Advanced Wet-Reprocessing System: Separation Experiments on Real Spent LWR Fuel Solutions

P. Goethals, L. Vos, J. Braet, A. Bruggeman, M. Gysemans, L. Vandevelde, L. Sannen,
H. Hoshi* and Y. Wei*
SCK•CEN, Boeretang 200, 2400 Mol, Belgium
**Institute for Research and Innovation (IRI), 1201 Takada, Kashiwa,277-0861 Japan.*

Abstract

In collaboration with the Japanese Institute of Research and Innovation (IRI), a project was set up to evaluate an aqueous reprocessing system which consists of anion exchange as main separation method, electrolytic reduction for reducing U^{6+} to U^{4+} and extraction chromatography for minor actinides (MA) partitioning. Hot tests were carried out for the main flow sheet (U and Pu recovery) using a concentrated nitric acid solution of a spent LWR-fuel. Firstly, a separation experiment was carried out using a column packed with AR-01 anion exchanger, and the separation behavior of the most important elements was examined. Secondly, electrolytic reduction of the U^{6+} effluent from the 1st column was performed using a novel flow type electrolysis cell. Subsequently, the reduced U solution was applied to the 2nd AR-01 column to separate the U^{4+} from remained fission products (FP). The test learned that Pu^{4+} and Np^{4+} recovered successfully on the 1ste column. In the electro-reduction cell, U^{6+}, $Np^{5+,6+}$ and a trace amounts of Pu^{6+} were reduced to U^{4+}, Np^{4+} and Pu^{4+}, respectively. On the 2nd column, U^{4+} Np^{4+} and Pu^{4+} were completely separated from FP. Finally, MA partitioning using extraction chromatography on a CMPO/SiO_2 column was evaluated preliminary.

These results confirmed that the proposed U and Pu recovery process is feasible and can be a worthy alternative for the Purex process.

Keywords: ***reprocessing, aqueous process, anion exchange, electro-reduction, spent LWR-fuel.***

1. Introduction

Essential for commercial reprocessing plants of nuclear fuel is the generation of as less as possible secondary radioactive waste (technical set up, solvent,…) due to the proposed technique. Although the Purex process has been developed and applied to commercial reprocessing plants for about 50 years, there are also some significant drawbacks such as the generation of a great amount of waste and the utilization of large scale extraction equipment.

In concentrated nitric acid solution, U, Np, and Pu form anionic nitrato complexes and exhibit distinct adsorption on anionic exchanger while the fission products (FP) and the minor actinides (MA) Am and Cm mostly exist as cations and show no or weak adsorption. Based on this knowledge, U, Np and Pu can be separated principally from FP and MA in nitric acid solution of spent nuclear fuels by anion exchange chromatography. Compared to the Purex process, the ion exchange process should have the following advantages: minimal organic solvent utilization, compact equip-ment, simultaneous separation of multi-element components.

The Japanese IRI is developing an advanced aqueous reprocessing process which consists of anion exchange as main separation technique, electro-reduction of U^{6+} to U^{4+} and extraction chromatography for MA partitioning[1,2]. The separations were based on a new type of anion exchanger, AR-01[3,4] and several novel extraction resins, containing a chelator such as CMPO[5].

These groups are immobilized on 50 μm diameter silica particles. Compared to the conventional polymeric matrix resins, these new type of resins have rapid adsorption-elution characteristics and high stability in concentrated nitric acid medium.

The experiments, carried out at SCK•CEN, were performed within the framework of a research contract with IRI. In this work, hot tests were carried out for the main flow sheet (U and Pu recovery) using a solution of spent commercial LWR-fuel. Firstly, a separation experiment was conducted using a column packed with AR-01 anion exchanger and the separation behavior of the most important elements was examined.

Then, electrolytic reduction for the U^{6+} effluent from the 1st column was performed using a novel flow type electrolytic cell. Subsequently, the reduced U solution was applied to the 2nd AR-01 column to separate the U^{4+} quantitatively from the FP.

Finally, an attempt was carried out to evaluate the separation between the FP and the MA & Ln on a 3rd column.

2. Aqueous Reprocessing System of IRI

Fig. 1 shows the schematic flow sheet of the by IRI proposed aqueous reprocessing system. This system consists of two anion exchange separation processes, one electrolytic reduction process and two extraction chromatography processes. The Pu in the spent fuel solution containing 6M HNO_3 is firstly adjusted to Pu^{4+} by the intro-duction of $NaNO_2$. The resulting solution is applied to the main separation column (1st column) packed with AR-01 anion exchanger. The elements, contained in the spent fuel solution, are separated into the following five groups:

(1): FP, Ln (lanthanides) and MA (Am and Cm);

(2): U, $Np^{5+,6+}$ and FP;

(3): Pu and Np^{4+};

(4): Pd and

(5): Tc.

