# Development of the extraction chromatography system for separation of americium and curium

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#### Abstract

Japan Atomic Energy Agency is conducting research and development on the extraction chromatography system for separation of americium and curium from a highly active raffinate generated in fast breeder reactor fuel reprocessing. Solvent extraction has been considered as the technology of main stream for that purpose and intensively investigated by researchers world wide. On the other hand, extraction chromatography will provide some advantages, such as no need of a diluent that means free from phase compatibility issue concerning highly functionalised extractants and a higher temperature limit concerning fire hazard, and a simple and small column equipment that processes a highly active solution, over solvent extraction. In order to evaluate the feasibility of the extraction chromatography for the reprocessing, several drawbacks/difficulties were investigated including a large column packed with an organic resin that would cause a deformed stationary phase by swelling and shrinking of resin itself, safety for fire and explosion hazard caused by decay heat and hydrogen radiolytically generated, and also a remote handling of adsorbent particles.

The adsorbents consist of the porous silica support coated with styrene-divinylbenzene polymer and an extractant, and have a uniform diameter. Concerning separation of Am and Cm, several extractants were studied to choose the combination of TODGA and a BTP derivative for trivalent actinides recovery and their separation from lanthanides, respectively, as the most promising at present. The extractant kept in the support will be degraded by acid and radiation as well as be lost into effluents due to its solubility in aqueous solutions. These factors were experimentally studied to estimate the life of adsorbents as a limit for replacing it. It was found that the adsorbents are suitable to obtain a stationary phase that allows a uniform flow essential to a good separation. The adsorbent is packed or discharged from the column by transporting it as slurry and the way was found to be feasible. Safety for fire and explosion is assured by transporting decay heat and hydrogen with eluents that results in maintaining the operating temperature and also a low concentration of hydrogen in the column. Some foreign particles that are often generated from fission products in the upper stream may plug the column and/or pipes to stop the flow of feeds and eluents. The behaviour of plugging the column was examined to provide a method to keep a steady operation.

# Introduction

Separation technology for Am and Cm, An(III), from a highly active waste solution has been a major concern on the nuclear chemical engineering. For that purpose, solvent extraction is widely studied and many kinds of extractant were developed. Chromatography provides potential performance thanks to numerous theoretical plates, however, its nuclear application other than analysis was limited, for example, Am/Cm separation by ion exchange [1] and by extraction with Am oxidation [2]. The chromatography technique is useful for difficult separation, therefore, Japan Atomic Energy Agency is developing the Am and Cm separation system for a future reprocessing plant.

A diluent used in solvent extraction is not needed for chromatography. This will contribute to ease the limiting temperature concerning safety operation and to provide an opportunity to employ a highly functionalised extractant without phase compatibility problem. A column for chromatography is structurally simple when compared with extractors for solvent extraction. On the other hand, chromatography process is operated in batch-wise different from that of solvent extraction. The operating procedure must be established with consideration on remote operation and periodical exchange of adsorbent that is degraded along with its use. Decay heat and hydrogen generated from radioactivities in the column are not diffused by dilution. This feature is different from solvent extraction and a counter-measure should be exploited. In order to establish an engineering system of extraction chromatography, its process and equipment system were investigated.

# System outline

The extraction chromatography system is supposed to be incorporated into a future FBR fuel reprocessing plant. The chemical process is based on the NEXT process [3]. A spent fuel is dissolved and a part of uranium is separated as uranium nitrate hexahydrate (UNH) by the crystallisation process. The resulted mother solution is fed to the solvent extraction of one cycle and a U-Np-Pu mixed product solution is recovered. The raffinate from the solvent extraction is treated by the extraction chromatography.

The adsorbent is a particle of 50  $\mu$ m in diameter and a composite material [4]. Different from a conventional organic resin, its matrix is porous silica and is coated with styrene-divinylbenzene polymer, then, impregnated with an extractant. Many extractants for solvent extraction are utilised. The flow sheet for solvent extraction is a basis for chromatographic or adsorption-elution cycle operation. Am and Cm should be separated from a concentrated nitric acid solution and be decontaminated from fission products (FP), including lanthanides (Ln), which chemically behave similar to actinides(III).

