ANL/CSE-13/37

Dissolution of U-Mo-Alloy Scrap from Fuel Fabrication

Chemical Science and Engineering Division

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DISSOLUTION OF U-Mo-ALLOY SCRAP FROM FUEL FABRICATION

1 INTRODUCTION

The mission of the National Nuclear Security Agency Global Threat Reduction Initiative (GTRI) is minimization of the civilian use of highly enriched uranium (HEU) worldwide. One of the key components of this effort is the conversion of research reactors from HEU to low-enriched uranium (LEU) fuels. The program is cooperating with research reactor operators to achieve the goal of HEU to LEU conversion without significant reduction in reactor performance. The programmatic goal is to convert all civilian research reactors by 2014. The GTR-Conversion program is currently engaged in the development of nuclear fuel that would enable conversion of high-performance reactors to LEU fuel. The fuel design is based on a monolithic uranium-molybdenum (U-Mo) fuel alloy, enclosed in Al-6061 cladding, with a diffusion/bonding interlayer composed of zirconium or aluminum-silicon alloy material.

The average Al to U molar ratio in the U-Mo targets (when taking into account numbers of different plates required annually by the National Institute of Standarts and Technology (NIST), Missouri University Research Reactor (MURR), and Advanced Test Reactor (ATR) reactors, plate geometries, and the amount of aluminum cladding) is 4.9 (Appendix 1). A process is required for the recovery of uranium from the scrap metal in the fabrication plant and potentially for uranium from irradiated fuel elements. To achieve this goal, a dissolution technique for U-Mo fuel elements is required in order to prepare feed solutions suitable for processing by a tributyl phosphate (TBP)-based solvent extraction process, which calls for dissolving the fuel meat in nitric acid media.

In this report, dissolution methods for U-Mo fuel and its cladding are described, and the most appropriate method for dissolving the fuel elements is suggested. Furthermore, special considerations and potential challenges in the dissolution of U-Mo fuel, such as limited solubility of Mo in uranyl nitrate solution, formation of zirconium-uranium intermetallic compounds that might cause explosive reactions during the dissolution, and formation of gelatinous solids during dissolution of aluminum-silicon alloy material are discussed. Recovery of uranium from casting runners, spent yttria-coated graphite crucibles, etching solutions from ingot and rolling operations, and slag formed during downblending and alloy formation are also discussed.

2 DISSOLUTION OF U-Mo ALLOY

An important consideration for designing a U-Mo fuel dissolution process is the limited solubility of molybdenum in uranyl nitrate solutions. One of the first studies of U-Mo alloy dissolution was done at Hanford for low-acid solvent extraction processing feed solutions (Schulz & Duke 1959; Schulz et al. 1962). When dissolution of 3–10% (w/w) U-Mo alloys in nitric acid was attempted, a flocculent, yellow precipitate (believed to be uranyl molybdate/polymolybdate) was obtained. The composition of the yellow solids was approximately the same under the entire range of conditions investigated (<1 M terminal HNO_3); however, when higher nitric acid and lower molybdenum concentrations were used, a lower weight percent of solid was obtained. The precipitate from U-Mo alloy dissolution is easily centrifuged, and uranium can be recovered from the precipitate by dissolving it in 0.5 M Na_2CO_3. It can then be converted to sodium diuranate solid and molybdate solution by treatment with sodium hydroxide. The Hanford report concludes that because the maximum uranium concentration attainable without precipitation of solids—when dissolving U alloy containing 3% (w/w) Mo, at terminal acidity of 1 M HNO_3—is about 0.4 M U, a complete dissolution of U-Mo alloy in nitric acid alone is not practical for the desired operation (Schulz & Duke 1959). Furthermore, the extent of dissolution of U-Mo alloy is considerably lower for 10% (w/w) Mo alloy and at lower acidities. This report also noted that the solubility of Mo in uranyl nitrate solution is lower at boiling temperatures than at room temperature.

The extent of dissolution of U-Mo alloy increases significantly in the presence of $Fe(NO_3)_3$ (Schulz & Duke 1959; Schulz et al. 1962). The U-Mo alloys are dissolved to higher terminal uranium and lower terminal acids concentrations, without solid formation. For example, when dissolving U alloy with 3% (w/w) Mo in the presence of 1 M $Fe(NO_3)_3$, a 1.3 M $UO_2(NO_3)_2$ in 0.4 M HNO_3 solution is obtained without precipitate formation. In the absence of $Fe(NO_3)_3$, only 0.1 M $UO_2(NO_3)_2$ and 0.58 M HNO_3 solution is prepared without precipitate formation. When dissolving U alloy with 10% (w/w) Mo in the presence of 1 M $Fe(NO_3)_3$, a 0.56 M $UO_2(NO_3)_2$ and 1.0 M HNO_3 solution is obtained. The solubility of Mo, at 100°C, in the presence of 1 M $Fe(NO_3)_3$ and uranium peaks at ~1.75 M HNO_3; for a 50 g/L U solution, it is ~26 g/L Mo; and for 100 g/L U, it is ~22.8 g/L Mo (Zeyfang 1979). The increased solubility of U-Mo alloy in presence of $Fe(NO_3)_3$ is attributed to formation of a negatively charged iron-molybdenum complex (Schulz & Duke 1959; Schulz et al. 1962).

