, sodium hypochlorite, or bleach, to oxidize the chips to produce an inert waste. Uranium turnings react rapidly with dilute solutions of sodium hypochlorite to form an insoluble uranium (VI) oxide as a finely divided bright yellow powder.

No soluble uranium products are formed. The oxidation is mild, occurs with dilute hypochlorite solutions, and is rapid. The resulting uranium oxide can be dissolved in dilute acids (pH 2 nitric acid) and readily separated from impurities, or reprocessed. The product oxide is suitable for either disposal after solidification, the Laboratory's option, or, for ^{235}U, allows recycling back into the uranium process scheme and eliminating the oxide as a waste form. Oxide coatings (UO_2), formed when the reactive metal is exposed to air, do not deter the oxidation of the metal, and in fact are oxidized with the uranium as well.

Low-temperature solution oxidation can also be used to selectively dissolve uranium away from impurity phases. Of special interest is applying this chemistry to separating uranium from uranium alloys containing less reactive metals like niobium or tungsten.

The Chemistry of the Process

The process developed for the Laboratory is based on the use of sodium hypochlorite in an aqueous environment. The process is based on the following reactions.

Uranium turnings from machining bulk metals reacts readily with dilute solutions of hypochlorite to initially give UO_2, which is subsequently converted to uranyl hydroxide. In the first reaction, uranium is oxidized using sodium hypochlorite:

$$U + 3NaClO + H_2O \rightarrow UO_2(OH)_2 + 3NaCl$$

The stoichiometry of the reaction dictates that three moles of sodium hypochlorite are needed to complete the uranium oxidation reaction. The laboratory process studies show that excess hypochlorite is necessary for complete reaction.

In the second reaction, uranyl hydroxide is reduced to uranium dioxide using thiosulfate:

$$4UO_2(OH)_2 + Na_2S_2O_3 \rightarrow UO_2 + H_2SO_4 + Na_2SO_4 + H_2O$$

This intermediate step may be added to reduce the uranyl hydroxide to uranium dioxide, which is a less soluble form of uranium and might settle faster, with a reducing agent such as sodium hyposulfite ($Na_2S_2O_4$) or thiosulfate ($Na_2S_2O_3$). Filtration and settling of the uranyl hydroxide could be very slow; reducing to uranium oxide may improve the treatment time and filtration or settling of the slurry.

In the third reaction, sodium thiosulfate reduces the excess sodium hypochlorite to sodium chloride:

$$4NaClO + Na_2S_2O_3 + H_2O \rightarrow H_2SO_4 + Na_2SO_4 + 4NaCl$$

In the fourth reaction, excess sulfuric acid is neutralized with sodium hydroxide to maintain correct pH control in the reactor.

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

When all reactions are complete, the reaction slurry is allowed to settle. Settling separates the solids from the liquid. The thickened slurry, which can be filtered to produce a filter cake is a solid product that can be recycled using a number of sophisticated recycling steps. The concentrated solids can also be mixed with cement and disposed of at the solid waste disposal area at the Laboratory. The solids are metered into a 55-gal. drum containing a premeasured amount of cement and sand. The drum lid is secured, the drum placed on a tumbler mixer, and the drum thoroughly mixed. The matrix is allowed to cure inside the sealed drum. If necessary, a sample of the mixture can be withdrawn through the bunghole.

Once separated, the liquid portion is transferred to the radioactive liquid waste treatment facility.

Mitigating the Hazards Involved in Treatment Using a Skid-mounted System

One hazard of the treatment process is exposure of the uranium chips and turnings to air, although even on the remote chance that the chips were exposed to the air during treatment, it is unlikely that they would ignite because they are covered with a thin film of diesel fuel. The drums are opened in a sealed chemical reactor under a nitrogen atmosphere.

Another hazard is that small quantities of chlorine are also released during the reaction. The chemical reactor is under slight negative pressure from a blower and the chlorine passes through a scrubber that removes more than 99.9% of the chlorine.

