DEVELOPMENT OF THE FOUR GROUP PARTITIONING PROCESS AT JAERI

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Abstract

At the Japan Atomic Energy Research Institute (JAERI), a partitioning process has been developed to separate elements in a high-level liquid waste (HLLW) into four groups; transuranium elements (TRU), Tc-platinum group metals (PGM), Sr-Cs and the others. The present paper deals with objects of the partitioning, main characteristics of four group partitioning process, generation of solid materials after the partitioning and its positive effects on the management of high-level waste (HLW), and recent study on the four group partitioning process.

Objectives

The first objective of the partitioning is the reduction of long-term radiotoxicity of HLW to be disposed of into deep underground. The second one is the volume reduction of HLW by separate treatment of heat generating nuclides such as ^{90}Sr and ^{137}Cs. The third objective is the development of advanced waste management methods because the other groups containing about 70wt% of fission and corrosion products in HLLW might be disposed of directly without long-term cooling. The fourth objective is resourcefication of HLW by promoting beneficial uses of radioisotopes and noble metals in HLLW.

Basic way of thinking for the construction of the partitioning process

For the satisfaction of above objects the four group partitioning process has been developed at JAERI since 1985.

Following items have been considered for the construction of the partitioning process.

1. First priority separation of the TRU group because of its long-term and dominant radiotoxicity and suppressing its dispersion into other groups.

2. Waste minimisation, especially for the separation of the Tc-PGM and the Sr-Cs groups.

3. Use of reagents with high radiation durability and chemical stability.

4. No possibility of firing and explosion of the reagent and its degradation products. No use of reagent with phenyl group which has a possibility of forming explosive compounds such as nitrobenzene as its degradation product.

5. Compatibility to a fuel reprocessing plant. No use of reagent such as hydrochloric acid and organic reagent with chlorine which causes corrosion of stainless steel. Increasing a possibility of using a waste treatment facility in the fuel reprocessing plant for the treatment of the wastes generated from partitioning.
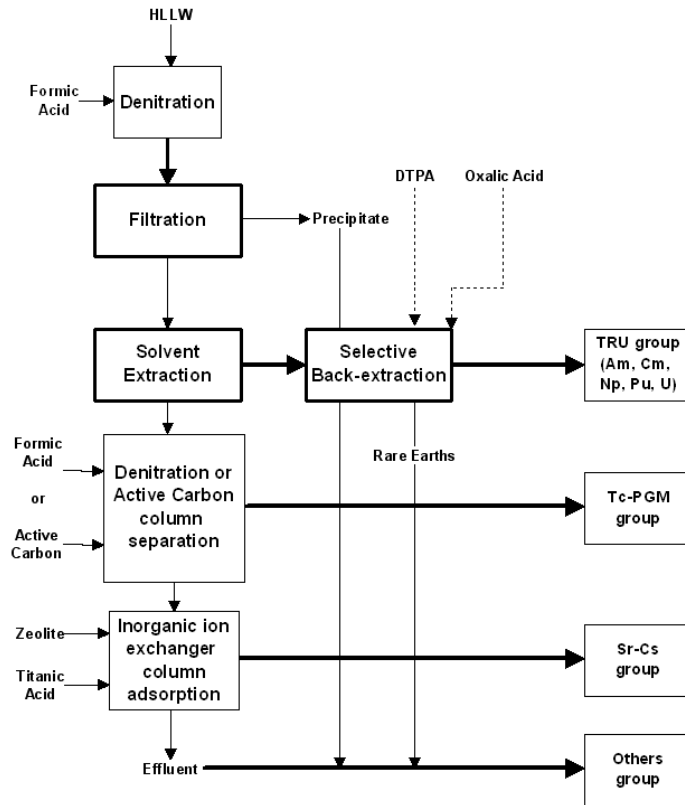
Four group partitioning process

Through the fundamental study, the four group partitioning process has been constructed as shown in Figures 1 and 2. Main characteristics of the four group partitioning process are as follows:

1. All TRU elements including pentavalent Np are extracted with DIDPA after the denitration of HLLW, reducing the nitric acid concentration from 2 M to 0.5 M.