An extensive study on solubility of Mo in nitrate-based media in the presence of uranyl nitrate, ferric nitrate, and other metal salts was done by Faugeras et al. (1961). The Faugeras report illustrates the complexity of U-Mo alloy dissolution. The study shows that Mo solubility in the presence of U peaks at ~1.5 M HNO_3 and that the solubility of Mo is dependent on uranium concentration and peaks at 120 g/L U. At 100°C and 1.5 M HNO_3, a solution of ~120 g/L U and ~9.6 g/L Mo is obtained. However, at the same temperature and nitric acid concentration but 100 g/L U, only 7.5 g/L Mo is dissolved. Thus, decreasing or increasing the uranium concentration from 120 g/L decreases the amount of Mo that can be dissolved in a solution containing uranyl nitrate and nitric acid. Faugeras et al. (1961) also did extensive studies of Mo solubility in uranyl nitrate–nitric acid solutions in the presence of 0.5 and 1 M $Fe(NO_3)_3$ at 100°C as a function of nitric acid and uranium concentration. From the data presented, it appears

that >11 g/L Mo can be dissolved in 100 g/L U and 2.5 M HNO_3 solution in presence of 0.5 M $Fe(NO_3)_3$.

Faugeras et al. (1961) also studied the solubility of Mo in the presence of $Al(NO_3)_3$, without uranium. Mo solubility decreases in presence of $Al(NO_3)_3$; in 1 M HNO_3 and 0.5 M $Al(NO_3)_3$, it is ~1.7 g/L, and in 1 M HNO_3 and 1 M $Al(NO_3)_3$, it is ~1 g/L. Therefore, dissolution of Al cladding with the U-Mo alloy will require less-concentrated solutions.

Ferris also looked at the solubility of molybdic oxide dihydrate in solutions of nitric acid and uranyl nitrate at 26°C using equilibration of the molybdic oxide with three series of nitric acid-uranyl nitrate solutions (Ferris 1961a,b). Uranyl nitrate concentrations of 0.28, 0.65, and 0.95 M were used, and for each U concentration the HNO_3 concentrations varied between 1 and 5 M. The data obtained by Ferris (1961a,b) indicate that a U alloy with 10% (w/w) Mo can be dissolved without forming a precipitate in 2 or 3 M HNO_3, obtaining 67 g/L U and up to 7.6 and 10 g/L Mo, respectively. Ferris (1961a,b) observed a yellow precipitate forming in solutions of low acidity and, consistently with other authors, identified it as uranyl molybdate; however, at higher nitric acid concentrations of >4 M, a white precipitate was identified by chemical and x-ray analysis as molybdic oxide monohydrate.

Dissolution of U alloy with 3% (w/w) Mo in 12–14 M HNO_3 was achieved where 85–95% of the molybdenum content precipitates as MoO_3 (Schulz et al. 1962; Schulz 1960). When lower concentrations of nitric acid are used, the precipitates are a mixture of molybdic oxide and uranyl molybdate. The dissolved solutions range in composition from 1.0 to 1.5 M $UO_2(NO_3)_2$ and 4 to 8 M HNO_3. When silicon is present in the alloy (0.2% (w/w) Si), it precipitates under the dissolving conditions (~90%). The main disadvantage of dissolving U-Mo fuel in concentrated HNO_3 is that the precipitates are bulky and do not settle well. They also adhere to container surfaces. The solids can be separated by centrifugation, but volumes of centrifuged unwashed precipitates range from 10 to 20% of initial solution. After thorough washing with water and 1 M HNO_3 the precipitates contain 0.06–0.5% U. However, in solution that contained 0.0004–0.002 M $Pu(NO_3)_4$, the amount of plutonium retained in washed precipitate was 2.4%. Uranium can be recovered from partially washed precipitates by treatment with 19 M NaOH and then 11 M HNO_3 at 90°C. Sodium hydroxide metathesizes the precipitate to soluble molybdate and insoluble $Na_2U_2O_7$, which is then dissolved in 11 M HNO_3.

