

AQUEOUS REPROCESSING OF U-Pu-Zr METAL FUELS – DISSOLUTION CONSIDERATIONS

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ABSTRACT

Aqueous processing of spent stainless-steel-clad U-Pu-Zr metal fuels from a GNEP sodium-cooled fast reactor would enable application of the UREX+1a solvent extraction processes that will separate cesium and strontium into a separate stream, in addition to separating the transuranics (TRUs). The Cs and Sr can be disposed by subsurface storage for a few centuries while TRUs are recycled to an advanced burner reactor, solving the heat generation limitations for Yucca Mountain and minimizing space needs. We evaluate dissolution processes for the individual metal constituents and, then, consider the chemistry required to dissolve the combination of metals, including vessel material aspects, that will enable utilization of solvent extraction separations processes.

Key Words: U-Pu-Zr metal fuels, reprocessing, dissolution, solvent extraction

INTRODUCTION

The sodium-cooled, metal-fueled fast reactor is a contender in the GNEP program. Aqueous processing of the spent nuclear fuel (SNF) can separate the Cs and Sr into a separate non-TRU stream¹ utilizing the UREX+1a GNEP separations flowsheet, which also separates the long-lived transuranics (TRUs), Tc, and I. Heat generation from Cs

and Sr limit the short term loading capacity of SNF in a repository while heat from the transuranics Pu, Am, and Cm limit the long-term loading. Neptunium and Tc are the maximum dose contributors in 250,000 years. Utilizing UREX+1a separations would enable disposition of the Cs and Sr in a subsurface storage facility in a few hundred years, while the TRUs, Tc, and I could be recycled to a fast burner reactor, reducing repository space needs by a factor of 20 to 100 from direct disposal requirements.

Technologies to dissolve the fuel to enable application of the solvent extraction separation processes are discussed here. The metal fuel, comprised of 20 weight % transuranics (TRU), 10 weight % Zr, and balance U, requires consideration of the dissolution chemistries of the three metals in order to develop a process flowsheet. For purposes of the discussion, the TRU component will be treated as all Pu as it is the most predominant and the most challenging to dissolve. We will first discuss dissolution of each of the metals, and, then, consider the chemistry required to dissolve the combination of metals, including vessel material aspects. This composition of fuel components has not been tested in aqueous dissolution previously; U-Zr alloys have been dissolved and plutonium dissolution chemistry is documented in the literature.

CLADDING SEPARATION

The fuels will be clad in 20 mil thick stainless steel tubes. A chop-leach process will be assumed for a base case, in which the fuel rods are sheared into short segments and the acid dissolvent attacks the metal fuel constituents from the open ends. The

cladding hulls would be compacted and would likely be classified and disposed as low-level waste.* If it is found necessary to first chemically de-clad the fuel in order to expose the surface, it can be dissolved in sulfuric acid (H_2SO_4). A penetration rate of 6 mils/hr can be achieved in 4 M H_2SO_4 at $95^\circ C$.² Modern high-nickel alloys such as Alloy C-22 would be suitable for a vessel material for this operation as well as for subsequent fuel dissolutions in nitric and hydrofluoric acids. The Idaho Chemical Processing Plant (ICPP) dissolved stainless steel fuel components in 6.8 M H_2SO_4 at $80^\circ C$ in a Hastelloy C-4 dissolver, yielding a penetration rate of 1 mil/hr; sulfamic acid was added to scavenge nitrous acid in equilibrium with small concentrations of nitric acid in the rinsed dissolver heels. Otherwise, a zirconium vessel for the de-cladding step would be completely resistant to attack by H_2SO_4 .^{3,4} It may be possible to enhance the dissolution rates in H_2SO_4 even further by adding small amounts of hypophosphorous acid, H_3PO_2 . Dissolution times for M-1 type 347 stainless steel in 300 to 400 % excess boiling 5 to 6 M H_2SO_4 were decreased by 56 to 79% when 0.1 M H_3PO_2 was added and by 87% with 0.2 M H_3PO_2 .⁵

Tests of de-cladding stainless-steel-clad oxide fuels with H_2SO_4 dissolvent showed negligible losses of uranium. Dissolution of plutonium oxide was even less.² Dilute (6 N) H_2SO_4 does not attack U metal.⁶ Concentrated H_2SO_4 forms a protective coating

* Advanced low-nickel metal claddings being developed would likely not be activated to greater-than-class C waste. Characterization of residual TRU contaminants from the metal fuels may be needed to determine whether the hulls must be dispositioned in a Federal repository. If contamination levels exceed LLW limits following fuel dissolution, further treatment may be possible to decontaminate them (see "Management of Cladding Hulls and Fuel Hardware," IAEA Technical Report Series No. 258, 1985. Note that data presented for stainless steel hulls are for oxide fuels.)

that slows the reaction. A moderate concentration of 5 N H_2SO_4 exhibits slow attack on metallic Pu.⁷ It is likely that the plutonium reaction would be similar to that of uranium.

