Molybdenum solubility in aluminium nitrate solutions

Xavier Hérès, Danièle Sans, Murielle Bertrand, Catherine Eysseric, Emmanuelle Brackx, Renaud Domenger, Emmanuel Excoffier, Jean François Valery

▶ **To cite this version:**

Xavier Hérès, Danièle Sans, Murielle Bertrand, Catherine Eysseric, Emmanuelle Brackx, et al.. Molybdenum solubility in aluminium nitrate solutions. Procedia Chemistry, 2016, 21, pp.46 - 53. 10.1016/j.proche.2016.10.007 . cea-03541209

HAL Id: cea-03541209
https://cea.hal.science/cea-03541209

Submitted on 24 Jan 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

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.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Peer-review under responsibility of the organizing committee of ATALANTE 2016

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

1876-6196 © 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
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,

- Start of agitation and heating to reach the nominal dissolution temperature,
- Sample collection and filtration of a sample using a 0.2 µm syringe filter,
- Dilution (after cooling of the sample in a water bath at 5 °C for 5 seconds)
- Stop heating and stirring and cool in water bath at 20 °C for 15 seconds,
- Filtration of bulk liquor using a vacuum pump through a 0.2 µm filter (previously weighed),
- Filter dried in an oven at 45 °C for more than 3 days,
- Measurement of free acidity by potentiometry using saturated ammonium oxalate and sodium hydroxide solution, analysis of uranium, aluminium and molybdenum concentrations by ICP-AES.

In order to be as precise and repeatable as possible, each point is the average of 8 tests on 2 samples at equilibrium (after 19.5 hours and 20 hours of stirring, 4 dilutions of samples). These results were obtained over several weeks of experience, with a renewed calibration for each series.

Parameters studied here were aluminium, uranium or gadolinium concentrations. Molybdenum solubility has been measured in high concentrations of aluminium nitrate from 37.5 g/L to 43.5 g/L. Acidity was fixed at 3 mol/L. Gadolinium was added up to 5 times its minimum concentration. The uranium concentration was increased from the nominal value up to 4.6 times.

2.2. Solution analysis

ICP-AES was calibrated daily with fresh standards for each measurement. Selected peaks are: Mo: 202.030 nm, U: 385.958 nm, Al: 396.152 nm, Gd: 335.048 nm. For the calibration curves, 5 standards (0, 1, 3, 5 and 10 mg/L) were prepared independently from commercial ICP standard solution 1 g/L (Aldrich). The determination coefficient of the calibration curve was > 0.9999, with a reproducibility of elemental peak < 3% (3 peaks per element). After a series of analysis, a standard was analysed to check for any drift. These precautions can detect a bad preparation of a standard or a failure of the ICP-AES unit. In this case, the results were obviously disregarded.

Uncertainty of ICP-AES analyses is < 4% and acidity is measured by potentiometric method with an error < 5%.

2.3. Solid analysis

In Table 1 are listed sample preparation and experimental conditions for SEM observations and XRD analyses.

Table 1. Sample preparation and experimental conditions for SEM observations and XRD analyses

Preparation for morphology	Dilution of the powder in 90% ethanol, 10% distilled water. Use or not of ultrasonic bath
Observation	Deposit of two-three drops onto an aluminium pad
Preparation for analysis	Coating in a transparent resin, ion polishing to 5kV during 1 h 30 to 3 h, carbon metallization of 15 nm.
MEB used	Carl Zeiss Merlin.
Voltage	2 kV for observation, 15 kV for analysis.
Intensity	70 Pa for observation, 5nA for analysis.
Picture Mode	HE-SE2 (secondary electrons) and AsB (backscattered electrons).
Preparation	After manual grinding and dilution in ethanol, a few drops deposit on a plane mirror.
DRX used	Diffractometer D8 Advance from Bruker AXS.
Cathode ray tube used	1600W power cathode copper.
Angular range	5° – 140°
Experimental conditions	3 s in steps of 0.03°, 40 kV voltage, 40 mA current.

2.4. Preliminary studies

Dealing with the first step of the experimental procedure, studies were carried out under several operating conditions to assess the time required to reach the equilibrium state for the dissolution of molybdenum point of view. Once the experiment is started according to the protocol described in paragraph 2.1, samples were regularly collected using a pipette, taking care to quickly close the hole to limit evaporation (the final volume decreases by less than 4 % compared to the initial one). The influence of the initial concentration of aluminium and molybdenum and the stirring speed (500 rpm and 200 rpm) were investigated.

Fig. 1 shows that whatever the concentration of excess molybdenum, added in metallic form, its dissolution is total after 30 minutes stirring but after molybdenum slowly precipitated as a solid assumed to be MoO_3 [2].