3 DISSOLUTION RATES

The dissolution rates for U-Mo alloys in nitric acid are higher than those for ingot uranium metal (Schulz & Duke 1959; Ferris 1961b). The dissolution rates for 3% (w/w) Mo alloy are 5–20 times higher then for U metal at corresponding nitric acid concentrations, and the dissolution rate increases with nitric acid concentration and alloy content of molybdenum.

The dissolution rate at boiling temperature for 10% (w/w) Mo alloy follows a third-power dependence on nitric acid concentration and is ~100 mg/min-cm^2 in 6 M HNO_3. It drops to about 2 mg/min-cm^2 in boiling 2 M HNO_3. Additionally, iron catalyzes the dissolution of U-Mo alloy at low acidities. At comparable pH (0.2) and nitrate ion concentrations, the dissolution rate in 1.0 M $Fe(NO_3)_3$ in about 1000 times greater than in $NaNO_3$–HNO_3 solution.

4 DISSOLUTION PROCESSES FOR U-Mo ALLOY

The dissolution flowsheet for U alloy with 3% (w/w) Mo, which was designed at Hanford for a REDOX-type solvent extraction process, allows complete dissolution of the alloy without precipitation of uranyl molybdate (Schulz & Duke 1959; Schulz et al. 1962). The resultant solution contains 0.75 M $UO_2(NO_3)_2$, 5.6 g/L Mo, 0.75 M $Fe(NO_3)_3$, and 1 M HNO_3. To dissolve U alloy with 10% (w/w) Mo adjustments in terminal uranium and/or terminal nitric-acid concentrations would be required. For example, to obtain a precipitate-free solution that is 1 M HNO_3 and 0.75 M $Fe(NO_3)_3$, the solution would have to be less than 0.4 M in uranium concentration.

The dissolution flowsheet designed at Oak Ridge National Laboratory (ORNL) for a TBP-based solvent extraction process parallels the flowsheet designed at Hanford (Ferris 1961b). The process for dissolution of Al canned fuel of U-Mo alloy containing 3% (w/w) Mo involves the dissolution of the aluminum can in boiling NaOH-$NaNO_3$ solution followed by dissolution of the alloy in boiling 6 M HNO_3. Less than 0.1% of the uranium was lost to the decladding solution. Dissolution of the 1-cm-diameter alloy requires about 6 hr. The resulting solution composition was 0.6 M uranium, 3.8 g/L Mo, and 3.4 M H^+, without formation of any precipitate. An alternative process for dissolution of U-Mo alloy containing 3% (w/w) Mo was achieved by boiling it in 8 M HNO_3 and 0.5 M $Fe(NO_3)_3$. That method achieves a solvent extraction feed containing 1 M uranium and 3 M H^+. However, for this process, the addition of iron is considered disadvantageous because large waste volumes are produced from solvent extraction.

The dissolution flowsheet designed at ORNL for a TBP-based solvent extraction process for U-Mo alloy containing 10% (w/w) Mo involved dissolution in boiling 11 M HNO_3 after the aluminum can was removed in boiling NaOH-$NaNO_3$ solution (with less then 0.1% uranium losses to the decladding solution) (Ferris 1961b). The 1.5-cm-diameter core was dissolved in 5 hr, producing a solution containing 260 g/L U and 6 M HNO_3. Most of the molybdenum precipitated as MoO_3 during dissolution. After centrifugation, it occupied 20–30% of the original solution volume, and after three washes, contained 5–10% U. Recovery of uranium was greatly improved when the solids were separated by vacuum filtration before washing with three portions of 1 M HNO_3. The residual uranium can be further recovered when the molybdenum precipitate is dissolved in NaOH solution. The main advantage of this method, which involves separating most of the molybdenum prior to solvent extraction, is that lower volumes of waste would be generated in the solvent extraction process. However, this advantage is a minor one when considering the centrifugation and washing of precipitate steps. U-Mo alloy containing 10% (w/w) Mo can be also dissolved in 5.5 M HNO_3 and 1 M $Fe(NO_3)_3$ solution, without precipitate formation, resulting in a feed solution containing 0.5 M uranium, 13.4 g/L molybdenum, and 3 M HNO_3.

