

PRODUCTS AND WASTES FROM FOUR GROUP PARTITIONING PROCESS DEVELOPED IN JAERI

M.Kubota and Y.Morita

Radioactive Waste Partitioning Research Laboratory
Department of Chemistry and Fuel Research
Japan Atomic Energy Research Institute

In 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 the partitioning process flow sheet, behaviors of objective elements and other constituents in the process, recoveries of objective elements, chemical purities of the products, the sorts and constituents of the secondary wastes, and the volume of solid materials generated from HLLW after the partitioning process.

The complete separation of TRU elements, including pentavalent Np, might be accomplished by using the partitioning process. However, further improvement will be required in the separation of Am and Cm from rare earths, back-extraction of U and Y from the DIDPA solvent, etc. to reduce the secondary waste generation and the handling liquid volume.

1. Introduction

Nuclear energy is the most promising option for the future generation when considering the global environmental protection. The management of high-level radioactive waste containing long-lived nuclides is one of the most important problems to be solved before the future deployment of nuclear energy in the global scale.

In 1988, Japan's Atomic Energy Commission published the report entitled "Long Term Program for Research and Development on Nuclide Partitioning and Transmutation Technology". In this program, a partitioning technology should be developed for separating elements in high-level liquid waste (HLLW) into four groups; transuranium elements (TRU), Tc-platinum group metals (PGM), Sr-Cs and the others. Among them, long-lived nuclides such as TRU nuclides should be transmuted by using an actinide burner reactor, FBR, etc.

2. Development of partitioning process

At JAERI, development of a partitioning method started about 23 years ago. From 1973 to 1984, a partitioning process was developed for separating elements in HLLW into 3 groups; TRU, Sr-Cs and others. The partitioning process consists of three steps; solvent extraction of U and Pu with tributylphosphate (TBP), solvent extraction of Am and Cm with diisodecylphosphoric acid (DIDPA), and adsorption of Sr and Cs with inorganic ion exchangers. The process was demonstrated by using an actual HLLW.

Since 1985, a four group partitioning process has been developed, in which a step for separating the Tc-PGM group was developed in addition to the three group separation. Effective methods for separating TRU, especially Np, and Tc have been developed.

3. Four group partitioning process

Through the fundamental study, the four group partitioning process has been constructed as shown in Fig.1. Main characteristics of this flow sheet 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, titanate acid and zeolite, respectively.

3.1 TRU separation

The TRU elements in the DIDPA solvent are sequentially back-extracted with 4 M nitric acid for Am, Cm and rare earths, 0.8 M oxalic acid solution for Np and Pu, and 1.5M sodium carbonate solution for U. A chemical flow sheet is shown in Fig.2. Back-extracted Am, Cm and rare earths are extracted again with DIDPA, and then Am and Cm are preferentially back-extracted with 0.05 M diethylenetriaminepentaacetic acid (DTPA) solution, leaving rare earths in the DIDPA solvent.

Recoveries of TRU elements and chemical behaviors of fission products and corrosion products in each chemical step can be estimated with data so far obtained through experiments with actual or simulated HLLW. Following results might be expected under optimized process conditions.

Recoveries of Am, Cm, Pu and U are more than 99.99% and Np more than 99.95% in the DIDPA extraction step. More than 99.99% of Am, Cm and rare earths are back-extracted with 4 M nitric acid, more than 99.9% of Np and Pu with the 0.8 M oxalic acid solution, more than 99.9% of U with the sodium carbonate solution and more than 99.99% of Am and Cm with the DTPA solution.

As to the chemical behaviors of fission and corrosion products, rare earths and Fe are quantitatively extracted with the DIDPA solvent. Rare earths behave like Am and Cm, but finally are separated from them in the DTPA back-extraction step. The rare earth content in the Am and Cm fraction might be reduced to lower than 25% under the operating condition of 99.99% recoveries of Am and Cm. Among rare earths, the chemical behavior of Y fairly differs from those of other rare earths. Most Y is back-extracted along with U in the sodium carbonate back-extraction step. The Fe is back-extracted along with Np and Pu with the 0.8 M oxalic acid solution.