The throughput of the plant is assumed to be 200 tHM/y for design study [3], then, a column system of engineering scale for 50 tHM/y was aimed at for the study. The column system will treat a raffinate of several m<sup>3</sup>. On the assumption that operation is conducted for 10 cycles/d in separating An(III) and Ln from the raffinate, the size of the column was 48 cm in ID and 65 cm in height.

#### Adsorbent development

#### Flow sheet

Among various extractants developed for solvent extraction, five compounds, namely CMPO, TODGA, HDEHP, R-BTP and TRPEN were chosen to evaluate them. CMPO [5] and TODGA [6] are used for An(III)-Ln recovery, and, HDEHP [7], R-BTP [8] and TRPEN [9] for An(III)/Ln separation. 2,6-bis(5,6-di-isohexyl-1,2,4-triazine-3-yl)pyridine and N,N,N',N'- tetrakis((5-octyloxypyridin-2-yl)methyl)ethylenediamine are used for R-BTP and TRPEN, respectively.

Feeding the raffinate without adjustment of acidity, such as denitration or dilution, is preferred. The nitric acid concentration of the raffinate from the NEXT process is higher than the PUREX process because it is from the mother solution of UNH crystallisation. CMPO and TODGA adsorbents can adsorb Am and Cm from such a solution. Some FP are adsorbed in some extent, thus it is required to wash them. Zr and Mo should be considered for CMPO treatment, and, Pd and Sr are for TODGA treatment. In order to decontaminate those elements, a chelating reagent is added to the feed to mask them, otherwise those are washed after adsorption.

The intermediate product of An(III) and Ln is a nitric acid solution, and is provided for the second cycle with HDEHP, R-BTP or TRPEN to separate An(III) from Ln. In the case of HDEHP adsorbent, DTPA which preferentially co-ordinate with An(III) is used. R-BTP and TRPEN have moieties that are selective to An(III) and adsorb them as nitrate complex.

Column separation and batch-wise adsorption experiments using Am and Cm at a tracer concentration were carried out to compare recovery of Am-Cm and FP decontamination [10,11]. Consequently the combination of TODGA and R-BTP adsorbent was evaluated as the primary candidate. Figure 1 shows the flow sheet of the result. It is expected to decontaminate FP including Cs, Sr, Zr, Mo, Pd and Ln such as Nd and Eu, and to separate Am and Cm at a high recovery.

# Figure 1: The combined flow sheet for Am and Cm separation using TODGA and R-BTP adsorbent



First cycle for An(III)–Ln(III) recovery

\*1 Volume is dependent on composition of the feed. Operation of 10 cycle/d was assumed.

# Durability

The extractant of adsorbent is dissolved into the effluent since it is not chemically bonded to the support. The extent is dependent on solubility of the extractant into an aqueous solution. The extractant concentration in the effluent is constant against effluent volume, thus, the rate of losing extractant can be predicted. Exposure to nitric acid and/or radiation induces degradation of the adsorbents besides dissolution into effluents and adsorption performance including distribution coefficient, capacity, kinetics and holding extractant. Therefore, it needs periodical

exchange of adsorbents. Change of adsorption capacity after exposure to nitric acid for several ten days or to gamma radiation was investigated. Figure 2 shows the capacity decrease of TODGA adsorbent after <sup>60</sup>Co gamma-ray irradiation in a nitric acid solution. Supposing the limited capacity for use as 80% of the initial value, the expected duration was estimated at about 14 and 7 d for TODGA and R-BTP adsorbent, respectively.

TODGA and R-BTP adsorbent were provided for TG/DTA. Their mass was almost constant under 100°C, then, they are stable under operating condition since operation is conducted under the boiling point of water. Beyond 100°C, an exothermic peak was observed around 220 and 140°C for TODGA and R-BTP adsorbent, respectively, and mass decreases with temperature. This tendency was also observed for irradiated samples, while the exothermic peak was rather diminished.