A flowsheet for efficient dissolution of Super Kukla (SK) Prompt Burst Reactor material operated at the Nevada Site was designed at Savannah River National Laboratory (SRNL) (Pierce 2007). The objective is to dissolve a Ni plated U-Mo alloy containing 10% (w/w) Mo in nitric acid without precipitate formation or flammable gas formation. Based on literature reports

and SRNL tests, SK material can be dissolved in boiling 4.5–5 M HNO_3 (starting acid concentration) at 100–105°C to yield a U concentration of 15–20 g/L, Mo concentration of 1.7–2.2 g/L, and final 4.0–4.5 M HNO_3. The terminal nitric acid concentration in the fuel solution allows H-Canyon Operations to avoid adjusting the feed from the dissolver prior to solvent extraction, while providing the maximum margin for avoiding precipitate formation. The material is charged to the dissolver in carbon steel cans, which contribute 1.0–2.3 g/L iron to the solution. Aluminum is not part of the feed stream. If the H-Canyon dissolver solution deviates from the flowsheet target of 4.5–5.0 M HNO_3, the amount of Mo that might precipitate is a small fraction of total Mo, as Mo is soluble at 2.2 g/L Mo in acid concentrations ranging from 2.2 to 5.0 M HNO_3 and 20 g/L U. Therefore, acid concentrations ranging from as low as 3.0–6.0 M encompass acceptable operating range and should not yield a precipitate.

Declad Hallam Nuclear Power Facility fuel slugs containing U-Mo alloy that has 10% (w/w) Mo enclosed in aluminum cans were dissolved in the H-Canyon dissolver at 100°C (Zeyfang 1979). The aluminum cans were dissolved in the nitric acid solution, along with the fuel, in the presence of mercury catalyst. The dissolvent was initially ~4.5 M HNO_3 and 1 M $Fe(NO_3)_3$. In this case, the increased solubility of Mo in the presence of ferric ion was seen as a way to reduce the amount of process solutions. The composition of the final solution was not described.

Dissolution experiments of irradiated and non-irradiated U-Mo fuels containing 7% Mo were performed by CEA/VALRHO in France (Herlet et al. 2005). During this dissolution, the Al cladding was dissolved with fuel meat; however; process details were omitted. In order to obtain a solution free of precipitate, non-irradiated materials were dissolved in boiling 5 M HNO_3. The target aluminum concentration was 15 g/L and the combined U-Mo concentration was also 15 g/L. The NO_x gases were recombined using a condenser. When irradiated fuel was dissolved under the same conditions, after overnight cooling the solution became slightly cloudy. Upon filtration, 0.6 w% of the spent fuel was collected. The insoluble species were composed of more then 90 w% molybdenum and aluminum.

Piqua fuel composed of U-Mo alloy (4w% Mo) clad in aluminum and containing 0.5% (w/w) Ni as a bonding agent was dissolved by SRNL (1972). The initial dissolving conditions were 5.8 M HNO_3 and 0.004 M $Hg(NO_3)_2$ and resulted in a solution containing 30 g/L U, 1.3 g/L Mo, 0.15 M Al, 0.008 M Ni, and 4.8 M HNO_3. The solution was concentrated by evaporation to 38 g/L U, 1.5 g/L Mo, and 5.8 M HNO_3 without precipitate formation. Although aluminum depresses the solubility of Mo above 0.5 M Al, the low Al concentration from Piqua cladding (0.1 M) did not have a significant effect.

5 CORROSION OF STAINLESS STEEL IN PRESENCE OF $Fe(NO_3)_3$

Corrosion of stainless steel by nitric acid is accelerated by the presence of ferric ions. The maximum corrosion rate in boiling 4.5 M HNO_3 and 1 M $Fe(NO_3)_3$ is 0.025 mm per month (MPM) and decreases to 0.005 MPM as fuel dissolution progresses. The average corrosion rate is approximately 0.015 MMP (Zeyfang 1979). Manness (1959) suggests that dissolution of U-Mo alloy in solutions containing more then 0.7–0.8 M $Fe(NO_3)_3$ requires incremental addition of nitric acid due to corrosivity of stainless steel construction materials.

6 DISSOLUTION OF Al-6061 CLADDING

Aluminum cladding can be rapidly removed from U-Mo alloy by caustic solution (Blanco & Watson 1961). However, this reaction forms H_2 which represents an explosion and fire hazard. Evolution of H_2 can be suppressed by adding sodium nitrate and is kept to a minimum when the molar ratio of Al/NaOH/$NaNO_3$ is 1/0.85/1.05. The dissolution rate of aluminum cladding increases with increasing caustic concentration and temperature. The penetration rate triples between 60 and 100°C. In 10% NaOH and 20% $NaNO_3$ and 100°C, the penetration rate for aluminum is 0.4–0.6 cm/hr (gresky 1952). Dissolution of unirradiated U-Mo alloy containing 3% (w/w) Mo in boiling 10w% NaOH and 20w% $NaNO_3$ is 0.15 mg/cm^2 hr (Schulz & Duke 1959; Schulz et al. 1962).