3.2 Tc and PGM separation

Two chemical methods have been developed for the Tc and PGM separation from the DIDPA raffinate; the precipitation method by a denitration with formic acid and the adsorption method with active carbon column. The former method might be more effective in practical use because of no generation of secondary wastes even though the recovery of Tc is estimated to be about 95% as compared with more than 99.9% in the latter method and the former method is not applicable to the solution in which concentration of Rh and Pd is lower than 0.005 M. More than 90% of Tc might be preferentially leached out, leaving PGM in the precipitate, with a hydrogen peroxide solution.

3.3 Sr and Cs separation

The adsorption method with inorganic ion exchangers, titanate acid and zeolite, has been developed for the Sr and Cs separation. More than 99.9% of Sr and Cs might be separated from the filtrate by this adsorption method after the Tc and PGM separation.

4. Products from four group partitioning process

4.1 TRU products

4.1.1 Am and Cm

The recovery which is the ratio of the amount in the product to the initial amount in HLLW might be more than 99.97% for Am and Cm under the estimation that less than 0.03% of them are lost in the chemical steps; DIDPA extraction, 4 M nitric acid back-extraction, DIDPA re-extraction and DTPA back-extraction. About 1 % of rare earths might be contained in the Am and Cm product and the chemical purity of the product might become about 75%.

In the chemical flow sheet as shown in Fig. 2, the Am and Cm product is obtained as the DTPA solution. Finally, a conversion method to oxide or nitride to be subjected to the nuclide transmutation should be developed.

4.1.2 Np and Pu

The recovery of Np might be more than 99.85% under the estimation that less than 0.05% is lost in the DIDPA extraction step and less than 0.1% in the 0.8 M oxalic acid back-extraction step. Almost all Fe and slight amounts of Rh, Ru, Zr and Mo might be contained in the Np and Pu product. The purification of the product from Fe and other impurities should be considered in the conversion step from the oxalic acid solution to oxide or nitride to be subjected to the nuclide transmutation.

Estimation of the Pu recovery is very difficult because more than 70% of Pu might be precipitated during the preparation step of HLLW from the TBP raffinate generated in the Purex

process, long-term storage of HLLW and the denitration step of HLLW prior to the DIDPA extraction even though the recovery of Pu from the filtrate after the denitration of HLLW is more than 99.9%. In order to accomplish the complete recovery of Pu, the dissolution of the precipitate and the separation of Pu from the resulting solution should be developed.

4.1.3 U

The recovery of U might be more than 99.9% under the estimation that less than 0.01% is lost in the DIDPA extraction step and less than 0.1% in the sodium carbonate back-extraction step. Almost all Y, slight amount of Fe, less than 0.1% of Np and less than 0.01% of Am and Cm might be contained in the U product which is obtained as the sodium carbonate solution. This product should be recycled to a fuel reprocessing plant.

4.2 Tc and PGM products

Estimation of the recoveries of Tc and PGM is difficult as the same as in the case of Pu because about 10% of Tc and about 20% of Ru and Rh might be precipitated during long term storage of HLLW and the denitration step of HLLW prior to the DIDPA extraction. In order to increase the recoveries of Tc and PGM up to more than 90%, a treatment method for the precipitate should be developed. However, higher recovery more than 90% for Tc will not be needed from the standpoint of reducing the potential hazard index of a vitrified HLLW.

