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MOLYBDENUM BEHAVIOUR DURING U-AL RESEARCH REACTOR SPENT FUEL DISSOLUTION

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ABSTRACT

In the frame of Research Reactors Spent Fuel (RRSF) treatment by hydrometallurgy, the dissolution in nitric acid of irradiated U-Al, is a key issue because of the low solubility of molybdenum fission product in presence of high concentration of aluminium. In this study, the values of molybdenum solubility have been accurately measured in different operating conditions. Studies have carried out with non-active materials. To be more representative of metallic fuel, uranium-molybdenum alloy powder and molybdenum metal have been dissolved in aluminium nitrate solutions at high temperature. In order to be sure that molybdenum solubility has been reached, experiments have been carried out with an excess of molybdenum metal. In spite of this excess addition, metallic elements have been dissolved completely after stirring time of thirty minutes with a magnetic stirrer. Shortly after this total dissolution, a slow molybdenum precipitation has been observed for almost 15 hours. An experimental protocol has been developed to properly wash precipitates in order to determine their elemental composition. No uranium has been detected in the washed precipitate by ICP-AES measurements performed after redissolution of solids in aluminium free nitric acid solutions. Further analyses by Scanning Electron Microscope have shown a needle-like morphology. Energy-dispersive X-ray spectroscopy analyses on several selected areas have confirmed the absence of uranium in precipitates. EDX semi-quantification has been carried out on ionically polished particles. They are composed of 75% oxygen and 25% molybdenum, suggesting MoO_3 compounds. X-ray diffraction spectra of powders have confirmed this result: all samples matched the crystallographic form of MoO_3.

1. Introduction

Research Reactor Spent Fuel (RRSF) consists of plates or cylinders of uranium-aluminium alloy (U-Al) clad with pure aluminium. These fuels are processed in AREVA's La Hague plant by liquid-liquid extraction, after batch dissolution in high concentrated nitric acid [1]. The dissolution capacity is limited by the solubility of aluminium and molybdenum in nitric medium. The objectives of that work were to determine the solubility of molybdenum in concentrated nitric acid and aluminium nitrate solution and to see if uranium could be included in a molybdenum precipitate. We focused here on solid analysis and the protocol for washing precipitates before analyses, in order to retrieve every element soaked on solid. Determination of molybdenum solubility in nitric acid containing aluminium solutions and studies of the impact of parameters such as aluminium concentration, acidity, gadolinium presence or uranium content are detailed in [2].

After development of washing protocols, several analytical techniques were used for the elemental analysis or chemical characterization of a sample. First, Inductively Coupled Plasma with Atomic Emission Spectroscopy (ICP-AES) gave element concentrations in the solid after complete dissolution in nitric acid. Then, others techniques as Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive X-ray Spectroscopy (EDS) or X-Ray crystal Diffraction (XRD) were used to characterize the solid directly.

2. Experimental

2.1 Procedure

In order to determine the solubility of molybdenum and to be representative of a metal fuel, uranium-aluminium alloy powder and molybdenum metal were dissolved in nitric acid solutions containing aluminium nitrate [2].

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 is described in [2]. To ensure that solubility is reached, every experiment was carried out with a large excess of molybdenum powder. For instance, in our operating conditions, molybdenum maximum solubility was 0.45 g/L and we try to dissolve 2 g/L of molybdenum in order to form a solid. At the beginning of each experiment, the whole powder was completely dissolved but after an induction period of about 30 minutes, a slow precipitation was observed. At the end, the bulk liquor was filtrated thanks to a 0.2 μm filter and a vacuum pump. The filters were dried in an oven at 45°C for more than 3 days.

The effect of different parameters on molybdenum solubility was studied such as concentration of aluminium, uranium and nitric acid.

Several solids were obtained from Mo solubility studies described in [2]. The objective was to develop a washing procedure in order to be sure that we could describe elements included in solids and not those which could be soaked on the precipitate.

Distilled water and nitric acid were tested to wash solids. Two protocols were carried out: firstly powder was mixed in aqueous solution in order to evenly disperse it in the liquid; secondly, washing solution was put through filter containing the powder. In the last case, the solid could be less efficiently washed.