According to Blanco & Watson (1961), mercury-catalyzed nitric acid dissolution of aluminum-jacketed uranium fuel has been successfully demonstrated at a pilot-plant scale; however, this process is unattractive because mercury is a U.S. Environmental Protection Agency (EPA) listed Resource Conservation and Recovery Act (RCRA) hazardous waste (Blanco & Watson 1961). To obtain complete dissolution, mercuric nitrate is added in amount equal to 5% of aluminum to be dissolved. The advantages of the simultaneous dissolution of Al clad and fuel meat is that the production rates are increased through continuous dissolution; however, the amount of aluminum limits the volume to which the nitric acid waste can be reduced (Bradford & Adler 1954).

A more environmentally benign substitute for dissolution of aluminum cladding in nitric acid was developed at the Idaho National Engineering and Environmental Laboratory (Anderson & Christian 1998). The substitute, fluoboric acid (HBF_4), penetrates the protective oxide film that continuously forms on the Al surface in HNO_3. The postulated mechanism of this process involves dissolution of the alumina film with 0.006 M HF, which is in equilibrium with 0.15 M HBF_4 at 100°C. The presence of HBF_4 provides a large semi-buffered supply of HF and allows attack of HNO_3 on the aluminum metal.

At concentrations up to 0.2 M, HF enhances aluminum dissolution, with more additional aluminum dissolved then is stoichiometrically associated with HF alone. At HF concentrations 0.5 M and higher, the additional amount of aluminum dissolved decreases relative to the quantity of added HF (Anderson & Christian 1998). HF is also gradually consumed during the course of Al dissolution and its effect diminishes. HBF_4 is advantageous to HF itself because it provides a buffered source of HF and sustains the dissolution rate longer than an equal molar amount of HF. The penetration rate of Al-6061 obtained in a continuous dissolution process at 100°C using 0.15 M HBF_4 in 7 M HNO_3 is 40 mg/cm^2 hr. The dissolution rate of 0.1–0.2 M HBF_4 in 7 M HNO_3 at ~90°C is comparable to that of 0.007 M $Hg(NO_3)_2$ catalyst under the same conditions. At boiling temperatures, however, the Hg(II) effect becomes much greater than that of HBF_4. However, the excess rate possible with mercury catalyst is not needed for continuous dissolution, and in fact some if not all continuous-flow dissolvers cannot accommodate it. The corrosion rate of a stainless steel dissolver from 0.15 M HBF_4 in 7 M HNO_3 is 0.015 mm/mo.

Crooks et al. (2003) approached dissolution of aluminum/plutonium oxide material by adding boric acid, calcium fluoride, and nitric acid separately. Boric acid is mainly added to dissolved irradiated fuel solution as a neutron poison. The concentration range of boric acid investigated, 0.1–0.3 M, had no effect on the aluminum dissolution rates. The dissolution rate of aluminum increases linearly with calcium fluoride concentration. However, because HNO_3 is consumed by the oxidation of aluminum and fluoride ions are complexed by the aluminum cations, the dissolution rate decreases with time. Laboratory test results show that complete dissolution is achieved with Al/F ratio of 1.3 and 0.25 M fluoride. For a full-scale dissolution of aluminum/plutonium oxide, 8 M HNO_3 solution containing 0.38 M F^- was used because of uncertainties in the fluoride determination. The corrosion rates of stainless steel were found to be acceptable at 0.07 to 0.83 mm/year.

7 DISSOLUTION OF ZIRCONIUM DIFFUSION BARRIER

When zirconium-uranium alloys containing low percentage of zirconium are dissolved in nitric acid, explosive reactions may occur (Schulz et al. 1954a, b; Culler 1958). These reactions are a result of zirconium-uranium intermetallic compounds and may be initiated by mechanical shock. The presence of fluoride eliminates the hazard of explosive reactions. Uranium-zirconium alloys are completely dissolved in nitric acid when 4 moles of fluoride ion are added per mole of zirconium. The source of fluoride ion can be hydrofluoric acid or ammonium fluoro-silicate.

8 DISSOLUTION OF ALUMINUM-SILICON BONDING MATERIAL

Sodium hydroxide dissolves the aluminum-silicon bonding alloy (Blanco & Watson 1961). The siliceous material derived from the bonding alloy forms gelatinous solids during caustic dissolution, which might have to be separated by centrifugation.

When fuel elements containing aluminum, silicon, and uranium are dissolved in nitric acid, the silicon remains as an insoluble residue. Two distinct forms of particles appear in solutions: black (crystalline silicon) and brown (amorphous silicon with some form of alumina) (Parrett & Rohde 1958). During simultaneous dissolution of aluminum cladding and uranium alloy in nitric acid catalyzed by mercuric nitrate, the siliceous materials form solids and have to be separated from the solution by centrifugation prior to solvent extraction (Blanco & Watson 1961). Alumina forms slowly dissolve in acids and silicon is soluble in HF and HF/HNO_3 solutions (Weast et al. 1964).

