Journal of Nuclear Materials 466 (2015) 502–508

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Actinides recovery from irradiated metallic fuel in LiCl–KCl melts

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A R T I C L E I N F O

Article history:
Received 5 July 2015
Received in revised form
12 August 2015
Accepted 23 August 2015
Available online 28 August 2015

Keywords:
Irradiated metallic fuel
Electrorefining
LiCl–KCl
Pu
Minor actinides

A B S T R A C T

Electrorefining of irradiated metallic fuels was successfully demonstrated: Actinides (U, Pu, Np, Am and Cm) in the fuels were dissolved in LiCl–KCl melts with high dissolution ratios, while U was selectively deposited on a solid cathode and the simultaneous recovery of actinides in a liquid Cd cathode was confirmed. The behavior of actinides, the fuel matrix stabilizer Zr and fission products such as lanthanide, alkaline, alkaline earth and noble metal, at the electrorefining is discussed based on the ICP-MS analysis of the samples taken from molten salt electrolyte, anode fuel residues and cathode deposits.

1. Introduction

Since the pyro-process utilizing molten salts and liquid metals as reaction media has intrinsic properties, such as a high stability against radiation, a high proliferation resistance, a compact and flexible batch-process to be designed and so on, this technology has been developed worldwide as one of the most promising reprocessing methods for spent nuclear fuels [1,2]. Pyro-process is also applicable in partitioning and transmutation scenarios where actinides are supposed to be recovered from several types of spent nuclear fuels of various chemical forms, burn-ups and ratios of minor actinides (Np, Am, Cm) [3]. In addition, damaged nuclear fuels can possibly be stabilized using a pyro-process [4].

The primal step of the pyro-process is the electrorefining which is an electrochemical process in molten LiCl–KCl melts to recover actinides by separating them from fission products. The spent metallic fuels are loaded in a metallic basket which is used as the anode. Then, the actinides in the fuels are anodically dissolved in the melts,

$$\mathrm{An} \rightarrow \mathrm{An}^{3+} + 3e^- \quad (\mathrm{An: U,\ Pu,\ minor\ actinides(MA)}) \tag{1}$$

The U^{3+} ion is selectively reduced to U metal on an inert solid cathode,

$$\mathrm{U}^{3+} + 3e^- \rightarrow \mathrm{U} \tag{2}$$

Pu and minor actinides are recovered in a liquid Cd cathode together with U,

$$\left(\mathrm{U}^{3+},\ \mathrm{Pu}^{3+}\ \mathrm{or}\ \mathrm{MA}^{3+}\right) + 3e^- \rightarrow (\mathrm{U,\ Pu\ or\ MA})_{\mathrm{in\ Cd}} \tag{3}$$

Concerning rare earth, alkaline and alkaline earth fission products in the fuels, they are dissolved at the anode and accumulate in the melts in the form of their chlorides. Parts of the rare earth are deposited in the liquid Cd cathode according to their distribution behaviors [5–7]. By keeping the anode potential below the Zr metal dissolution potential, Zr and noble metal fission products remain in the anode basket [8–11]. The basic feasibility of the above mentioned electrorefining has been demonstrated by using simulating materials and non-irradiated fuels [12–14]. However, the knowledge on the electrorefining using irradiated fuels is still limited. Therefore, the authors have started collecting experimental data on the electrorefining of irradiated metallic fuels to design and optimize the process. The anodic behavior of irradiated metallic fuels is discussed in our previous study [11]. The present study is focusing on the actinides recovery from irradiated metallic fuels to investigate the behavior of important elements including minor actinides upon electrorefining.

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http://dx.doi.org/10.1016/j.jnucmat.2015.08.045
0022-3115/

2. Experimental

2.1. *Specification of the irradiated metallic U-19Pu-10Zr-2MA-2RE fuel*

The metallic fuel rod used in the present study was irradiated in the PHENIX reactor in France and the maximum burn-up was 2.5 at % [15–17]. The approximate composition of the fuel rod before the irradiation is as follows (number in wt%); 67-U, 19-Pu, 10-Zr, 2-MA (1.2-Np, 0.6-Am, 0.2-Cm), 2-RE (1.4-Nd, 0.2-Y, 0.2-Ce, 0.2-Gd). Part of the irradiated fuel rod (144 mm–173 mm from the top of the fuel rod) was cut into 5 segments. As summarized in Table 1, the weight and length of each segment are around 2 g and 6 mm, respectively. The outer diameter is 6.55 mm including the cladding. Before the irradiation, there was the gap between the fuel rod and the cladding. Due to the radial swelling of the fuel rod, no gap is observed after the irradiation as seen in the metallographic section shown in Fig. 1. The fuel segments were used in the present study without any pretreatments. The initial composition in the fuel segments was calculated using the ORIGEN code [18].