The separation is based on their different adsorption-elution kinetics.

The purpose of the electrolytic reduction process is to reduce U^{6+} and $Np^{5+,6+}$ to U^{4+} and Np^{4+}, respectively. Subsequently, the reduced solution is fed to the 2nd column also packed with AR-01 to separate the U^{4+} and Np^{4+} from the remained FP due to the great difference in their adsorbability on the resin. In order to isolate the trivalent MA, the effluent containing FP and MA from the anion exchange columns is supplied to the extraction chromatographic column. This column is packed with CMPO/SiO_2, a bi functional organophosphorus impregnated resin, allowing to separate the elements into three groups, i.e. FP, Ln-MA and Zr-Mo[5].

3. Experimental

3.1. Main Process in the hot cell.

For the hot separation experiments, AR-01, an anion exchanger containing 4-(1-methylbenzimidazol-2-yl)phenyl (weak-base group) and 4-(1,3-methylbenzi- midazolium-2-yl)phenyl (strong-base group) as functional groups, was used. The total exchange capacity is 3.4 meq/g-resin and the strong-base capacity is 2.0 meq/g-resin. Details of the property and preparation method of AR-01 were given previously.

A piece of spent fuel rod discharged from a commercial LWR was dissolved in 8M HNO_3 solution by refluxing for 8 h. After filtration, the resulting solution was adjusted to approximately 0.7 M U^{6+} in 6M HNO_3. A small amount of $NaNO_2$ (to 0.05 M) was added to the solution to hold the Pu in tetravalent state (Pu^{4+}). The analytical composition of the sample solution is summarized in Table 1. The separation experiments were carried out using Pyrex-glass columns (20 mm $Ø_{int}$, 100 cm length). The column was packed with the AR-01 anion exchanger to about 90 cm (resin height) corresponding to a bed volume (BV) of 283 ml, and installed in a hot cell. Prior to the chromatographic operation, the anion exchanger was conditioned by passing 6 M HNO_3 solution (about 5 BV) through the column to convert the exchange sites to the nitrate form. About 40 ml of the sample solution was pumped to the column at a constant flow rate of 20 ml/min. Then eluents and washing solutions were supplied to the column at the same flow rate, successively. Effluent fractions of 10 ml from the column were collected and in each fraction the concentration of the elements of interest were measured by ICP-MS, α- or γ-spectrometry, after appropriate dilution.

Electrolytic reduction experiments were carried out using a special flow type electrolysis cell. The cathode of glassy carbon fibers filled in a cylindrical column of Vycor glass (a porous silica glass) is the working electrode. The U^{6+} - FP eluent obtained from the 1st column was introduced into the cathode compartment at a constant flow rate of 2 ml/min. The anode compartment was filled with 6M HNO_3 solution. As a holding reducing agent of U^{4+}, 0.2 M N_2H_4 was added to the cathodic solution. The electrolysis cell was connected to a potentio/galvano-static D.C. power supply and the electrolytic reduction was conducted at a constant potential of -300mV vs. Ag/AgCl. The outlet solution of the electrolysis cell was then applied to the 2nd AR-01 column for the separation of U^{4+} from FP. At the outlet of the electrolysis cell, the spectrofotometric detection cell was placed to controll the efficienty of the reduction reaction (convertion U^{6+} to U^{4+}).

The polled fractions containing the U^{4+} & FP were brouhgt on top of the 2nd column and the fractions of interest were separated.

The fractions of the 1st column, containing the highest fractions of the FP & MA and Ln were adsorbed on a 3rd column, filled with CMPO-SiO_2 resin, eluted to separate the FP. CMPO can efficiently extract trivalent actinides and lanthanides from aquous solutions containing concentrated nitric acid.

3.2 Results and Discussion

Figure 2. shows the individual elution profiles (1st column) of the hot separation experiment for the spent fuel solution. Looking at the elution curves, one notices that immediately after the front (dead volume), most of the M^{a+} ions are concentrated in the fraction range before the U and Pu peaks appears. The elements Am, Eu, Nd, Pr, Cs, Rh, and Y leave the column first and are eluted in a narrow band. For these elements, at least 97 % of the mass amount was recuperated in the effluent. All the U was adsorbed on the anion exchange resin and eluted off with 1M HNO_3 solutions. The total amount of effluent, containing the quantitatively recuperated U, was about 180 ml. Most of the above FP and MA elements were separated from U. However, a fraction of particularly Ru, Zr, Nb and several Ln (weakly adsorptive FP) were adsorbed and mixed with the U eluent. Ru presented a complicate elution behavior and a small portion finally appeared in the final eluate (0.1M and 9M HNO_3). Pu^{4+} was quantitatively adsorbed on the stationary phase and eluted effectively by 1 M HCOOH as eluent, showing a sharp elution peak achieving a successful