The first protocol consists in introducing the precipitate resulting from one of the experiments from [2] into tubes containing washing solution. The tube is then stirred at room temperature (T=25°C. approximately) for 5 minutes with a vibrating stirrer. The solution is then filtered using a vacuum pump on a 0.2 μm filter. Concentrations of uranium, aluminium and molybdenum are then measured using ICP-AES in each of the recovered solutions after dilutions of 10,100 or 1000 doubled. In order to make a balance on the total quantity of element initially present, dissolution of the washed solid was carried out in a Becher covered with a Mylar type film (polyethylene terephthalate) and heated on a magnetic stirrer heating to 70 °C, either with 5 mol/L of NaOH or with 3 mol/L of HNO_3, stirred with a magnetic bar for one hour. The left part of Fig. 1 shows a block diagram of this protocol.

In the second protocol, the powder was first mixed in deionized water by means of a vibrating agitator and then filtered on a filter with a porosity of 0.2 μm above an Erlenmeyer equipped with a vacuum pump. Then, the solid on the filter was successively impregnated by washing solutions without mechanical agitation. The final solid is then totally dissolved in 3 mol/L of nitric acid at 70 °C, with magnetic stirring for one hour in a Becher. The right part of Fig. 1 shows the synoptic diagram of this protocol.
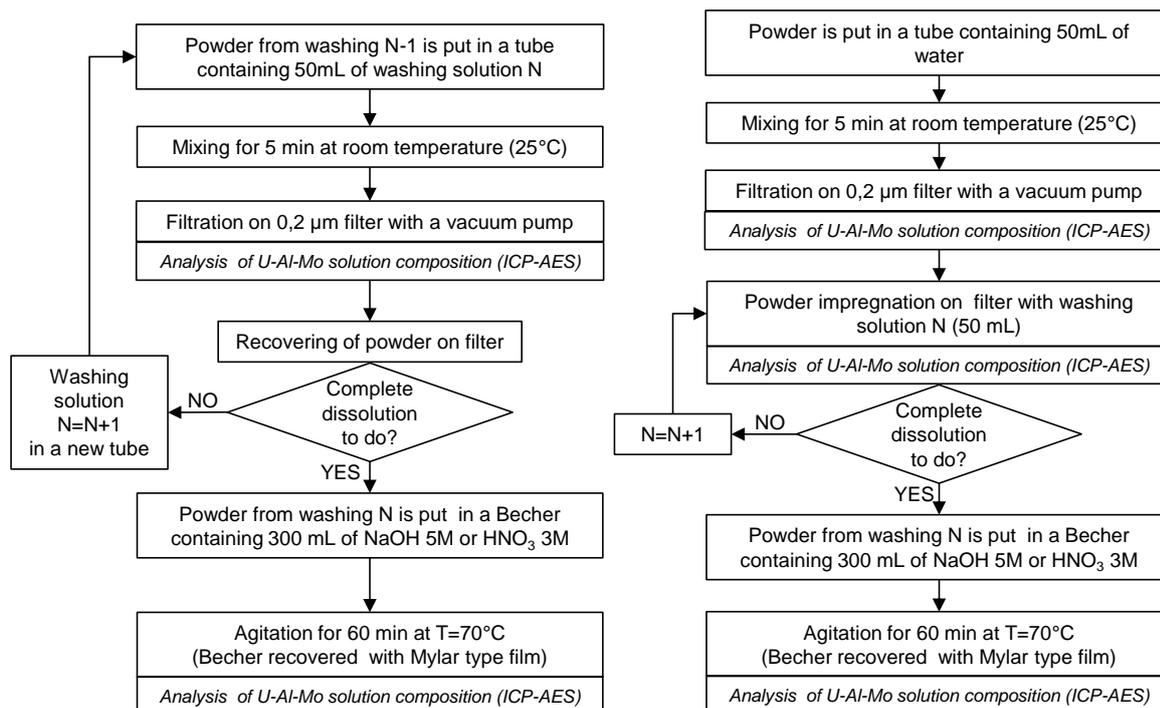
Fig. 1. Experimental washing protocols with mechanical agitation (left) or by impregnation (right)

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. 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.

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.