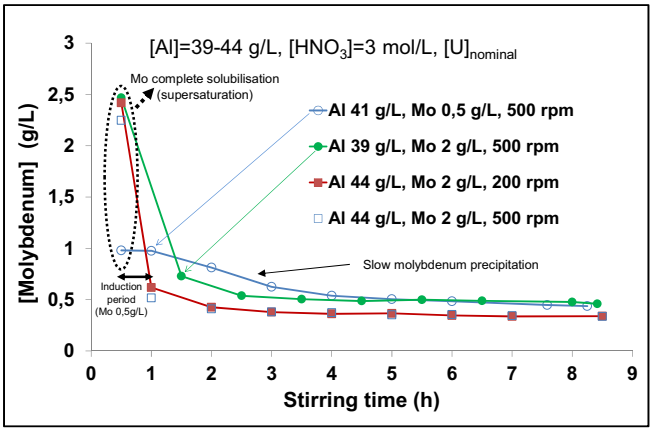

Fig. 1. Evolution of the Mo concentration in solution after total dissolution of the U-Al powder.

According to Fig. 1, the excess of molybdenum metal reduces the induction period before the progressive precipitation of molybdenum. Furthermore we can notice that precipitation is faster when the concentrations are higher. Indeed, with high concentrations, the kinetics of nucleation, growth and agglomeration are faster due to higher supersaturations[3]. That's why the experimental protocol includes an excess of molybdenum metal for all experiments described in this article, up to 2 g/L at maximum possible dissolution.

Fig. 1 points out that the studied range of the stirring speed corresponds to a fully turbulent flow so that there is little impact of the stirring speed. We choose to operate at 500 rpm.

After 6 to 7 hours, the values obtained were very close to the equilibrium solubility; there remains a very slight decrease in Mo concentration in solution. The equilibrium state was reached after > 15 hours. That is why, all experiments were carried out for 20 hours.

3. Results

3.1. Influence of aluminium concentration

Results clearly points out the decrease in molybdenum solubility with increasing aluminium concentration (see Fig 3.). This could be the result of increased ionic strength associated with the aluminium concentration. Another hypothesis is the formation of an insoluble Mo-Al type compound, facilitated by increasing aluminium concentration, is the cause of the decrease.

According to Fig. 3, the molybdenum solubility seems to be directly linked to the aluminium concentration as the experimental points gather in a straight line.

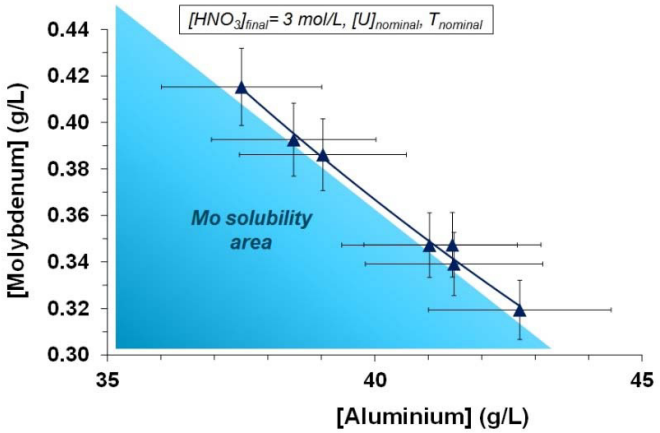

Fig. 2. Molybdenum solubility with respect to the aluminium concentration, at 3 mol/L of nitric acid. Blue shaded area represents the domain of molybdenum solubility

Fig. 2 graphically represents the 4% analytical uncertainties on experimental points. As expected, due to the need to be precise and to work on a limited operating range, the calculated uncertainties are close to the variation in concentrations. However, the protocol used, requiring separate experiments over several days with analyses spread over several weeks and systematic calibration of instruments for each day of analysis, gives some confidence in the values.

3.2. Influence of gadolinium

Gadolinium is currently added as a neutron-absorbing substance to compensate for the excess neutron reactivity in nuclear power plants. It is therefore important to see whether it has a significant impact on the values of molybdenum solubility in high nitric acid and aluminium concentration solutions.

The series of experiments consisted in varying the concentration of gadolinium and nitric acid as described in Table 2.

Table 2. Impact of gadolinium on molybdenum solubility at different acidities.