9 RECOVERY OF U FROM CRUCIBLES, CONDENSERS, SLUG, AND FURNACE AIR FILTERS

Graphite crucibles are currently used for melting and casting of uranium alloys (Reiner 1987). Graphite components in direct contact with uranium are coated with ceramic paint (usually yttria, zirconia, or magnesium zirconate) to prolong component life and minimize carbon contamination. When these protective coatings are applied, the components are reusable and economical. Although the protective coatings reduce contact of uranium with graphite, the use of graphite crucibles does produce carbon contamination in U alloys due to imperfections in the ceramic coating, delamination, scratches, and by reaction of protective coating with graphite.

The recovery of uranium from graphite crucibles could be achieved by methods similar to those used for leaching uranium from graphite-based reactor fuel. In this process, the fuel is simultaneously pulverized, and uranium is leached in 90% HNO_3. The uranium losses are greater then 1% when uranium content in graphite based fuel is 1.5% (w/w) and 0.15% when the uranium content is 5% (Bradley & Ferris 1961).

Methods have been developed for recovery of plutonium from slag and crucibles by dissolution of the slag and crucible followed by solvent extraction (Blaine 1961). However, these methods do not seem economically feasible for recovery of LEU from crucibles and slug.

Under the current Y-12 National Security Complex practices, the uranium lost to crucibles, condensers, air filters, and slag (uranium oxides which are of lower density than the metal and float on top of the melt) is considered below-economically-recoverable quantities and is disposed as low-level waste (Wachs et al. 2008).

10 RECOVERY OF CAST RUNNERS AND U-Mo ALLOY WITHOUT BONDING LAYERS OR CLADDING

The U-10Mo alloy has a melting point of around 1200°C, which is much lower than the melting point of Mo (2623°C) (Wachs et al. 2008). Re-melting scrap material is a common practice but should be kept to 50% virgin materials and 50% re-meltable scrap in order to keep carbon within acceptable levels (Stanley & Binstock 1960). Therefore, the cast runners and uncoated U-Mo scrap material could be recycled to the melting step in the alloying process.

11 GAS FORMATION

The off-gas from dissolution of U-Mo alloys in nitric acid is mainly NO_x, and only traces of H_2 are evolved (0–0.2 volume percent) (Schulz & Duke 1959). The main components of the off-gas (>1%) are NO ~ 70–72%; NO_2 ~ 21–25%; and N_2 ~ 3–5%. The hydrogen generation for dissolution of Hallam Fuel (U-Mo alloy containing 10% (w/w) Mo) in an Al can is less than 2% and is attributed to the dissolution of aluminum in presence of Hg catalyst (Pierce 2007). Hydrogen-gas generation for dissolution of U-Mo alloy with aluminum in nitric acid did not approach the safety limits of 4% in the dissolver off-gas.

12 SUGGESTED DISSOLUTION METHODS

In the recommendations given here, it is assumed that a process involving filtration or centrifugation steps is not preferred in a process facility. In addition, use of mercury is not considered due to health hazards and the high costs of hazardous waste disposal.

12.1 DISSOLUTION OF U-Mo ALLOY WITH Zr DIFFUSION BARRIER AND WITH OR WITHOUT Al-6061 CLADDING

The most suitable method for dissolving scrap metal containing Zr appears to be dissolution in HNO_3 containing a fluoride source such as HF, CaF_2, or HBF_4. All components of the scrap, U-Mo alloy, Zr, and Al cladding can be soluble under these conditions. Hallam Nuclear Power Facility, SRNL, and CEA/VALRHO in France studied dissolution of U-Mo with aluminum clad/can in nitric acid (Zeyfang 1979; Herlet et al. 2005; SRNL 1972). However, none of the U-Mo fuels dissolved had Zr components. Aluminum clad/can dissolution in Hallam Facility and SRNL utilized mercury. The French report did not give details of reagents used.