2. Tc and PGM are separated by precipitation through denitration or by adsorption with an active carbon.

3. Sr and Cs are separated by adsorption with inorganic ion exchangers, titanic acid and zeolite, respectively.

4. The TRU elements extracted in the DIDPA solvent are sequentially back-extracted with 4 M nitric acid for Am, Cm and lanthanides, 0.8 M oxalic acid solution for Np and Pu, and 1.5M sodium carbonate solution for U.

5. Back-extracted Am, Cm and lanthanides are extracted again with DIDPA, and then Am and Cm are preferentially back-extracted with 0.05 M dietylentriaminepentaacetic acid (DTPA) solution, leaving lanthanides in the DIDPA solvent.

Figure 1. **Four group partitioning process**

Effectiveness of the partitioning process

Separation efficiency obtained experimentally with mainly simulated HLLW and the estimated recovery through whole partitioning process are shown in Table 1 along with the target recovery, where the separation efficiency of the element means the recovery in the first chemical step for its separation and the target recovery of TRU elements was determined to make the potential radiotoxicity of a vitrified HLW after storage for 1000 years comparable to that for naturally occurring mineral containing 3wt% of U.

The separation efficiency and the estimated recovery of TRU elements are quite high and almost satisfied with the target recovery. The recoveries of Tc and PGM are around 90 to 95% which is lower than the target recovery. This lower recovery is not so important because of their little contribution to the potential radiotoxicity of HLW.

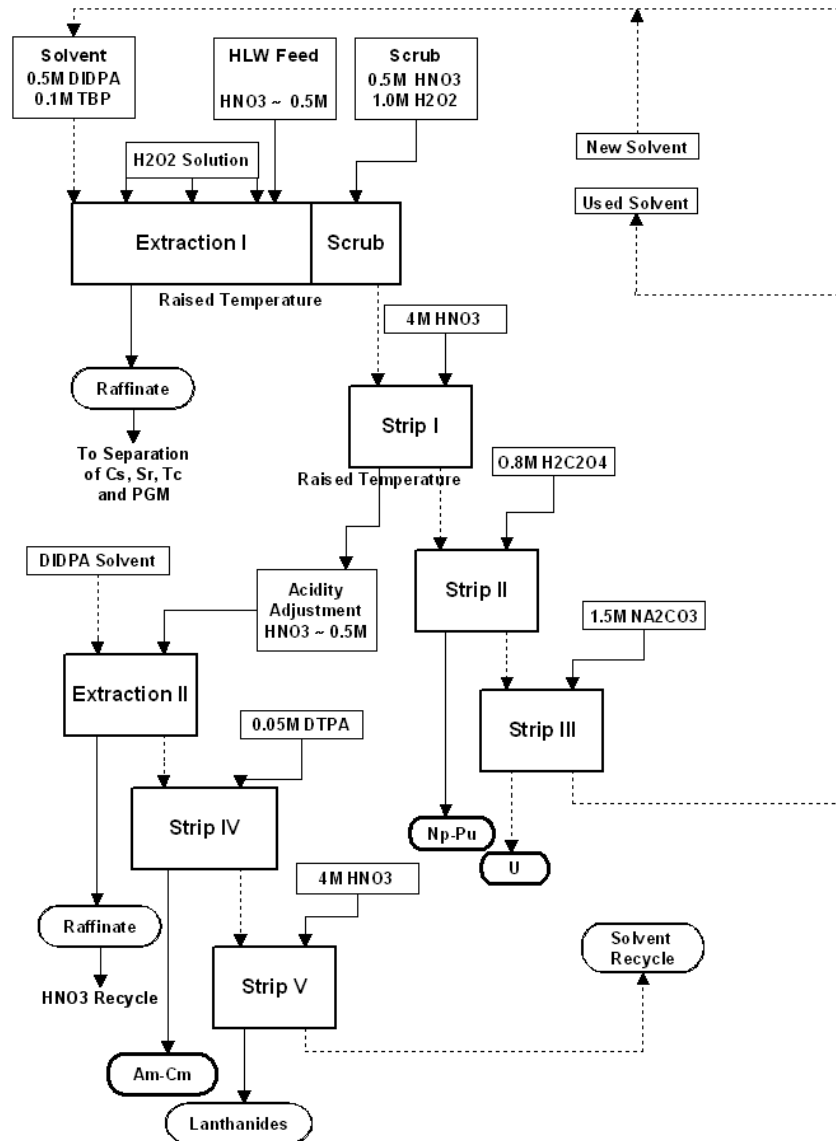Figure 2. **The DIDPA extraction process including mutual separation of TRU**