Element in solution	Final concentrations					
Nitric acid (mol/L)	2.5	2.5	3	3.1	3.3	3.6
Gadolinium (g/L)	1	0	0.5	0	0.2	0
Aluminium (g/L)	42.1	42.5	42.8	42.4	41.8	42.2
Uranium (g/L)	Nominal	Nominal	Nominal	Nominal	Nominal	Nominal
Molybdenum (g/L)	0.373	0.342	0.335	0.322	0.332	0.295

The values obtained show that the addition of gadolinium has very little impact on the solubility of molybdenum (close to analytical uncertainty). This experiment shows that the increase in acidity leads to a small decrease in Mo solubility. However, it appears that, for the conditions tested, the molybdenum is somewhat more soluble in the

presence of gadolinium with similar levels of aluminium and acidity: Thus, any addition of gadolinium in the solution of dissolution does not increase the risk of precipitation of molybdenum.

3.3. Uranium impact on solubility

Previous values were acquired with nominal uranium concentration. To ensure that this actinide is not involved in the precipitation of molybdenum, experiments were made with higher concentrations of uranium. The fact that molybdenum is less soluble if uranium is more concentrated might be a clue to the formation of a mixed U-Mo precipitate, as, for example, UO_2MoO_4 proposed by Ferris[2].

Preliminary experiments were carried out by increasing the mass of U-Al powder in the dissolution medium. Two solutions of aluminium nitrate in nitric acid are used. Varying masses of U-Al powder were added in each aluminium-nitric solution.

Table 3. Impact of uranium on molybdenum solubility

Element in solution	Final concentrations						
Aluminium (g/L)	41.7	41.8	41.5	41.6	43.5	43.5	43.6
Uranium (g/L)	0	Nominal	2.4 x Nom.	4.6 x Nom.	Nominal	2.4 x Nom.	4.6 x Nom.
Molybdenum (g/L)	0.354	0.355	0.354	0.358	0.288	0.283	0.286

As for gadolinium, it is seen in Table 3 that the increase in uranium concentration has very little impact on the solubility of molybdenum; the values appear to be stable with respect to analytical uncertainties. Constant values of molybdenum solubility despite the increase in the concentration of uranium suggest that this actinide would not form additional mixed precipitate Mo-U. This hypothesis will be validated by XRD and SEM analyses of precipitates from these experiences (see paragraph 3.4).

3.4. Powder analysis

After filtration, several precipitates from previous experiments were washed with pure water and 10 mol/L nitric acid. The first washing of the precipitate eliminates about 95 % of residual aluminium and 70 % of residual uranium. The second washing removes the remaining 30 % of residual uranium. The precipitate could then be dissolved in 3 mol/L nitric acid at 70 °C for 1 hour. The analyses by ICP-AES of 10 dissolution solutions from various operating conditions, show that the washed precipitate is composed, in mass, of 96 % of molybdenum and 4 % of aluminium. Uranium is unquantifiable by ICP-AES in the precipitate.

Additional analyses were carried out by SEM to observe the morphology of powders. Regardless of the initial composition, all powders consisted of a multitude of small needles. The needle length ranged from 2 µm to 12 µm. The preparation using ultrasonic bath tended to break these needles. EDS spectroscopy gave spectra and elemental analyses on small selected area. In the example given in Fig. 3, titanium and aluminium come from ion polishing holder, chloride and silicon come from resin coating. Apart from some elements due to sample preparation or support, oxygen and molybdenum were the only elements found. This confirms the results from ICP analyses where uranium is not in the precipitate. Quantification was achieved on some solid ionically polished. The composition was 75% oxygen and 25% molybdenum, corresponding to molybdenic acid MoO_3.

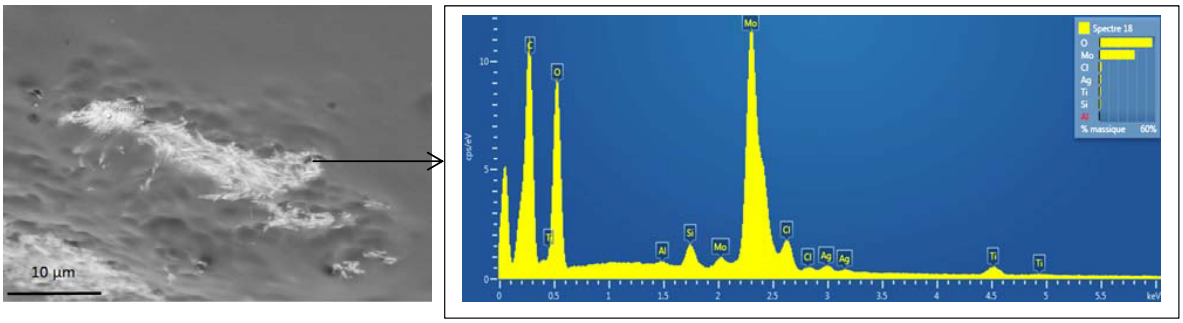

Fig. 3. Example of Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS) on a cross section area of powder

Then, X-ray diffraction of powders was used to determine the crystallographic form in solids. All samples corresponded to the same crystallographic form of MoO_3 (Fig. 4), all the peaks are indexed.