ZIRCONIUM DISSOLUTION

Zirconium is dissolved in hydrofluoric acid. A solubility exceeding 1.7 molar can be achieved at elevated temperature. In order to assure solution stability at ambient temperature, it is diluted to 0.5 molar when solution adjustments are made. Zirconium metal is not appreciably attacked by nitric acid.

URANIUM DISSOLUTION

Uranium dissolves at a moderate rate in nitric acid (HNO_3), forming the very soluble and extractable uranyl nitrate in solution $[\text{UO}_2(\text{NO}_3)_2]$. Hydrofluoric acid (HF) will also dissolve uranium as uranium tetrafluoride (UF_4). The UF_4 solubility is limited and a precipitate forms. This is readily dissolved by complexing excess fluoride with aluminum nitrate $[\text{Al}(\text{NO}_3)_3]$ and adding HNO_3 , which oxidizes the uranium to the uranyl ion. Uranium and zirconium metals together in the fuel can result in formation of epsilon phase uranium-zirconium, UZr_3 . This can react explosively with HNO_3 .^{8,9} To prevent this, addition of a small amount of fluoride is necessary and sufficient.⁹

PLUTONIUM DISSOLUTION

Plutonium dissolves slowly in HNO_3 . Nitric acid is an oxidizing acid. When Pu metal is dissolved in it, an oxide film is formed on the metal that inhibits the dissolution,^{7,10} similar to what happens when aluminum is dissolved in HNO_3 . Aluminum fuels are rapidly dissolved in HNO_3 by adding small concentrations of mercuric nitrate [$\text{Hg}(\text{NO}_3)_2$] catalyst.¹¹ An alternative to the use of $\text{Hg}(\text{NO}_3)_2$ is fluoboric acid (HBF_4).¹² A small concentration of HF in equilibrium with the BF_4^- in HNO_3 reacts with the oxide film to enable the HNO_3 to react with the metal. The HNO_3 reaction predominates over any small reaction of the Al metal with HF.

Pu metal dissolution in HNO_3 has been enhanced some by addition of HF,^{7,10} which destroys the passivating layer by forming strong Pu(IV) fluoride complexes. It is important to keep the HNO_3 concentration below about 5 molar to minimize the oxidation of the metal surface. An optimum concentration is about 3 M HNO_3 with 0.13 M HF. (The HF concentration of 0.13 molar was the highest tested; the rate increased linearly with increased HF concentration.) Sulfamic acid in HNO_3 increases the rate more, leading to rapid dissolution. The sulfamic acid scavenges nitrous acid, HNO_2 , preventing Pu(III) oxidation and passivating layer formation.^{7,10} Plutonium alloys dissolve rapidly at ambient temperature in 3.5 M HNO_3 –3 M HCOOH (formic acid),¹³ with penetration rates of 0.3 to 0.6 cm/hr. However, at this concentration of HCOOH , denitration occurs after dissolution, which leads to formation of HNO_2 with concomitant

difficulties. This is avoided by using smaller concentrations of HCOOH, but the dissolution rate drops off considerably.¹⁴

Moisy et al.¹⁵ have observed a promising technique for achieving rapid dissolution of Pu metal at ambient temperature in dilute solutions of HNO₃-HCOOH by applying ultrasonic irradiation that erodes away the passivating layer and increases mass transfer at the metal-liquid interface. A metal penetration rate of about 1.7 cm/hr was observed in 0.5-1.0 M HNO₃, 1 M HCOOH. At higher HNO₃ concentrations, the dissolution rate drops off rapidly due to sonochemical oxidation of Pu(III) to Pu(IV).