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

3. Results

3.1 Development of washing procedure

A complete dissolution of unwashed solids showed they contained uranium. The objective was to see if the uranium present in unwashed solids was included in the precipitate or was only impregnated on its surface. First, the protocol with mechanical agitation (left part of fig. 1) was carried out with washings at high acidities, 5 and 10 mol/L. The precipitates from experiments with nominal concentration of uranium (E1) and with four times more uranium (E2) were used for this study. Fig. 2 shows elemental distributions of molybdenum, aluminium and uranium in the washing or dissolution solutions. This distribution was determined for each element in mass percentage relative to the total measured in the washing/dissolving solutions (the last solution being clear, all the powder is supposed to be dissolved). The mass fraction of Mo, Al and U in the unwashed precipitate was between 36 and 40%
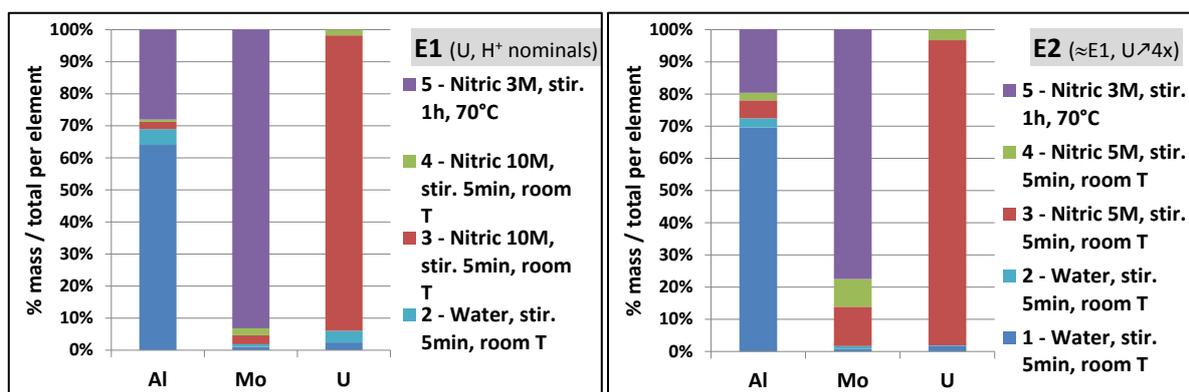

Fig. 2. Distribution of Mo, Al, U in aqueous stirred washing or dissolution solutions tested for powders from experiments carried out with nominal uranium concentration (E1) or with 4 times higher (E2)

The values measured by ICP-AES showed that:
- Uranium was quantitatively removed in the first HNO_3 5 mol/L or 10 mol/L acid washing.
- Molybdenum was less solubilized in the washing solutions as the nitric acid increases (9-12% solubilized with 5 mol/L of HNO_3 while 2-3% solubilized with 10 mol/L of HNO_3).
- Washing with water strongly solubilized the aluminium and increase in acidity reduced the solubilisation of the residual aluminium. It was therefore possible that aluminium was included in the molybdenum precipitate in minority.

The washed precipitate was composed of 96% Mo and 4% Al in percent by weight of the total weight of the washed solid, without taking into account the oxygen not measured here.

Washings with water to remove the impregnated aluminium and with 10 mol/L nitric acid, to remove the uranium were therefore recommended.

In the following experiments, the second protocol with impregnation of solids (right part of Fig. 1) was followed in order to see if lack of agitation could change distribution of elements in washing solutions.

The precipitates from experiments E3, E4, E5 and E6 were used for this study. E3 was similar to E1 with twice more uranium. E4 was similar to E3 with additionally 1 mol/L of nitric acid. E5 was comparable to E2 with 0.8 mol/L of nitric acid less. E6 is an experiment without any uranium.

