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Chemical Science and Engineering Division

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DISSOLUTION OF IRRADIATED U-Mo ALLOY MONOLITHIC FUEL CONTAINING 10% (w/w) MO

The Global Threat Reduction- (GTR)-Conversion program is currently engaged developing nuclear fuel that would enable the conversion of high-performance research reactors (HPRRs) to low enriched uranium (LEU) fuel. The fuel design is based on a monolithic uranium-molybdenum fuel alloy, which contains 10% (w/w) Mo (U-10Mo), enclosed in Al-6061 cladding, with a diffusion/bonding interlayer composed of zirconium or aluminum-silicon alloy material (Wachs et al. 2008). Taking into account the numbers of different plates; plate geometries being proposed; and the amount of aluminum cladding in the National Institute of Standards and Technology (NIST), Missouri University Research Reactor (MURR), and Advanced Test Reactor (ATR) fuel elements, the average Al/U molar ratio in the fuel targets is 4.9 (Stepinski et al. 2008). Reprocessing might be required for recovery of uranium from these irradiated fuel elements. Therefore, a nitric-acid-based dissolution technique for U-Mo fuel elements is required to prepare feed solutions for a tributyl phosphate- (TBP-) based solvent extraction process.

In this report, a dissolution method for irradiated U-Mo fuel elements is recommended, based on findings summarized in a preceding report, "Dissolution of U-Mo Alloy Scrap Metal" (Stepinski et al. 2008). In the recommendations given here, dissolutions of irradiated fuel are assumed to be conducted at the Savannah River Plant, which is designed for single-batch dissolutions, where cladding is dissolved along with the fuel using a mercury catalyst.

To completely dissolve Mo-alloy irradiated fuel containing 10% (w/w) Mo with aluminum cladding, the Al concentration needs to be less than 0.5 M, because at concentrations above 0.5 M, Al depresses solubility of Mo (Perkins 1972). To obtain Al concentration of 0.21–0.41 M, assuming the average Al/U molar ratio of about 4.9, the fuel needs to be dissolved to 10–20 g/L of U. From the data presented by Faugeras, it appears that, to achieve the dissolution of U-10Mo at terminal U concentration of 10-20 g/L, a terminal HNO_3 concentration of 3 M is required (Faugeras et al. 1961). (Up to 5 M terminal HNO_3 concentration was used in the dissolution flowsheet for Super Kukla (SK) Prompt Burst Reactor material designed at Savannah River National Lab [Zeyfang 1979].) Using a terminal nitric acid concentration of 3 M, up to 2.75 g/L of Mo can be dissolved in a 20 g/L U solution at 100°C 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 and 1-M HNO_3, and up to 12 g of Mo can be dissolved in a 10–20 g/L U and 2-M HNO_3 solution. The effect of $Fe(NO_3)_3$ on Mo solubility is even greater at higher concentrations, and the uranium and nitric-acid concentrations can vary from 0 to 75 gU/L and 1 to 3 M HNO_3 without precipitate formation (Faugeras et al. 1961). It is also possible that U-10Mo can be dissolved to higher terminal U and Mo concentrations 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, therefore lowering 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. At this point, addition of $Fe(NO_3)_3$ is not recommended.

The closest dissolution conditions to the ones discussed in this report have been investigated by CEA (Commissariat à l'Energie Atomique) VALRHO Marcoule (Herlet et al. 2005). In the reported experiments, Al-clad irradiated and non-irradiated U7Mo foils were 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. Since the parameters of current U-Mo alloy containing U-10Mo differ from those for which processes were previously developed, small-scale dissolution experiments will need to be performed in order to confirm dissolution conditions for the irradiated targets.

Dissolution of U-10Mo fuel plates with a Zr diffusion barrier should be done in the presence of sufficient F^- to prevent the formation of explosive U-Zr intermetallic compounds. The recommended Zr/F mole ratio is 4 (Schultz et al. 1954a,b; Culler 1958). This requirement is challenging because Al is also complexed by F^-; therefore, higher amounts of F^- will be required. In addition, the effects of fluoride on the solubility of uranyl molybdate or molybdic oxide are not known. Small-scale experiments are recommended for optimizing conditions for dissolution of U-Mo alloy in presence of Zr and Al in respect to concentrations of nitric acid, hydrofluoric acid, and, perhaps, $Fe(NO_3)_3$.