Table 1. **Target recovery, experimentally obtained separation efficiency and estimated recovery of elements in the four group partitioning process**

Elements		Target recovery (%)	Separation efficiency (%)	Estimated recovery (%)
T R U	Np	99.5	>99.95	99.85
	Pu	99.9	>99.99	99.85
	Am	99.99	>99.99	99.97
	Cm	99.9	>99.99	99.97
Tc		99	~98	~95
Sr, Cs		99	>99.9	>99.9

As for the separation of actinides, Am and Cm, from lanthanides, it is possible to reduce the lanthanide content less than 25wt% under the condition of 99.99% separation efficiency of actinides, which is fully satisfied with the purification suitable for nuclide transmutation.

The radiation durability of the DIDPA solvent is about 7 times higher than TBP and its degradation products give hardly drawback effects on the TRU extraction because most of the products are organophosphoric acid compound like DIDPA. Thus there is no frequent need to purify the DIDPA solvent prior to its recycle use, which greatly contributes to the reduction of a secondary waste generation.

Generation of solid materials after the partitioning and its positive effects on the management of HLW

Table 2 shows the volume of solid materials after partitioning of HLLW2. The volumes of the TRU group and the Tc-PGM group were estimated as oxide and metal respectively. The volume of the Sr-Cs group was estimated for the solid material generated by the direct calcination of the inorganic ion exchangers loaded with Sr and Cs, and the volume of the others group for the vitrified material containing 30wt% of oxides of fission and corrosion products. Cementation was considered for the secondary wastes such as $CaHPO_4$ and $NaNO_3$.

Table 2. **Volume of solid materials after the four group partitioning for one ton of the spent fuel burned up to 33 GWd/t**

Group	Main nuclides or elements	Solid form	Volume (L)
TRU	^{237}Np, ^{241}Am	oxide	0.09
Tc-PGM	^{99}Tc, Ru, Rh, Pd	metal	0.39
Sr-Cs	^{90}Sr, ^{137}Cs	calcined product	14
Others	Zr, Mo, Fe, rare earths	vitrified material	31
Total volume of high-level waste after the partitioning			~45
High-level waste volume without partitioning			~150
Secondary waste after the partitioning		cemented material	330

In relation to Table 2 positive effects of the partitioning on the management of HLW can be described as follows:

1. Most of nuclides with long-term radiotoxicity are collected in the TRU group whose volume is only 0.06% of a vitrified HLW without partitioning. The long-term radiotoxicity of HLW can be greatly reduced by the separation of the TRU group and its nuclide transmutation.

2. Most of nuclides contributing to the heat generation of HLW are collected in the Sr-Cs group whose volume is only 10% of the vitrified HLW. This means, from a view-point of volume only, a storaging capacity for cooling of the vitrified HLW for 30 years can be used for the storage of the Sr-Cs group for 300 years, during which the activities of ^{90}Sr and ^{137}Cs with half-live of about 30 years are reduced by a factor of about 1000.

3. The solid materials obtained from a direct calcination of inorganic ion exchangers loaded with Sr and Cs over 1 000 C possess extremely higher thermal stability and lower leachability by a factor of about three orders of magnitude than the vitrified HLW.

4. In the vitrification of the others group, it is possible to increase an elemental concentration as compared with that in the vitrified HLW because of no presence of heat generating nuclides such as ^{90}Sr and ^{137}Cs, thus contributing to the volume reduction of the other group, about 20vol% of the vitrified HLW. For the others group it might be possible to dispose of directly into deep underground without any long-term cooling.

5. Total volume of the four groups is estimated to be 45 L for one ton of the spent fuel, which is smaller by a factor of 3.3 compared with that of the vitrified HLW. Extremely higher volume reduction of HLW might be expected by the four group partitioning.

6. Volume of the cemented waste is only about 20% of that generated in a reprocessing plant.

Moreover, an alpha activity concentration of the cemented waste becomes lower than 1 GBq/ton and its shallow land disposal might be expected.