Fig. 3 and Fig. 4 show elemental distributions of molybdenum, aluminium and uranium in the washing or dissolution solutions. This distribution was determined for each element in mass percentage relative to the total measured in the washing/dissolving solutions (the last solution being clear, all the powder is supposed to be dissolved).
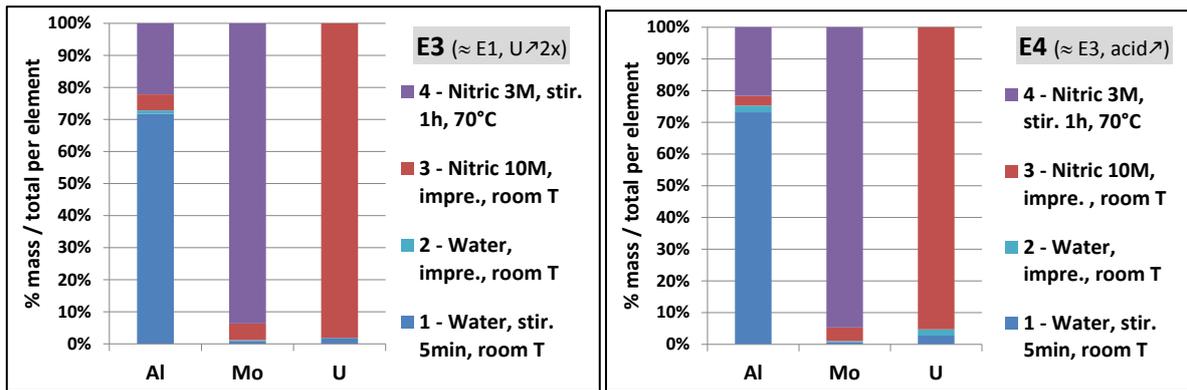
Fig. 3. Distribution of Mo, Al, U in aqueous impregnation washing or dissolution solutions for powders from experiments E3 (like E1 with more uranium) and E4 (like E3 with more acid)
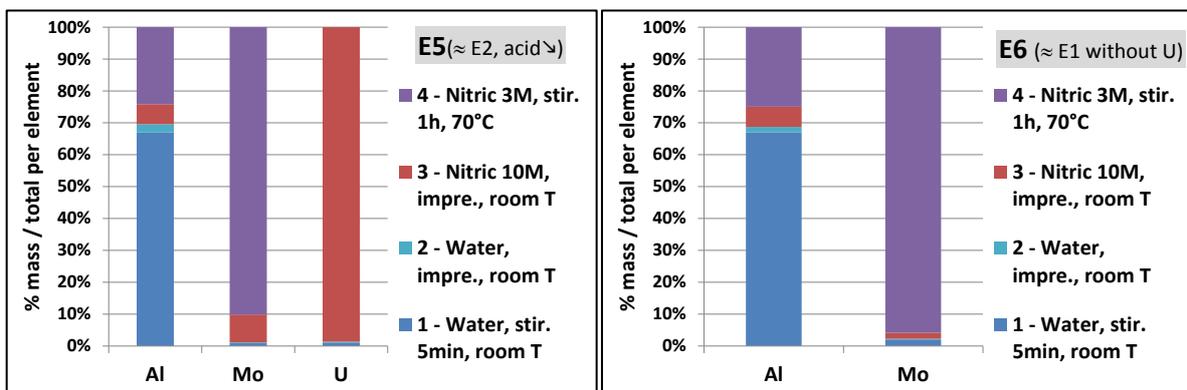

Fig. 4. Distribution of Mo, Al, U in aqueous impregnation washing or dissolution solutions for powders from experiments E5 (like E2 with less acid) and E6 (like E1 without uranium)

The measurements confirmed washing efficiency of solids with water to remove aluminium on the one hand and with 10 mol/L of nitric acid to solubilize the uranium on the other hand. Washing with simple impregnation of nitric solution on the filter solubilized the same quantity of uranium as with stirring: uranium was likely impregnated on the solid and not included in it because, otherwise, the quantities of uranium measured in the filter washing solution would be lower than with homogeneous agitation of the powder in solution.

Whatever concentrations of nitric acid, aluminium or uranium, every washed precipitate was composed, according to ICP-AES measurements, of 96% molybdenum and 4% aluminium as an elemental mass percentage relative to the total mass of the washed solid, without taking account of the oxygen not measured here. It would appear that a small proportion of aluminium is included in the solid.

The uranium is undetectable by ICP-AES in the solution of redissolution of the washed solid (with the limit of quantification by this analytical technique, the mass of uranium is less than 0.2% of the total mass of the precipitate).

To confirm the absence of uranium in the solid and to characterize directly the precipitates, Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive X-ray Spectroscopy (EDS) or X-Ray crystal Diffraction (XRD) were used.