2.2. *Demonstrations of U recovery on a solid cathode (RUN1) and TRU recovery in a liquid Cd cathode (RUN2)*

All electrorefining tests were performed in a hot cell at JRC-ITU. The atmosphere inside the hot cell is Ar which is purified to keep the concentration of impurities, oxygen and water, below 20 ppm. A selective U metal recovery from fuel segments No. 1, 2 and 3 using a solid cathode was carried out at RUN1. At RUN2, a liquid Cd cathode was used to demonstrate the simultaneous recovery of U, Pu and minor actinides (Np, Am and Cm) from the fuel segments No. 4 and 5. The salts around 112 g after the previous electrorefining test of irradiated metallic fuels [11] was used as the electrolyte at 773 K in the present study. Thus, the eutectic LiCl–KCl melts initially contain actinides and fission products such as lanthanides, alkaline and alkaline earth elements. Fuel segments were loaded in a steel mesh basket (40 mesh, 10 mm outer diameter, 15 mm height) which was used as the anode. A low carbon steel rod (3 mm diameter) was used as solid cathode. The solid cathode was rotated at 50 rpm during the electrolysis. Two solid cathodes were used at RUN1; the first one was replaced with the second one after the passed charge reached 2556 C. A liquid Cd cathode was composed of Cd metal 4.153 g, which was loaded in an alumina crucible (9 mm inner diameter, 18 mm height). The lead of the liquid Cd cathode was a Ta wire (1 mm diameter) which was covered by an alumina insulator not to contact the melts directly. Conventionally, a Ag/AgCl reference electrode is used to investigate the electrochemical behavior of actinides in LiCl–KCl melts. The Ag/AgCl reference electrode consists of a Ag wire immersed in a LiCl–KCl eutectic melts containing 1 wt% AgCl loaded in a Pyrex tube with a thin bottom wall. Unfortunately, it is found that a high radiation from the irradiated materials might shorten the life time of the Ag/AgCl reference electrode significantly [19]. Therefore, a $Ni/NiCl_2$ reference electrode was used in the present study on a trial base. The constitution of the $Ni/NiCl_2$ reference electrode was similar with Ag/AgCl one: Ni lead wire was immersed in LiCl–KCl-5.4wt%$NiCl_2$ melts which was loaded in a mullite tube. The potential of the $Ni/NiCl_2$ electrode was measured against a Ag/AgCl reference electrode by immersing the Ag/AgCl reference electrode shortly in the melts, and it was shown that the $Ni/NiCl_2$ electrode potential (= around 80 mV vs. Ag^+/Ag) was stable until the end of the electrorefining tests in the present study. However, to discuss its stability against high radiation, it is necessary to use the $Ni/NiCl_2$ reference electrode for much longer time. Potential values presented in this paper are calibrated to that of a Ag/AgCl reference electrode (= around −1.2 V vs. Cl_2/Cl^-).

Table 1
Weight and length of the fuel segments. Weights of fuel segments without cladding are calculated values.

RUN	Segment ID	Weight (without cladding)/g	Length/mm
RUN1	No. 1	1.976 (1.565)	5.8
	No. 2	2.061 (1.642)	5.9
	No. 3	2.025 (1.621)	5.7
RUN2	No. 4	2.013 (1.614)	5.6
	No. 5	1.961 (1.562)	5.6

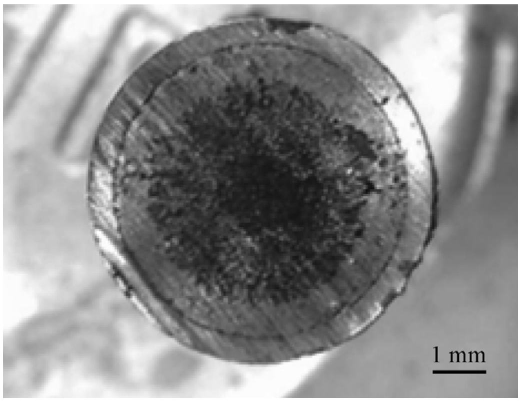

Fig. 1. Photo of the edge phase of irradiated metallic fuel segment No. 2.

2.3. *Analytical procedure*

For the evaluation of the experiment, the following samples were analyzed quantitatively; molten salt electrolytes, precipitates in the salt taken at the bottom of the crucible after RUN1, deposits on the solid cathodes after RUN1, the Cd ingot after RUN2 and fuel segments in the anode basket after RUN1 called as anode residues. The samples were dissolved in acids to be analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) as described in our previous paper [11]: salts, deposits on the solid cathodes and the Cd ingot were dissolved in 1 mol% HNO_3. Anode residues were separated into fuel residues and cladding materials using a dedicated tool. Then, high pressure dissolution was carried out; the fuel residues were dissolved in the mixture of 8 mol% HNO_3 and 0.2 mol% HF in a tight container at around 453 K for 12 h. The precipitates were also dissolved by the high pressure dissolution. To remove the adhered salts on the solid cathode deposits, fuel residues, the Cd ingot and precipitates, they were washed by distilled water before dissolving them in acids.

3. Results and discussion

3.1. *U recovery on solid cathodes at RUN1*

As seen in the polarization curves of the anode basket containing the fuel segments No. 1, 2 and 3 and a Zr plate in the melts (Fig. 2), the actinide dissolution (reaction 1) proceeds at more positive potential than −1.35 V (vs. Ag^+/Ag) together with the dissolution of rare earths, alkalines and alkaline earths, and Zr is dissolved at more positive potential than −1.05 V (reaction 4),

$$Zr \rightarrow Zr^{n+} + ne^- \quad (n = 2 \text{ or } 4) \tag{4}$$

Based on the polarization curves, the potential of the anode at