Available online at www.sciencedirect.com

ScienceDirect

Procedia Chemistry 21 (2016) 46 – 53

Procedia Chemistry

5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

Molybdenum solubility in aluminium nitrate solutions

Xavier Hérès *[a], Danièle Sans[a], Murielle Bertrand[a], Catherine Eysseric[a], Emmanuelle Brackx[b], Renaud Domenger[b], Emmanuel Excoffier[b], Jean François Valery[c]

[a]*CEA, Nuclear Energy Division,DRCP, Marcoule, France*
[b]*CEA, Nuclear Energy Division,DTEC, Marcoule, France*
[b]*AREVA-NC, DOR/RDP, La Défense, France*

Abstract

For over 60 years, research reactors (RR or RTR for research testing reactors) have been used as neutron sources for research, radioisotope production (^{99}Mo/^{99m}Tc), nuclear medicine, materials characterization, etc… Currently, over 240 of these reactors are in operation in 56 countries. They are simpler than power reactors and operate at lower temperature (cooled to below 100 °C). The fuel assemblies are typically plates or cylinders of uranium alloy and aluminium (U-Al) coated with pure aluminium. These fuels can be processed in AREVA La Hague plant after batch dissolution in concentrated nitric acid and mixing with UOX fuel streams. The aim of this study is to accurately measure the solubility of molybdenum in nitric acid solution containing high concentrations of aluminium. The higher the molybdenum solubility is, the more flexible reprocessing operations are, especially when the spent fuels contain high amounts of molybdenum. To be most representative of the dissolution process, uranium-molybdenum alloy and molybdenum metal powder were dissolved in solutions of aluminium nitrate at the nominal dissolution temperature. The experiments showed complete dissolution of metallic elements after 30 minutes stirring, even if molybdenum metal was added in excess. After an induction period, a slow precipitation of molybdic acid occurs for about 15 hours. The data obtained show the molybdenum solubility decreases with increasing aluminium concentration. The solubility law follows an exponential relation around 40 g/L of aluminium with a high determination coefficient. Molybdenum solubility is not impacted by the presence of gadolinium, or by an increasing concentration of uranium.

Peer-review under responsibility of the organizing committee of ATALANTE 2016

* Corresponding author. Tel.: +33-466797700.
E-mail address: xavier.heres@cea.fr

Peer-review under responsibility of the organizing committee of ATALANTE 2016
doi:10.1016/j.proche.2016.10.007

Keywords: molybdenum, aluminium, solubility

1. Introduction

This study deals with the reprocessing of Research Reactor Spent Fuel (RRSF) consisting of plates or cylinders of uranium-aluminium alloy (U-Al) clad with pure aluminium. These fuels would be processed in AREVA's La Hague plant by liquid-liquid extraction, after dissolution in concentrated nitric acid and mixing with dissolution solution from Light Water Reactor (LWR) spent fuel[1]. Between 2005 and 2014, more than 7.25 tons of U-Al RRSF were reprocessed at La Hague while until the 1990s, 18 tons were processed at Marcoule. During reprocessing, the dissolution step can be impacted by the solubility of aluminium and molybdenum in nitric medium. In order to provide more flexible conditions for the dissolution operations in the case of treatment of fuels with a high molybdenum content, it is important to accurately determine the solubility of molybdenum under the operating conditions of fuel dissolution including; concentrated nitric acid and aluminium nitrate solution with uranium. This paper focuses on the experimental determination of the molybdenum solubility in nitric acid and aluminium solutions and on the identification of the impact of parameters such as aluminium concentration, acidity, gadolinium presence or uranium content.

After the description of the experimental procedure, the time required to reach the equilibrium state of the dissolution process is estimated. The maximum allowable concentration of aluminium is then determined to avoid precipitation phenomena with respect to the Mo/Al mass ratio. The increase in uranium concentration on this solubility is also studied. Finally, powder analyses by Scanning Electron Microscopy with X-ray microanalysis and X-Ray crystal Diffraction were carried out to characterize the type of solid obtained beyond Mo solubility.

Nomenclature

EDS	Energy-dispersive X-ray spectroscopy
HEU	High Enriched Uranium (fuels with typically up to 20% ^{235}U)
LEU	Low Enriched Uranium (fuels with less than 20% ^{235}U)
RERTR	Reduced Enrichment for Research and Test Reactors
RTR	Research and Test Reactors
RRSF	Research Reactor Spent Fuel
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
U-Al	Unirradiated fuel containing 63% uranium and 37% aluminium
XRD	X-Ray crystal Diffraction

2. Experimental

2.1. Procedure

The type of powder used can lead to notable differences in solubility of the same element. Thus, to be most representative of a metal fuel; uranium-aluminium alloy powder and molybdenum metal were dissolved in nitric acid solutions containing aluminium previously prepared from commercial aluminium nitrate powder with in certain cases gadolinium powder.

The dissolution apparatus consisted of a stirred tank reactor equipped with a heating jacket and a water cooled condenser above in order to retain vapour. The experimental protocol included the following steps:

- In the heating mantle, addition of U-Al (>99%) and Mo (Aldrich, >99.99% purity) powders, followed by addition of aluminium nitrate solution (Sigma Aldrich, >98,5% purity) or aluminium and gadolinium nitrate solution,