# Figure 2: Decrease of adsorption capacity of TODGA adsorbent for Nd after gamma-ray irradiation in the nitric acid solution

Solution : 4.76 M HNO\_-Eu, Temp. : 25°C, Contact time : 3 h

#### Treatment after use

The used adsorbent should be properly regenerated or treated as waste for disposal. After the used extractant is separated from the support by passing dichloromethane or acetone through the column, a genuine extractant can be retained again. The regenerated adsorbents of CMPO, TODGA, HDEHP and TRPEN reproduced their adsorption capacity, whereas for R-BTP adsorbent, an improved procedure is needed to reproduce the initial capacity. Figure 3 shows the capacity of the regenerated TODGA adsorbent. On disposal of the used support, heating the support decomposes the organic contained and provides silica particle that is stable and suitable to be disposed of.

In solvent extraction extractant is dissolved into an aqueous solution, then diluent washing is employed to reduce the concentration and to assure safety in concentrating wastes. Similarly, extraction chromatography requires treatment of eluates. Solid adsorbent does not have ability to capture dissolved extractant and their degraded products, diluent washing using hydrocarbon, such as n-dodecane, is required.

#### Figure 3: Comparison of isotherms of Nd for genuine and regenerated TODGA adsorbent

Contact time for adsorption = 180 min, temperature = 40°C, solution = 4.8 M HNO<sub>3</sub> containing Nd



#### Column system development

#### Packing adsorbent

It is important to obtain a good bed in order to attain a good separation. Remote operation of exchange adsorption including packing and discharging is essential because the used adsorbents is to be replaced periodically. Slurry transport was investigated on the method to exchange adsorbents without connecting and detaching the column. A column connected with double tube for slurry and solutions were fabricated for a testing system and a proper procedure and conditions of exchange were obtained. Figure 4 shows appearance of the column system for engineering scale testing. Pressure drop of the column increases while feeding the adsorbent slurry. Packing adsorbent is operated with monitoring pressure drop. After detecting the value of pressure, the bed is consolidated, then, another batch of adsorbent is filled with the vacancy on the top of the column. The performance of the bed was evaluated by calculating apparent HETP for elution curve of ion which is scarcely adsorbed. THe HETP for the column of 48 cm ID and 65 cm H is almost identical to that of 1 cm ID column, and is superior to the 20 cm column with connection of a different style.

# **Hydraulics**

Macroscopic hydraulics inside column was evaluated with HETP besides flow of mobile phase was examined to confirm its uniformity. Several sensors for electroconductivity were inserted to the column and tracer of electrolyte was fed. The axial flow rate obtained was almost constant for radial position. Near the wall, thin region has different flow rate.

Temperature control is also important to operate for a steady separation. Decay heat of radioactivities must be discharged from the column. Thermal conductivity of the stationary phase apparently depends on rate of mobile phase, and increases with flow rate [12]. On the course of operation for adsorption-elution, decay heat is transported via the mobile phase to the outside column. Tests using the column of 20 or 48 cm ID with electric heaters and thermocouples were revealed that the bed is maintained at the desired temperature. A jacket of column is needed to hold temperature near the column wall at constant.



Figure 4: Testing system of engineering scale column

The column was on the way of move assuming off-site inspection/maintenance

When a halt of mobile phase, radionuclides are retained in the column regardless of distribution coefficient, and forms a band of decay heat. Decay heat is accumulated around the band. In the test that used the column with electric heaters, temperature around the bar-shaped heater was locally raised due to a small thermal conductivity. From these data, a column model was devoted to calculation of temperature resulting in increase of about 20°C after 60 min halt of mobile phase as shown in Figure 5.



Figure 5: Increase of temperature in the column after the mobile phase stopped (calculated)

# Repeated operation

Chromatography attains a desired throughput by repeating cycles of adsorption-elution. A test of 10 times repeating was carried out with the column of 20 cm ID that was packed with CMPO or HDEHP adsorbent [13]. For the CMPO cycle Nd behaves with Am-Cm and as shown in Figure 6 the elution curves of Nd for 10 cycles are almost identical and operation with constant conditions is expected. On the other hand, elution curves for HDEHP column were deteriorated to exhibit low and wide peak as operation was repeated. It is essential to choose an extractant which solubility into aqueous solutions is so small that a large number of operation cycles can be achieved.