separation of Pu^{4+} from U and FP. A few % of Pu, which is considered to be Pu^{6+}, was mixed in the U eluate. Np showed a complicated elution behavior probably due to its different oxidation states. Np^{5+} and Np^{6+} were mostly mixed with the U fraction, while Np^{4+} (88% of the total Np) was found in the Pu eluate fraction. Pd and Tc were not detected in all the effluents, although they were expected to be eluted by 50 ml of 0.5 M EDA in 1M HNO_3 and 9M HNO_3 respectively. For Pd, as shown in Fig 1, originaly IRI proposed 1M $CS(HN_2)_2$ as eluate. The strong adsorption of those elements on the stationary phase can be considered as a quantitatively separation.

The incomplete separation between U and the FP elements on the 1st separation column is considered to be due to the relatively low adsorbability of U^{6+} in HNO_3 solution onto the anion exchanger. To enhance the separation factor between U and FP, the electrolytic reduction of uranyl (UO_2^{2+}) to uranous ion (U^{4+}) was investigated. The U^{6+}-FP eluate from the 1st column was introduced into the electrolysis cell and the electro reduction experiment was carried out at a constant potential of -300 mV vs. Ag/AgCl. The main goal of the electrolytic reduction is the transformation of U^{6+} to U^{4+}, which is much stronger adsorbed onto the AR-01 resin.

A separation experiment for the electrolytic reduced U^{4+}-FP eluate solution was conducted using the 2nd AR-01 packed column and the experimental results are shown in Figure 3. As seen, all the FP including Ru showed almost no adsorption and eluted from the column firstly. U^{4+} exhibited one sharp elution peak indicating that the electrolytic reduction was complete. It can be seen that the Np and Pu were eluted together with the U^{4+}, indicating that in the electro reduction the remained $Np^{5+,6+}$ and Pu^{6+} were reduced to Np^{4+} and Pu^{4+}, respectively and completely separated from all of the FP elements.

The pooled fractions of column 1 and 2 containing the FP, Ln and MA were injected on a glass column (50 cm length, 1 cm $Ø_{int}$) filled with CMPO/SiO_2-P adsorbent (packing height: 48 cm) to separate the MA and Ln from the FP. Three different groups of elements can be differentiated in the elution profile (Fig 5). Immediately after the dead volume, elements like Cs, Rh, and partly Ru were concentrated. The recuperation was quantitative, except for Ru (yield ~ 60 %).

In the middle group, the MA and Ln (Cm, Am, Nd, Pr, Ce, and La) eluted with diluted HNO_3 , followed by recuperation of Zr and Mo with diluted $H_2C_2O_4$.

For the behavior of Y (mass balance to low) and Sr (mass balance to high), no reasonable explanation could be found.

The fourth step in the IRI proposed separation has not yet been evaluated.

4. Conclusions

A new process has been investigated to develop an advanced aqueous reprocessing system using a minimal organic solvent and compact equipment for separating U, Pu and long-lived minor actinides from spent nuclear fuels. It consists of anion exchange as main separation method, electrolytic reduction for reducing U^{6+} to U^{4+} and extraction chromatography for MA partitioning. Hot tests were carried out for the main flow sheet (U and Pu recovery and for the group separation of lanthanides and trivalent actinides) using of a spent LWR-fuel solution.

The separation experiment for the spent fuel solution using AR-01 anion-exchanger column demonstrated that most of the FP and MA elements could be separated from U^{6+} in the first step (1st column). Some FP showed weak adsorption and contaminated the U eluate. Pu^{4+} was

eluted effectively by dilute HCOOH and successfully separated from U and FP. Np showed a complicated elution behavior due to its different oxidation states.

The electrolytic reduction test of the U^{6+}-FP eluate from the 1st column was successfully performed using an electrolysis cell with carbon fibers as working electrode and Vycor glass as separator. In the electrolysis cell, U^{6+}, $Np^{5+,6+}$ and Pu^{6+} were reduced to U^{4+}, Np^{4+}, and Pu^{4+}, respectively and the U^{4+}-Np^{4+}-Pu^{4+} in the U-FP eluate was completely separated from all of the FP elements during the 2nd column separation.

For the 3rd column, additional experiments are still necessary to optimize the separation.