To dissolve U-Mo alloy containing 10% (w/w) Mo with aluminum cladding, the Al concentration needs to be less then 0.5 M. At concentrations above 0.5 M, Al depresses solubility of Mo (SRNL 1972). Assuming an average Al/U molar ratio of about 4.9, at 10–20 g/L U, the Al concentration is 0.21–0.41 M. From the data presented by Faugeras et al. (1961), it appears that to achieve the dissolution of U-Mo alloy containing 10% (w/w) Mo at terminal U concentration of 10–20 g/L, a terminal HNO_3 concentration of 3 M (and up to 5 M based on the dissolution flowsheet for Super Kukla [SK] Prompt Burst Reactor material designed at Savannah River National Lab; Pierce 2007) is required. Under those conditions, at 100°C, up to 2.75 g/L of Mo can be dissolved in the alloy solution without precipitate formation. With the addition of 0.5 M $Fe(NO_3)_3$, up to 7 g of Mo can be dissolved in 10–20 g/L U solution and 1 M HNO_3 and up to12 g of Mo in 10–20 g/L U and 2 M HNO_3. The effect of $Fe(NO_3)_3$ on Mo solubility is even greater at higher concentrations. When 1 M $Fe(NO_3)_3$ is present in 1.5 M HNO_3 and 20 g/L U, up to 28 g/L of Mo can be dissolved. Therefore, it might be possible that U-Mo alloy containing 10% (w/w) Mo can be dissolved to higher terminal U concentrations than 10–20 g/L in the presence of high concentrations of Al, when $Fe(NO_3)_3$ is present. However, the addition of $Fe(NO_3)_3$ will increase the nitrate concentration in solution, and therefore lower the solubility of $Al(NO_3)_3$ due to the common-ion effect. Data for dissolution of U-Mo alloy in the presence of high concentrations of Al is not available and should be obtained experimentally; this is especially true when $Fe(NO_3)_3$ is present.

The closest dissolution conditions have been investigated by CEA/VALRHO, where U-Mo with 7% (w/w) Mo foils and Al cladding have been successfully dissolved, without $Fe(NO_3)_3$, in 5 M HNO_3 to obtain precipitate-free solutions containing 15 g/L U-Mo and 15 g/L Al (Herlet et al. 2005). Since the parameters of current U-Mo alloy containing 10% (w/w) Mo targets differ from those for which processes were previously developed, small-scale dissolution experiments will need to be performed in order to confirm dissolution conditions of the foils.

The recommended mole ratio of Al/F to ensure efficient dissolution is 1.3. In order to avoid explosive reactions of U-Zr, the required Zr/F mole ratio is 4 (Schulz et al. 1954a,b; Culler 1958). These conditions are challenging because Al is also complexed by F^-, and higher amounts of F^- are needed. HBF_4 provides a continuous source of HF; however, the effectiveness of HBF_4 in preventing formation of U-Zr compounds is not known. In addition, the effects of fluoride on the solubility of uranyl molybdate or molybdic oxide are not known. Therefore, small-scale experiments are recommended to optimize dissolution of U-Mo alloy in presence of Zr and Al in respect to nitric acid, the fluoride source, and perhaps $Fe(NO_3)_3$.

12.2 DISSOLUTION OF U-Mo ALLOY WITH Al-Si BONDING LAYER AND WITH OR WITHOUT Al-6061 CLADDING

The most efficient way to recycle this material is to remove the Al cladding and the Al-Si layer in caustic $NaOH/NaNO_3$ solution. Dissolution of unirradiated U-Mo 3% (w/w) Mo alloy in boiling 10% (w/w) NaOH and 20% (w/w) $NaNO_3$ is 0.15 mg/cm^2 hr (Schulz & Duke 1959; Schulz et al. 1962). The calculated loss of 0.025 mm U-Mo alloy foil, using this dissolution rate and assuming alloy density of 15.3 g/cm^3 results in U-Mo alloy loss of ~0.8% per hour. At this point the U-Mo alloy could be remelted with other scrap.

Without cladding, the U-Mo alloy can be also dissolved in HNO_3. From the data presented by Faugeras et al. (1961), it appears that >10 g/L Mo can be dissolved in 75 g/L U and 1–3 M HNO_3 can be dissolved in the presence of 1.0 M $Fe(NO_3)_3$. If the presence of $Fe(NO_3)_3$ is not desired, then up to 2.75 g of Mo can be dissolved in a solution with terminal U concentration 15–20 g/L and ≥3 M HNO_3.

Alternately, the U-Mo alloy with Al-Si layer and Al clad can be dissolved in HNO_3 in the presence of F^-. In the presence of a sufficient HF concentration, silicon will most likely be soluble, and removal of solids might not be necessary. The Al/F ratio required for efficient dissolution is 1.3. As described above, with the average Al/U molar ratio of about 4.9, to achieve the Al concentration of 0.21–0.41 M the alloy needs to be dissolved to 10–20 g/L U. From the data presented by Faugeras et al. (1961), it appears that a terminal HNO_3 concentration of 3 M (or higher) is required to achieve the dissolution of U-Mo alloy containing 10% (w/w) Mo at terminal U concentration of 10–20 g/L. Under those conditions, at 100°C, up to 2.75 g/L of Mo can be dissolved in the alloy solution without precipitate formation. The solubility of U-Mo alloy can be increased significantly, and the conditions under which a precipitate-free solution can be obtained can be expanded by addition of $Fe(NO_3)_3$, but its affect on aluminum solubility must be studied. Dissolution of fuel elements composed of U-Mo alloy with an Al-Si bonding layer and Al-cladding, without U-Mo precipitation or formation of silicon/alumina solids should tested experimentally.