If dissolution of U-10Mo fuel plates with an Al-Si bonding layer is done in the absence of F^-, then siliceous materials will have to be separated from the solution by centrifugation prior to solvent extraction (Blanco and Watson 1961; Parrett and Rohde 1958). In presence of a high enough F^- concentration, silicon will most likely be soluble, and removal of solids might not be necessary (Weast et al. 1964). Dissolution of fuel elements composed of U-10Mo Al-Si bonding layer and Al cladding should tested experimentally to determine optimum conditions for dissolution without U/Mo precipitation or formation of silicon/alumina solids.

Mercury-catalyzed nitric-acid dissolution of aluminum-jacketed uranium fuel has been successfully demonstrated at a pilot-plant scale (Perkins 1972; Zeyfang 1979; Blanco and Watson 1961), and dissolution of aluminum cans and cladding has been done routinely at Savannah River Site SRS. To obtain complete dissolution, mercuric nitrate is added in amount equal to 5% (w/w) 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 (1) a one- versus two-step process, and (2) the possibility of using continuous dissolution.

REFERENCES

Perkins, W., 1972, *Processing Piqua Fuel in 221-H*, DPST-72-540, Savannah River National Laboratory, November.

Blanco, R.E., and C.D. Watson, 1961, "Head-End Processes for Solid Fuels," *Reactor Handbook*. S.M. Stroller and R.B. Richards (editors). Interscience Publishers, Inc., New York.

Culler, F.L., 1958, *Explosive Reactions during Reprocessing of Reactor Fuels Containing Uranium and Zirconium or Niobium*, ORNL-58-11-31, Oak Ridge National Laboratory, November.

Faugeras, P., C. Lheureux, and P. Leroy, 1961, *Etude De Solubilite Du Molybdene en Miliieu Nitrique* CEA Report No.1823, Nuclear Study Center, Seclay, France.

Herlet, N., G. Ferlay, J.P. Dancausse, and A. Juvenelle, 2005, "Reprocessing of U-Mo Fuels: Dissolution Experiments on Non-Irradiated and Irradiated Materials," *9th International Topical Meeting on Research Reactor Fuel Management*, April, Budapest, Hungary. European Nuclear Society, Brussels, Belgium. Available at http://www.euronuclear.org/pdf/RRFM2005-Transactions.pdf.

Parrett, O.W., and K.L. Rohde, 1958, *The Effect of Silicon in the Reprocessing of a Uranium Aluminum Alloy*, IDO-14441, Phillips Petroleum Co. Atomic Energy Div., Idaho Falls, Idaho May.

Schultz, W.W., F.A. Scott, and E.E. Voiland, 1954a, *Explosive Hazards in the Nitric Acid Dissolution of Uranium-Zirconium Alloy Fuel Elements* HW-32365, Oak Ridge National Laboratory, July.

Schulz, W.W., F.A., Scott, and E.E. Voiland, 1954b, *The Identification and Characterization of Explosive Residues Produced by Dissolution of Uranium-Zirconium Alloys*, HW-32410, Oak Ridge National Laboratory, November.

Stepinski, D.C., J. Swanson, J. Stevens, and G.F. Vandegrift, 2008, *Dissolution of U-Mo-Alloy Scrap from Fuel Fabrication*, ANL/CSE-13/37, June.

Wachs, D.M., C.R. Clark, and R.J. Dunavant, 2008, *Conceptual Process Description for the Manufacture of Low-Enriched Uranium-Molybdenum Fuel*, INL/EXT-08-13840, February.

Weast, R.C., S.M. Selby, and C.D. Hodgman (editors), 1964, *Handbook of Chemistry and Physics*, 46th Ed., Chemical Rubber Publishing Company.

Zeyfang, R.W., 1979, *Hallam Uranium-Molybdenum Fuel Processing*, TA-2-967, Savanna River Site, September.

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