Figure 6: Elution curves of Nd those were obtained in the repeated operation of CMPO cycle using a simulated feed solution

### Hydrogen generation

In the solvent extraction system, hydrogen which is generated by radiolysis and travelled to gas phase is diluted with air and treated as a gaseous waste for discharge. Since hydrogen in a packed column cannot be diluted with air, another method must be employed. The G value for hydrogen was experimentally obtained by irradiating CMPO adsorbent statically in water with <sup>60</sup>Co gamma-ray. Figure 7 shows that the G value is dependent on the amount of adsorbent and water, and synergetic effect is observed when small amount of adsorbent is present. Increasing adsorbent amount induces decrease of G value. It is suggested that some precursors are consumed and hydrogen is physically trapped in adsorbent particles. G values for  $O_2$  and  $N_2$  from water is smaller that of  $H_2$ , thus, in the view of assuring safety it should be assumed that the concentration of  $H_2$  is in the range of explosion and the counter-measure should be considered. Nitrate ion reduces G value of  $H_2$  and it is applied for the system of adsorbent-water.

Figure 7: G value of H<sub>2</sub> from the mixture of water and CMPO adsorbent at different amount



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The G value for  $H_2$  is affected by the kind of extractant, although the difference is diminished by stirring water and adsorbent while irradiation. This suggests that a precursor interacts with extractant. According to the G values obtained, it was estimated that amount of  $H_2$  generated is not significant and hydrogen is absorbed in the mobile phase and discharged without making a bubble in the column.



Figure 8: Transport of hydrogen accumulated after the flow of the mobile phase was resumed

When the mobile phase is stopped, hydrogen is accumulated abound the band of radioactivities and, in the case of exceeding its solubility, forms gaseous phase. By resuming flow, transport of hydrogen to downstream is recovered to the concentration of the steady state. Figure 8 shows the calculation result of hydrogen transport after halt and resume of mobile phase. Since a bubble is difficult to move it by flow of mobile phase, in the case of fail to resume, opening column should be considered.

# Plugging

Stopped mobile phase induces accumulation of heat and hydrogen, therefore, it should be avoided. The major cause is solid particles contained in the feed solution. Although the feed is a raffinate processed by solvent extraction and solid particles is well removed, precipitation of FP such as zirconium molybdate hydrate would occur when the feed is retained for long than scheduled. Besides clarifying the feed, affect from introducing foreign solid should be investigated.

After feeding a water containing stainless steel particle as a stand-in to the column, it was observed that particles was accumulated on the filter of inlet and on the adsorbent bed and most of the bed was intact. The stationary phase acts like a filter and prevents its intrusion to the bed. Figure 9 shows that the filter and the bed at its top caught stainless steel particles. A simulated feed solution was heated to generate solid particles of fission product elements, and fed to the column of 1 cm ID. The eluate was again fed, then pressure drop was not increased and the resulted eluate did not contain solid. Based on the findings described above, a procedure to prevent a column plugging and to resume from the status was deduced as follows:

- periodically exchanging filter and adsorbent for prevention;
- back washing filter, washing radionuclides retained, exchanging adsorbent, disclosing column for resuming.

Column system test was conducted and confirmed that the procedure is feasible.



Figure 9: Accumulation of stainless steel particle at the top of the column of 1 cm ID after feeding water containing the particle

# Conclusion

Engineering of processing highly active liquid by extraction chromatography was investigated. Among extractants published, TODGA and R-BTP were chosen as the most promising at present for chromatography use. The adsorbent requires periodical exchange and is dedicated to recycle use. Mobile phase uniformly flows in the engineering column. Exchanging the adsorbent is based on transport of its slurry. Decay heat of radionuclides is discharged outside via mobile phase, and temperature inside the column is kept at constant. Hydrogen generated from radiolysis is also released in a similar manner. Plugging column must be avoided in order to prevent accumulation of heat and hydrogen. If it plugs, the column system safety for fire hazard is kept by the procedure proposed which includes back washing solids accumulated on the filter and washing radionuclides retained in the column. Based on the results, potential of extraction chromatography for nuclear engineering was confirmed.

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