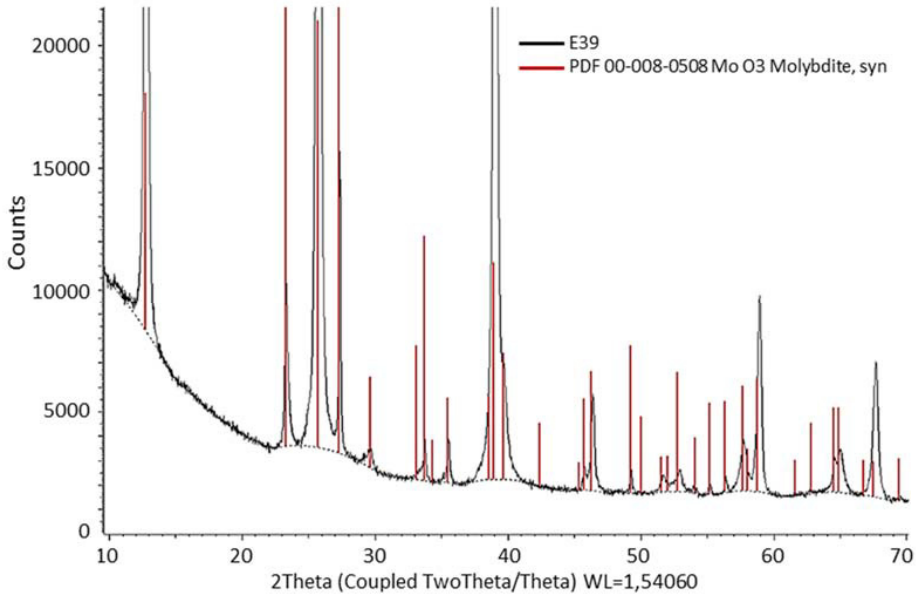

Fig. 4. Examples of X-ray diffraction of powders, all the peaks are indexed (red line: MoO_3 orthorhombic symmetry)

These results show that even in high concentration, uranium does not precipitate with molybdenum. The precipitate was basically composed of molybdenum trioxide MoO_3 proposed in literature[4,5,6] (no mixed U-Mo precipitate, as for example UO_2MoO_4 suggested by Ferris[2])

4. Conclusions

This study led to the accurate determination of the range of the molybdenum solubilities with respect to varying the aluminium concentration at the dissolution step for RTR U-Al spent fuels. It was observed that after total dissolution of molybdenum, slow precipitation of molybdenum occurs: therefore non-equilibrium dissolution leads to dissolving higher concentrations of molybdenum than those determined in this study. It appears that neither uranium nor gadolinium modify the solubility of molybdenum in the range of concentrations corresponding to the operating conditions of the dissolution.

Studies on solids showed that no uranium was in the precipitate, composed of MoO_3 hydrated solid as proposed in literature[4,5,6] .

Due to the composition of the ion polishing holder, it was not possible to point out the potential presence of aluminium inside the solid, in order to confirm the ICP-AES analysis with 4 % in mass of aluminium. An analysis of solids using a MET would confirm this result.

Acknowledgements

Financial support for this work was from AREVA-NC.

References

1. Valéry J.F., Domingo X., Landau P., Péchard C., Laloy V. Overview on RRSF reprocessing, from spent fuel transportation to vitrified residues storage. In *RRFM 2015 Conference Proceeding,* Bucharest, Romania, 19-23 April 2015, ENS conference 2015, p 806-818.
2. Ferris, L. Aqueous processes for dissolution of uranium-molybdenum alloy reactor fuel elements. Oak Ridge National Laboratory, 1961, ORNL-3068
3. Myerson A.S., editor. *Handbook of Industrial Crystallization.*Butterworth-Heinemann Publishing; 2002
4. Rempel K.U., Migdisov A.A., Williams-Jones A.E. The solubility and speciation of molybdenum in water vapour at elevated temperatures and pressures: Implications for ore genesis, *Geochimica et Cosmochimica Acta* **70,** 2006, 687–696
5. Schulz W., Burns R., Duke E.M.. Nitric acid dissolution of uranium molybdenum alloy reactor fuels, *Industrial & Engineering Chemistry Process Design and Development,* **1(2),** 1962, p.156-160
6. Visser A.E., Pierce R.A., Laurinat J.E. Purification of Uranium from a Uranium/Molybdenum Alloy, *Separation Science and Technology,* **43**, 2008, p. 2775–2785