3.2 Preparation and direct characterisation of solids
3.2a Solid production and ICP-AES results from washing protocol
In order to have a larger quantity of precipitate to be characterized, an experiment E6 was carried out according to the same protocol as described in [2] but with a larger dissolving volume and with a final uranium concentration above 20 g/L to increase the detection sensitivity of a potential uranium-molybdenum co-precipitate. The solid obtained was washed twice with water and then with 10 mol/L nitric acid directly on the filter, according to the block diagram of the left part of Fig. 1. To confirm that nitric acid didn't dissolve uranium included in

the precipitate, a fraction of this solid was not washed with 10 mol/L of nitric acid. A small fraction of the final washed solid was dissolved in HNO_3 3 mol/L by stirring for one hour at 70°C, in order to measure elemental residual composition by ICP-AES. The synoptic diagram of the washing protocol is given in Fig. 5
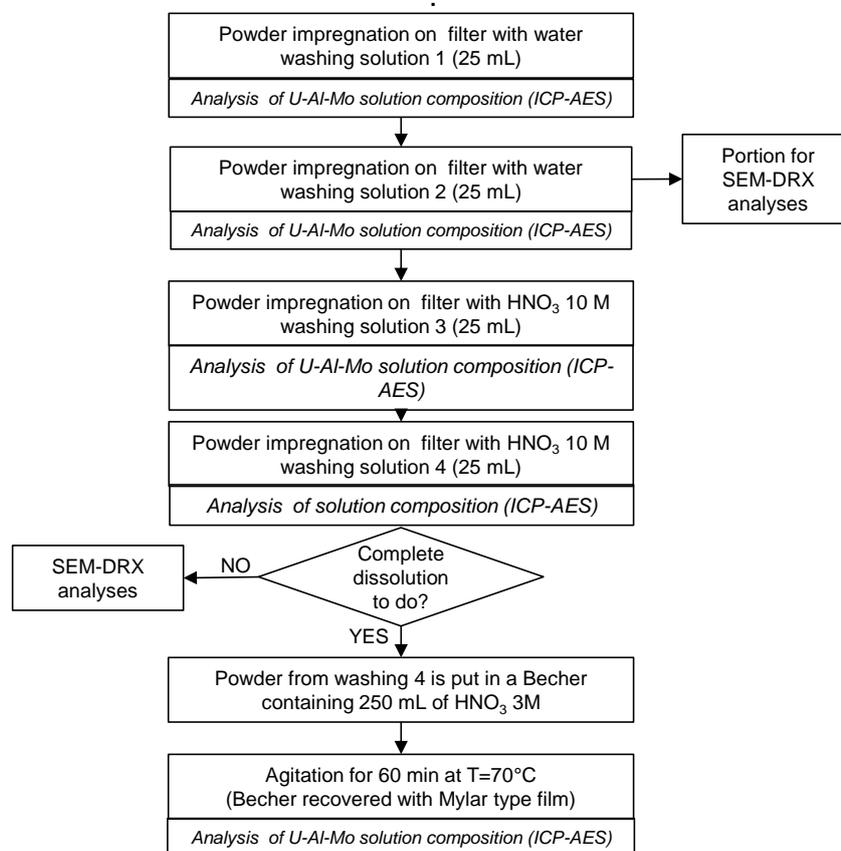

Fig. 5. Synoptic diagram of the washing protocol by impregnation of the powder from E6 for the MEB-DRX analyses

The results of ICP-AES analyses of washing and dissolution solutions are given in Tab. 2. Based on these values, water washing removes more uranium, molybdenum or aluminium from the freshly prepared precipitate than the previous precipitates which had been aged and dried several weeks before washing. About 70% of the uranium was washed with water instead of 1% to 13% in the case of previous experiments (column "1" in the "Material balance" of Tab. 2). 94% of aluminium was washed with water for E6 instead of 60% to 73% for the aged precipitates. These results seem to confirm that uranium was not included in the precipitate but was only impregnated on the surface of the precipitate. The less efficient washing of an aged solid could be explained by a phenomenon of slow dehydration and oxidation of the metals (Mo, Al and U) making their solubilisation more difficult in distilled water.

However, regardless of the aging time, washing with 10 mol/L of HNO_3 dissolved quantitatively the residual uranium. The final elemental proportion of the solid remains 97% molybdenum and 3% aluminium, closed to values already measured. The solid prepared here was comparable to those obtained previously.