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APPENDIX A:

HPRR FUEL CHARACTERISTICS AND AVERAGE Al/U MOLE RATIO

Reactor	Plate Type	Plates per year	Plate Length (cm)	Plate Width (cm)	Total Plate Thickness (cm)	U-Mo Fuel Meat Thickness (cm)	Clad Thickness - Sum of 2 Sides (cm)	U (mols)	Al (mols)	Al/U Mole Ratio
HFIR	0	1710	61	8.098	0.13	0.008-0.043	0.058-0.092	-	-	-
HFIR	1	3690	61	9.210	0.13	0.018-0.063	0.038-0.083	-	-	-
NIST	5	1140	33	7.094	0.10	0.026	0.08	401	2036	5.1
MIT	26	486	58	6.416	0.05	0.051	-	537	-	-
MURR	30	32	65	5.062	0.12	0.023	0.10	14	107	7.7
MURR	31	32	65	5.321	0.10	0.030	0.07	19	73	3.7
MURR	32	32	65	5.580	0.10	0.046	0.05	31	59	1.9
MURR	33	32	65	5.8	0.10	0.046	0.05	32	62	1.9
MURR	34	32	65	6.101	0.10	0.046	0.05	34	64	1.9
MURR	35	32	65	6.360	0.10	0.046	0.05	35	67	1.9
MURR	36	32	65	6.619	0.10	0.046	0.05	36	70	1.9
MURR	37	32	65	6.878	0.10	0.046	0.05	38	72	1.9
MURR	38	32	65	7.14	0.10	0.046	0.05	39	75	1.9
MURR	39	32	65	7.396	0.10	0.046	0.05	41	78	1.9
MURR	40	32	65	7.656	0.10	0.046	0.05	42	81	1.9
MURR	41	32	65	7.915	0.10	0.046	0.05	44	83	1.9
MURR	42	32	65	8.174	0.10	0.046	0.05	45	86	1.9
MURR	43	32	65	8.435	0.10	0.046	0.05	46	89	1.9
MURR	44	32	65	8.694	0.10	0.046	0.05	48	92	1.9
MURR	45	32	65	8.954	0.10	0.046	0.05	49	94	1.9
MURR	46	32	65	9.213	0.10	0.046	0.05	51	97	1.9
MURR	47	32	65	9.472	0.10	0.046	0.05	52	100	1.9
MURR	48	32	65	9.731	0.10	0.046	0.05	53	103	1.9
MURR	49	32	65	9.990	0.10	0.046	0.05	55	105	1.9
MURR	50	32	65	10.249	0.10	0.046	0.05	56	108	1.9
MURR	51	32	65	10.508	0.10	0.046	0.05	58	111	1.9
MURR	52	32	65	10.767	0.10	0.046	0.05	59	113	1.9
MURR	53	32	65	11.029	0.12	0.043	0.08	57	186	3.2
ATR	61	120	126	5.382	0.20	0.020	0.18	93	1490	16.0
ATR	62	120	126	5.517	0.13	0.026	0.10	128	838	6.6
ATR	63	120	126	5.771	0.13	0.030	0.10	150	848	5.6
ATR	64	120	126	6.027	0.13	0.030	0.10	157	885	5.6
ATR	65	120	126	6.281	0.13	0.033	0.09	182	891	4.9
ATR	66	120	126	6.538	0.13	0.033	0.09	189	928	4.9
ATR	67	120	126	6.792	0.13	0.033	0.09	196	964	4.9
ATR	68	120	126	7.049	0.13	0.033	0.09	204	1000	4.9
ATR	69	120	126	7.303	0.13	0.033	0.09	211	1036	4.9
ATR	70	120	126	7.559	0.13	0.033	0.09	218	1073	4.9
ATR	71	120	126	7.813	0.13	0.033	0.09	226	1109	4.9
ATR	72	120	126	8.070	0.13	0.033	0.09	233	1145	4.9
ATR	73	120	126	8.324	0.13	0.033	0.09	241	1181	4.9
ATR	74	120	126	8.580	0.13	0.033	0.09	248	1218	4.9
ATR	75	120	126	8.834	0.13	0.033	0.09	255	1254	4.9
ATR	76	120	126	9.091	0.13	0.030	0.10	236	1335	5.6
ATR	77	120	126	9.345	0.13	0.026	0.10	216	1419	6.6
ATR	78	**120**	126	9.60	0.13	0.020	0.11	166	1554	9.3
ATR	79	120	126	10.06	0.25	0.017	0.24	145	3607	24.8
Total								5667	27985	**4.9**

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