Recent Study on the four group partitioning process

Prevention of colloid formation and removal of the colloid in the pre-treatment step for the partitioning

Studies on pre-treatment of HLLW for the DIDPA extraction in the four group partitioning process showed that colloid was formed at denitration step when a simulated HLLW was heated before denitration. The heating step was added to make the precipitate easy-to-filter, which is very important from the chemical engineering point of view. Since the colloid disturbs the extraction with DIDPA by forming emulsion, the prevention of the colloid formation and the removal of the colloid was studied using simulated HLLW.

The main component of the colloid was Zr, which remains in the pre-treated HLLW in a yield of about 50%. Modification of heating and denitration condition in the pre-treatment could not prevent the formation of either the colloid or the very fine particles which is very difficult to filtrate. Addition of phosphoric acid, which is one of the reagents for Zr precipitation, was found to be effective. To prevent the emulsification in the DIDPA extraction, amount ratio of phosphoric acid to the initial Zr should be more than 0.8.

As for the removal of the colloid formed in the denitrated HLLW addition of reagents for Zr precipitation also is the most effective among the various methods examined except very direct method of ultra filtration. Four reagents of phosphoric acid, ammonium para-molybdate, sodium ortho-molybdate and telluric acid were examined for the colloid removal and all the reagents could convert the colloid to precipitate by heating the solution after the addition. It was concluded that ammonium para-molybdate would be the best reagent among the four reagents because Mo is already included in HLLW, ammonium para-molybdate does not induce extra salts, it makes easiest-to-filter precipitate and it does not change the acid concentration.

Construction of optimum separation process for Tc-PGM Group by precipitation through denitration

For the purpose of constructing the optimum separation process for Tc and PGM by precipitation through denitration, the acid concentration of the denitrated solution and the precipitation ratio of elements were examined using simulated DIDPA raffinates at the various concentrations of elements and nitric acid and in the various heating conditions.

When the simulated DIDPA raffinate was heated strongly at the denitration, the several-times concentration of the raffinate was required for efficient separation of PGM. If the twice concentrated raffinate was denitrated by the addition of formic acid with the ratio of [HCOOH] / [HNO$_3$] > 2.4, or if the 4-times concentrated raffinate was denitrated with the ratio of [HCCOH] / [HNO$_3$] > 2, pH of the denitrated solution increased to neutral region and then PGM was separated as precipitates.

In case the denitration was performed without the concentration of the simulated DIDPA raffinate, the temperature rising rate of the solution was found to be an important parameter. In order to increase the pH of the denitrated solution to neutral region and to separate PGM as precipitates by the denitration at [HCOOH] / [HNO$_3$] = 2.2, the temperature rising rate should be slower than a threshold value and the solution temperature after the rising should be over 95 C.

Tc behaviour in the four group partitioning process

A small scale partitioning test on the four group partitioning was performed using simulated HLLW with addition of a macro amount of Tc as a total test that summarises the previous studies on Tc separation and as a final confirmation about Tc behaviour before the partitioning test with real HLLW at the Nuclear Fuel Cycle Safety Engineering Research Facility (NUCEF).

At the pre-treatment step including denitration step and newly-introduced colloid removal step by addition of Mo, Tc remained in the solution. Ratios of Tc found in the precipitates was 0.23% at the denitration and 0.21% at the colloid removal. The loss of Tc to the precipitate was negligible.

At the DIDPA extraction step, 99.93% of Tc transferred to the raffinate. Calculated distribution ratio was 0.013.

At the precipitation step by denitration of the raffinate after concentration, 98.2% of Tc were precipitated. It was confirmed that the Tc precipitates even at a macro amount.

At the dissolution step for Tc from the precipitate with hydrogen peroxide, 84.6% of Tc were recovered as a solution. By repeated dissolution, the recovery can be increased.

Back-extraction of actinides from organophosphoric acid with hydrazine carbonate

Back-extraction of actinides from organophosphoric acid solvent with hydrazine carbonate is an attractive method to separate actinide from other actinides and lanthanides from the standpoint of reducing secondary waste because it is so-called salt-free. The back-extraction from HDEHP (di(2-ethylhexyl)phosphoric acid) and DIDPA was studied to elucidate its behaviour of actinides and lanthanides.