	1 - Water, impregnation, Room T		2 - HNO₃ 10M, impregnation, Room T		2 - HNO₃ 3M, dissolution 60min, T=70°C		Total (mg)	Material balance			%Element
								1	2	3	Total 3
[Al] (g/L)	0.88	0.87	0.04	0.04	0.02	0.02					
[Mo] (g/L)	0.69	0.68	0.03	0.03	0.48	0.50					
[U] (g/L)	0.07	0.08	0.03	0.03	0	0					
Al (mg)	43.1	42.5	1.9	1.8	0.7	0.9	45	94%	4%	2%	3%
Mo (mg)	33.8	33.1	1.2	1.2	22.7	23.4	58	58%	2%	40%	97%
U (mg)	3.7	3.7	1.7	1.7	0	0	5	69%	31%	0,0%	0%
Vol (mL)	49	49	49	49	47	47					

Tab. 2: ICP-AES results from aqueous washing solutions of the powder from E6

3.2b Elemental composition, structure and morphology by SEM/EDS

The powder was made up of small needles of length ranging from 2 to 12 µm. As shown, for example, in Fig. 6 (bottom photos), a pre-treatment using ultrasonic bath before SEM analysis tended to break these needles.
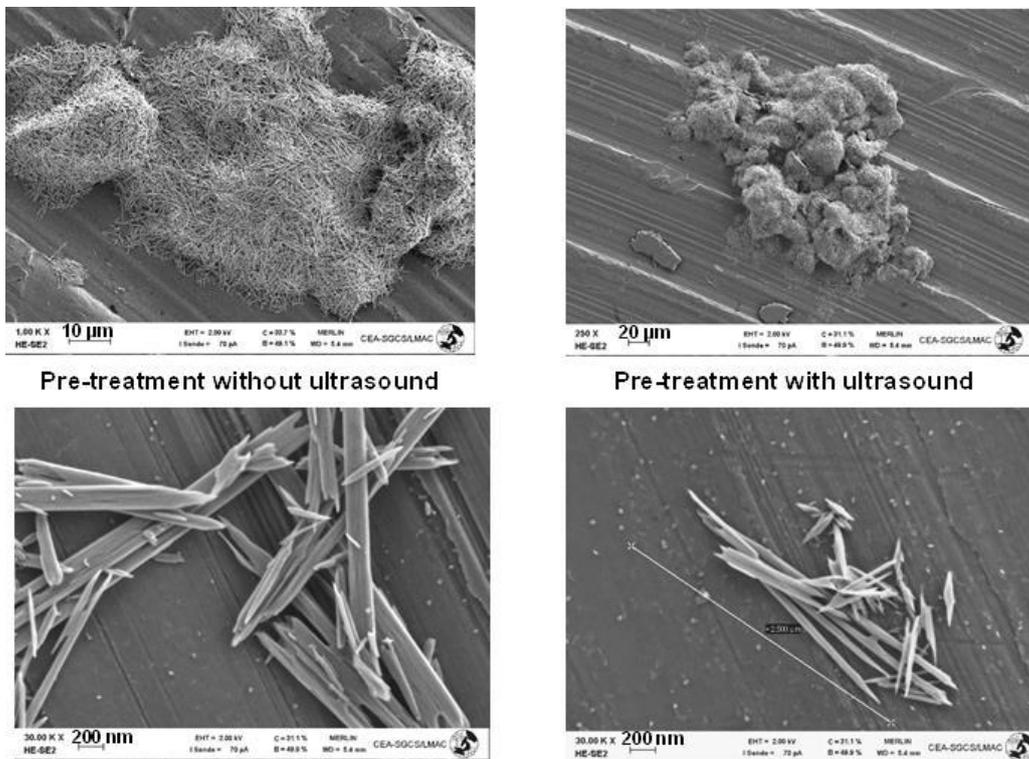

Fig. 6. Example of SEM images of solids, impact of pre-treatment using ultrasonic bath