Small quantities of hydrogen could be released under some conditions. Air is used to rapidly dilute the reactor exhaust gas to a level below the flammability limit, as indicated by an analyzer.

The slurry has low radioactivity: the uranium is "depleted," containing about 0.2% of the fissionable isotope U-235.

The chemical reactor will be mounted on a transportable treatment structure on a steel frame, or skid. This system was designed to be:

- inherently safe,
- transportable, so that it can be shipped to other sites and can be moved in and out of the Hazardous Waste Treatment Facility,
- flexible when running the pilot studies,
- easy to operate in either batch or continuous mode, and
- easy to decontaminate.

The equipment and portable skid will be made of stainless steel for easy decontamination. The chemical reactor itself is made of titanium, which resists the oxidation and corrosion inherent in the process.

When the diesel fuel is drained from the drum, the chips are uncovered and can accidentally ignite. Although diesel fuel is difficult to ignite, it, too, can burn. To ensure the safety of the operation, we will load a closed drum into a chemical reactor, which is then sealed and purged with nitrogen, a neutral gas; this step eliminates the air, which could react with the chips when the oil is drained. The drum of chips thus becomes a reactor within a reactor.

Hydraulically activated hollow spikes then pierce the lid and the bottom of the drum. The oil drains into the bottom of the reactor, where it is pumped through filters. Then it can be recycled or incinerated.

After draining the oil, we add water to the reactor and pump it through the top spikes onto the chips. The water drains through the bottom spikes to the bottom of the reactor; the water is then recirculated. We then slowly add a 12% solution of bleach to the circulating solution; the uranium begins to oxidize.

The reaction is complete when the concentration of bleach is constant, after about 8 hours. The reaction is exothermic; the reactor is water cooled, because the hypochlorite, stable at room temperature, decomposes and releases oxygen and chlorine at higher temperatures.

Finally, we open the reactor, retrieve the drum, and crush it to reduce its volume before we dispose of it. We can then repeat the operation with another drum of uranium chips and turnings.

Benefits of the Treatment Method

This treatment method provides a low-temperature, nonhazardous way to convert the reactive uranium metal to the metal oxide and has substantial safety advantages over potentially explosive roasting techniques or supercompaction.

Intractable or insoluble oxides that are typical of the roasting processes are not produced. Processing steps requiring concentrated acids for dissolution and the resulting acidic mixed wastes are avoided. Because no high pressure or temperatures will be used, the equipment expenses should be much less than those for a roasting or compaction operation.

With this process, the oxidant is an aqueous solution of hypochlorite, household bleach. Because this is a high-volume chemical in the United States, it is readily available and inexpensive. The process itself is simple. Reaction rate is controlled by the addition of oxidant, and there is no danger of a runaway reaction. The reaction conditions are such that no residual hypochlorite remains at the end of the treatment. Wastewater (roughly pH 7) from the process is sent directly to the wastewater treatment facility to remove any potential radioactive contamination. The oxide product from the process is suitable for storage because it is not reactive and is not a waste regulated under the Resource Conservation and Recovery Act, disposal, or recycling. The Laboratory will likely dispose of the uranium oxide. After treatment, the contents of a 30-gal. drum, up to 100 kilograms, will represent one 55-gallon drum of cemented oxide. If the oxide is stored for recycling, the volume of the cake will be about 100 liters or less. Drying would reduce the volume further.

Future Directions

Other DOE facilities have similar large inventories of uranium chips, sometimes thousands of drums, and the process affords the entire DOE complex a safe, cost-effective treatment method.

An attractive product of the metal deactivation of enriched uranium is the metal oxides, because they are inert and also the basic materials for metal reprocessing. Oxides produced at low temperature can be readily dissolved in dilute acid and brought into the front end of the currently used uranium reprocessing scheme.

We have also demonstrated that this chemistry will allow the separation of uranium from alloying metals such as niobium or titanium. Equipment for this process will be designed and constructed at Los Alamos.