In the case of HDEHP, the separation factor of Am(III) and Eu(III) was about three and Am might be separated from lanthanides in an appropriate hydrazine carbonate concentration from 0.6 M to 1.0 M.

Np(IV) and Pu(IV) were back-extracted with 0.6 M hydrazine carbonate solution from HDEHP with the distribution ratios of 0.11 and 0.47, respectively, whereas Am(III), Eu(III) and U(VI) were hardly back-extracted, whose distribution ratios were 2.3, 7.3 and 13.6 respectively.

Therefore, it is possible to separate actinides each other and to separate trivalent actinides from lanthanides by changing the hydrazine carbonate concentration.

Partitioning tests with simulated HLLW at NUCEF

Partitioning tests with simulated HLLW have been performed in the partitioning test facility at NUCEF which was constructed for the demonstration of the four group partitioning process with real HLLW. One of the purposes was to obtain the data on elemental behaviour to be compared with the results of the tests with real HLLW. Another purpose was to check the operability of the facility.

Table 3. **Fractional distribution (%) of each element at the mixer-settler**

Element	Raffinate	Back-extracted with 4M HNO_3	Solvent
Y	< 0.002	5.6	94.4
La	< 0.06	> 99.93	< 0.01
Ce	< 0.01	97.9	2.1
Pr	< 0.02	99.85	< 0.13
Nd	< 0.01	98.7	1.3
Sm	< 0.008	96.5	3.5
Eu	< 0.006	96.3	3.7
Gd	< 0.04	97.5	2.5
Fe	4.64	0.52	94.84
Zr	< 0.3	< 3.1	> 96.6
Mo	> 95.4	4.1	< 0.5
Te	88.8	11.6	< 0.6
Ru	98.7	0.2	1.1
Rh	> 99.0	0.9	< 0.1
Pd	98.2	0.8	1.0
Sr	> 99.98	0.02	< 0.001
Ba	> 99.99	0.01	< 0.001
Rb	> 99.96	< 0.03	< 0.01
Cs	> 99.91	< 0.07	< 0.02

Phosphoric acid was added to the simulated HLLW before denitration in the pre-treatment step for the DIDPA extraction in order to remove completely Zr not only in ionic form but also in colloidal form, which sometimes disturbs the aqueous - organic phase separation in the DIDPA extraction. About 99.5% of Zr, 98% of Mo, 42% of Te, 20% of Fe and 5% of Ru were removed from the simulated HLLW as a precipitate in this pre-treatment step.

In the DIDPA extraction a 16 stages mixer-settler was used and 7 stages used for extraction of TRU, 4 stages for scrubbing and 5 stages for back-extraction of Am and Cm. The fractional distribution of each element in this DIDPA extraction steps is shown in Table 3. Lanthanides could be almost completely extracted with DIDPA and back-extracted with 4 M HNO_3. Further complete back-extraction of lanthanides might be easily accomplished by increasing the number of the back-extraction stage. Other elements except Fe, Zr and Y were not extracted and therefore Sr and Cs were well separated from lanthanides. About 99.8% of Fe, 80% of Zr and 0.5% of Y were back-extracted with the oxalic acid solution.

The raffinate of the DIDPA extraction was fed to the separation step for PGM and Tc by precipitation through denitration. More than 90% of PGM was precipitated and almost all Cs was remained in the solution, but 20-30% of Sr was coprecipitated. These results well agreed with the results of previous experiments in a small scale. Recovery of Sr from the precipitate should be studied.

Partitioning tests with real HLLW at NUCEF

As the first step of the four group partitioning test with real HLLW, semi-hot test with tracer level of real HLLW has been performed at NUCEF. In this test more than 99.99% extraction of Am with DIDPA was confirmed and 99.92% was back-extracted with 4 M nitric acid. Chemical behaviours of other elements were also almost consistent with those in the partitioning test with simulated HLLW.

Conclusion

The four group partitioning greatly contributes to the reduction of the high-level waste volume and the establishment of an advanced HLW management technology as well as the promotion of the transmutation of long-lived nuclides which contributes to the reduction of long-term burden of HLW into natural environment.

Demonstration of the four group partitioning process with real HLLW is now in progress, the effectiveness of the process will be verified and the process will be optimised for its practical utilisation.

REFERENCES

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