Fig. 7 gives the images obtained for the precipitate not washed by 10 mol/L of nitric acid, after a three-hour ionic polishing. Shots 1 and 2, obtained with the detector HE-SE2 of secondary electrons (SE), show that the sample is perfectly plane. Images 3 to 6, with the AsB detector of backscattered electrons (BSE), indicate only one phase even if this solid was not washed with 10 mol/L of nitric acid. It confirms that residual uranium detected by ICP-AES in the 10 mol/L washing solution came from impregnation on the external surface of the solid and was not included into solid structure.
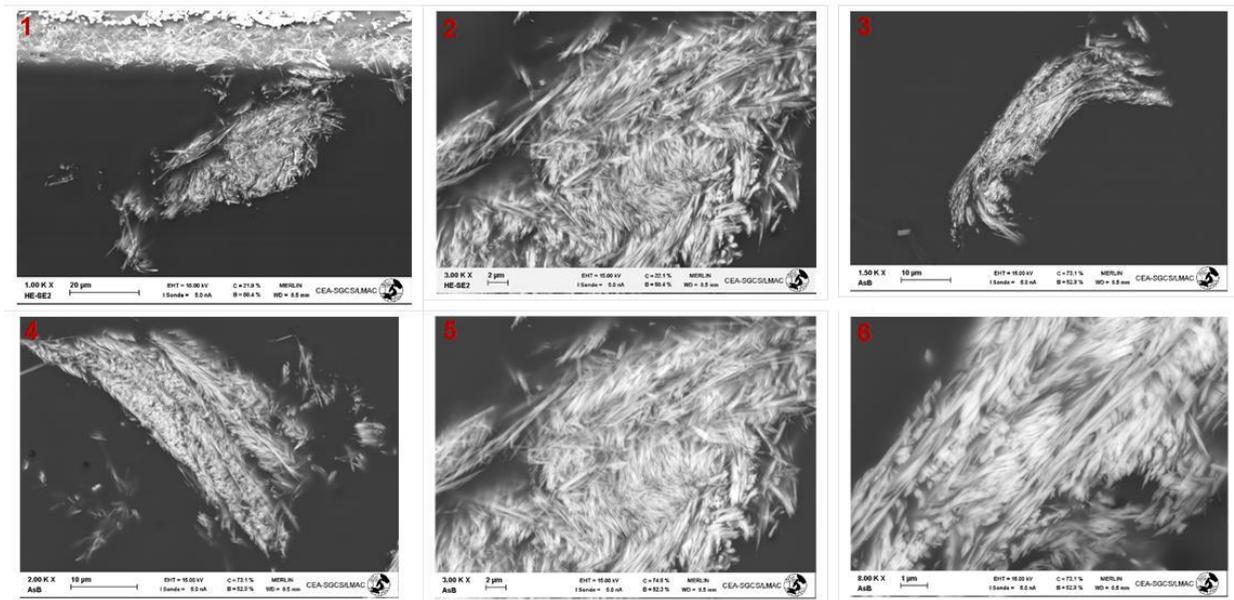
Fig. 7. SEM (SE or BSE) images of the solid unwashed with nitric acid 10 mol/L resulting from the experiment E6 after ionic polishing of 3 hours

With X-ray microanalysis using dispersive energy spectroscopy (EDS) it is possible to estimate qualitatively elementary composition of solid, apart from interferences coming from supports used for analyses. Fig. 8 shows examples of EDS spectra. These analyses reveal essentially molybdenum and oxygen. Aluminium and copper come from the ionic polishing support. Uranium is not detected, confirming ICP-AES results given in 3.2a.
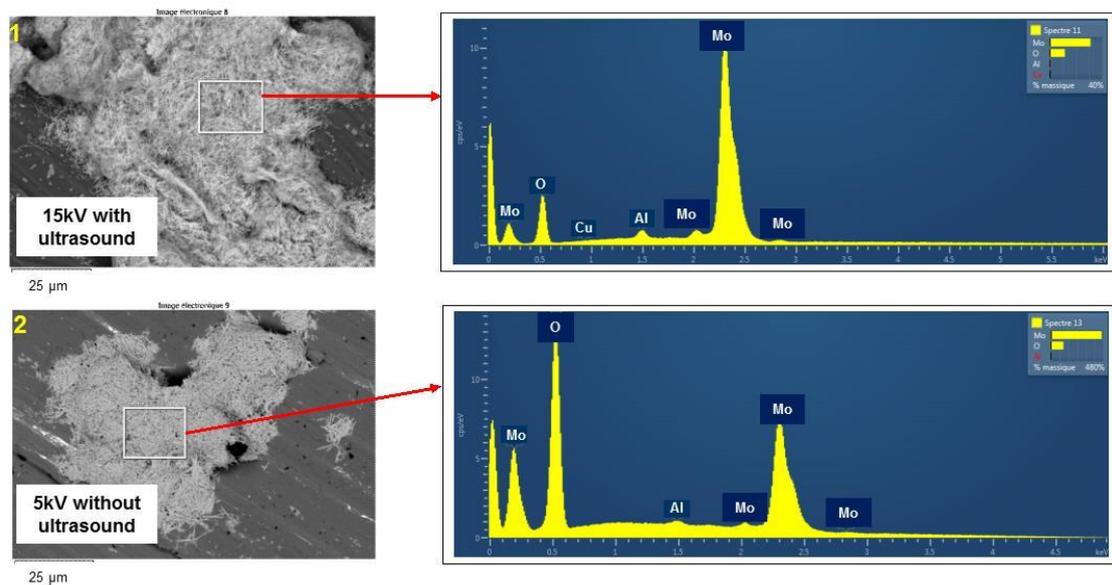