Based on the experiments, we may conclude that still a lot of details have to be controlled. From the practical point of view, some parts of the technical set up must be adapted to allow more gentle manipulations in the hot cell.

A better pre-adaptation of the valancies of Pu and Np would be wishfull. The dynamic dead volume of the electrolysis cell is still a problem.

The mass balance for some elements like Sr must be checked in detail. Pd and Tc presented significantly strong adsorption and can be considered as quantitatively accumulated on the stationary phase.

New experiments are planned to resolve those problems.

Table 1. : Analytical composition of the feed solution

Element	µg/g V0	mM	Method
U	120900	720	ICP-MS
U-236	884	5.30	ICP-MS
U-235	762	4.60	ICP-MS
Pu-240	295	1.74	ICP-MS
Pu-239	427	2.53	ICP-MS
Cm-244	4.8	0.028	ICP-MS, Alfa-spec
Am-243	17.6	0.103	ICP-MS
Am-241	60.6	0.355	Gamma-spec
Np-237	78.6	0.470	ICP-MS
Gd-157	3.34	0.030	ICP-MS
Eu-154	1.76	0.016	Gamma-spec
Eu-153	23.1	0.21	ICP-MS
Sm-149	0.34	0.0033	ICP-MS
Nd-146	149	1.45	ICP-MS
Nd-145	135	1.32	ICP-MS
Pr-141	241	2.43	ICP-MS

Element	µg/g V0	mM	Method
Ce-140	263	2.66	ICP-MS
La-139	271	2.77	ICP-MS
Cs-137	201	2.08	Gamma-spec
Cs-134	1.09	0.012	Gamma-spec
Cs-133	234	2.49	ICP-MS
Ag-109	13.4	0.174	ICP-MS
Pd-105	44.6	0.602	ICP-MS
Rh-103	51.6	0.710	ICP-MS
Ru-101	76.5	1.07	ICP-MS
Tc-99	137	1.96	ICP-MS
Mo-98	125	1.81	ICP-MS
Mo-95	119	1.78	ICP-MS
Nb-93	176	2.68	ICP-MS
Zr-91	125	1.95	ICP-MS
Y-89	106	1.69	ICP-MS
Sr-88	111	1.79	ICP-MS

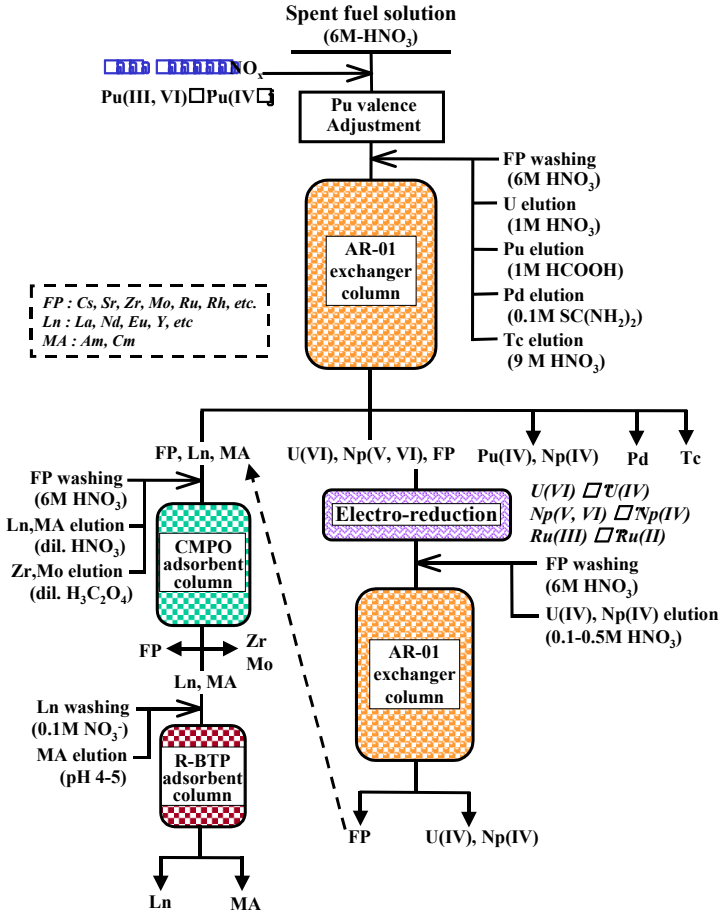

Fig. 1. The original IRI's aqueous reprocessing procedure for spent nuclear fuels.