FUEL DISSOLUTION

A practical approach may be to alternately expose the fuel to HF and HNO₃ solutions. Following HF exposure with vigorous sparging for mechanical agitation and/or sonication the Zr may be dissolved, along with some uranium. One would either partially complex the HF dissolver product with Al(NO₃)₃ or transfer it to another vessel, and then add HNO₃ to a concentration of 3 M HNO₃ with 0.13 M HF to dissolve the U and Pu. Even if incomplete dissolution occurs in the first cycle, upon addition of the next batch of fuel and going through another cycle, the initial fuel batch can be completely dissolved as zirconium and some uranium are dissolved in HF while plutonium and uranium are dissolved in HNO₃-HF. Following complete dissolution, HF is complexed down to about 0.02 molar to free up the uranium from complexation with fluoride to enable its extraction and to make the solution non-corrosive to downstream

stainless steel vessels. Zirconium will remain as largely inextractable complexed fluorides. Adjustment of the plutonium valence to Pu(IV) with nitrite ion (NO_2^-), added as NaNO_2 or gaseous NO_2 , will make it extractable with the uranium.

It is possible that the fluoride precipitates will result in a barrier to dissolvent reaction. That occurs when calcia-stabilized ternary $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ fuel is dissolved in HF- HNO_3 mixtures. Calcium hexafluorozirconate, CaZrF_6 , forms on the surface of the fuel pellets and dramatically slows the reaction. However, the reaction proceeded when the pellets were vigorously agitated to break the CaZrF_6 from the surface of the pellets.¹⁶ Sonication could be investigated, as well, for preventing formation of a diffusion barrier.

Another approach is to dissolve the fuel in nitric acid with fluoride added to prevent explosion of UZr_3 . Sufficient fluoride would be needed to accommodate reaction with the Zr. To enhance the reaction of the plutonium, formic acid with sonication could be utilized. Once dissolution is complete, any excess fluoride would be complexed with aluminum nitrate and the solution adjusted for solvent extraction. Fluoboric acid could be investigated as a fluoride source that could increase the plutonium dissolution rate, as it does for aluminum.

The Niflex process utilized 2 M HF, 1 M HNO_3 to dissolve Zircaloy-2 cladding and U-Zr alloy fuel.^{17, 18} Zircaloy dissolution rates of 0.33 cm/hr at 50 and 70°C and 0.93 cm/hr at 90°C were achieved. The process was developed to dissolve fuels in Type 309Cb stainless steel vessels and the HF was added incrementally. This is a condition that

may be suitable for Alloy-22 or Alloy-2000 vessel material with full concentration of HF in the HNO₃ initially and would likely dissolve the Pu successfully.

INSOLUBLE FISSION PRODUCTS

The noble metal fission products are largely insoluble in acids. Ruthenium, because of its high fission yield and substantial insolubility, is particularly significant. When U-Zr metal naval fuels processed at the Idaho Chemical Processing plant were dissolved sequentially in hydrofluoric and nitric acids, approximately 50% of the Ru and about 10% of the Rh remained as suspended solids in the accountability vessel following 30 minutes settling in the processing vessel prior to transfer to the accountability vessel. Evidently the solids settled out in the processing vessel are substantially dissolved during the next batch of fuel processing. Of those suspended solids in the product, about half eventually settled out over a period of days. While a small fraction of these solids may transport across the aqueous-organic interface during solvent extraction processing, most will remain in the high-level liquid waste. The 50% that ultimately settle to the bottom of the waste tank are readily resuspended and would be removed with the liquid waste for subsequent solidification treatment.

The noble metal solids in U-Zr-Pu metal fuels will likely be similarly finely divided. It will be necessary to characterize the undissolved solids for a particular adopted flowsheet.

VESSEL MATERIALS

Advanced high-nickel alloys are available (e.g., Alloy C-22, Alloy-2000) that are resistant to corrosion by HF and by HNO₃, and they will tolerate small concentrations of one in high concentrations of the other. If nitric acid is used as the initial dissolvent, the required HF addition in moderate concentrations may present a materials challenge. One may need to resort to plastic lined vessels. In the flowsheet concepts in which HF is the first dissolvent, the metal alloy vessels will be entirely adequate for long life use. These should be considered the first processes of choice to investigate and develop.

CONCLUSIONS

While no specific development has been done to dissolve the U-Pu-Zr fuels, sufficient data and experience are available to indicate that a successful flowsheet could be developed. As indicated in the discussion on fuel dissolution, a number of approaches could be investigated.

Once the fuel is in solution, fluoride solutions can be adjusted with aluminum nitrate, nitric acid, and water to provide a composition that will free the uranium and plutonium from fluoride for extractability, adjust the plutonium valence for extraction, provide nitrate for salting in the extraction, and result in stable solutions that are non-corrosive to downstream stainless steel vessels.

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