Fig. 8. Example of SEM/EDS spectra of washed solid from experiment E6 with or without ultrasonic pre-treatment

3.2b X-ray diffraction analysis

Fig. 9 gives an example of a X-Ray crystal Diffraction (XRD) spectrum of the solid sample. The powder was scraped on the filter and then deposited with alcohol on a mirror for analysis by DRX. All peaks are indexed with respect to the orthorhombic MoO_3. All the samples analysed by XRD corresponded to the same crystallographic sheet of molybdenum trioxide MoO_3, as expected in the literature [3]-[4]-[5].
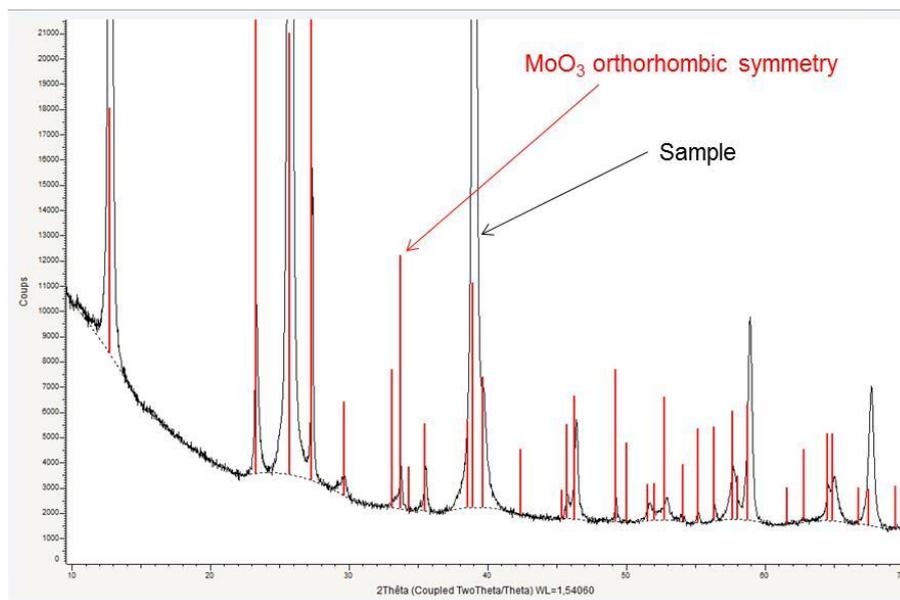
Fig. 9. XRD spectrum of washed solid from experiment E6

4. Conclusions

The SEM/EDS and XRD analyses showed that the precipitates obtained during the dissolution experiments of powder U-Al like, with only an excess of molybdenum metal, was always in MoO_3 form.

According to ICP-AES measurements on the redissolution solutions, the washed precipitates contained mainly molybdenum (96% in mass) and a little aluminium (4% mass), without considering oxygen which was not measured here. The uranium is undetectable by ICP-AES in the redissolution solution of the washed solid (mass of uranium <0.2% mass).

As for ICP-AES, no additional solid phase or inclusion of uranium was detected during these SEM/EDS measurements, even under conditions of concentrated uranium in the dissolution solution. This confirms that uranium was not included in the solid.

The presence of small amount of aluminium detected by ICP-AES could not be confirmed by SEM/EDS due to the use of a support containing this element. To characterize a fine structure of Mo-Al solid, analysis by transmission electron microscopy (TEM) would be necessary. It would be interesting to verify the existence of such a solid to explain in particular the decrease in molybdenum solubility with an increase in the concentration of aluminium in nitric acid.

It would also be useful to study the impact of zirconium on molybdenum solubility by some complementary experiments at different acidities in order to better simulate the operating conditions for the treatment of U-Al RRSF.

5. References

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