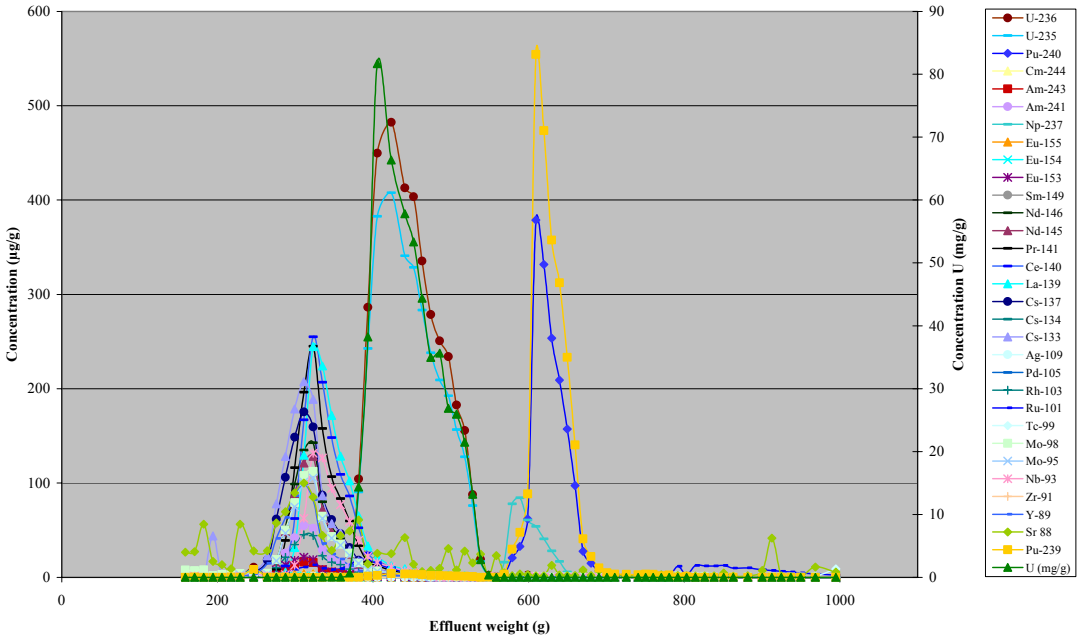

Fig. 2. Elution curves on AR-01 for spent LRW-fuel solution: column 1

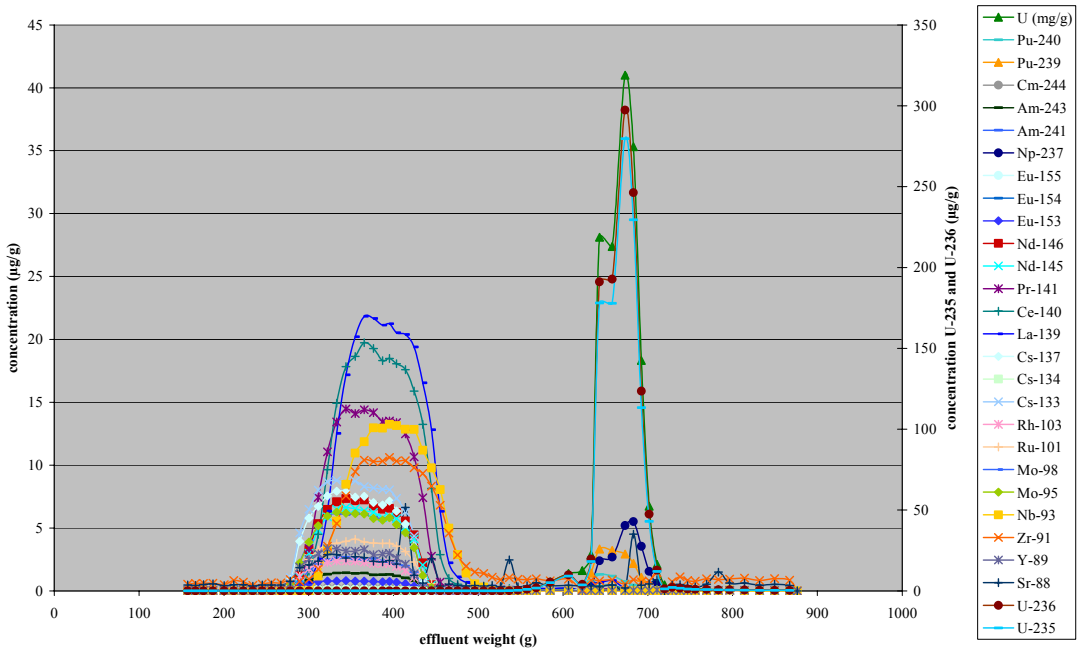

Fig. 3. Elution curves on AR-01 for spent LRW-fuel solution: column 2

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