The recoveries from the filtrate after the denitration of HLLW are estimated to be about 95% of Tc, 92% of Ru, 87% of Rh and 99% of Pd when the precipitation method is applied to the DIDPA raffinate. The Tc product obtained by the leaching of the precipitate with hydrogen peroxide might contain trace amount of PGM. Conversion of the Tc chemical form present in pertechnetate ion should be studied for the nuclide transmutation or a beneficial use. The PGM obtained as the precipitate might be present as a mixture of metal and oxide. Mutual separation of Ru, Rh and Pd should be studied for their beneficial uses. However, the necessity of this study might not be so urgent since the PGM contains long lived nuclides of which half-lives are longer than one year and a very long-term cooling will be needed before practical use.

4.3 Sr and Cs product

The recoveries of Sr and Cs might be more than 99.9%. Most Ba and Ni might be also adsorbed on the inorganic ion exchangers. The U and TRU contents compared to their initial amounts in HLLW might be less than 0.01% and less than 0.0001%, respectively.

The exchangers loaded with Sr and Cs can be solidified into a very stable form by direct calcination. This greatly contributes to the reduction of waste volume because the material used for the adsorption can be used as the mother material for the Sr and Cs solidification and the thermal stability of the product is very high compared with that of vitrified material. Therefore, large amount of heat generating nuclides can be included in the small volume of the solid material. Leachabilities of Sr and Cs are extremely low by a factor of four order of magnitude as compared with that for vitrified material.

The Sr and Cs product might be used as a heat source and a radiation source during the period of storage prior to a deep underground disposal.

5. Wastes from four group partitioning process

5.1 Others group

The others group in the four group partitioning process is waste in a direct sense. This group contains elements collected from 4 kinds of fractions; the precipitate after the denitration of HLLW, the rare earths fraction separated from Am and Cm, the effluent from the Sr and Cs adsorption column, the Fe and Y fractions separated from the Np and Pu fraction and the U fraction, respectively.

From the precipitate fraction, most Zr, Mo and Te are estimated to be recovered and transferred to the others group. The Pu quantity transferred to the others group is estimated to be less than 0.01%. The rare earth fraction is estimated to contain most rare earths and less than 0.01% of Am and Cm, the effluent fraction to contain Na which is released by an ion exchange reaction with Cs, and the Fe and Y fraction to contain most of them.

Total amount of elements to be contained in the others group is estimated to be 26 kg in their oxides for one ton of the spent fuel burned up to 33 GWd/t.

5.2 Solvent waste

The DIDPA solvent is estimated to contain less than 0.1% of U, less than 0.001% of TRU and trace amounts of Ru, Fe and Zr after treatment with the sodium carbonate solution. Total amount of the DIDPA solvent waste generated for one ton of the spent fuel is estimated to be 10 L, corresponding to 8.2 kg of CaHPO_4 , under the conditions that 3000 L and 4000 L of the DIDPA solvent are used respectively for the TRU extraction step from HLLW and the separation step of Am and Cm from rare earths and the number of its recycle use in each step is estimated to be 50 and 100 times, respectively.

5.3 Washing solution

The DIDPA solvent after the treatment with the sodium carbonate solution should be washed with nitric acid to convert the Na form to H form for its recycle use. Therefore, the waste of the washing solution contains sodium ion of which amount is estimated to be 128 kg in NaNO_3 for one ton of the spent fuel. Amounts of U and Pu-TRU are estimated to be less than 0.0001% and less than 0.00001%, respectively.

5.4 Sodium carbonate solution and other wastes

In the U back-extraction step with sodium carbonate solution, about half of Na remains in the carbonate solution. Therefore, the amount of Na in the carbonate solution after the U back-extraction is estimated to be 128 kg in NaNO_3 for one ton of the spent fuel.

The liquid wastes generated after treatment of the Am and Cm fraction and the Np and Pu fraction are the DTPA solution and the oxalic acid solution, respectively. For these liquid wastes it might be possible to decompose to water and carbon dioxide which enable no generation of solid wastes.

6. Volume of the solid materials

Table 1 shows the volume of the solid materials generated in the four group partitioning process.

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 most Sr, Cs, Rb, Ba and Ni, and the volume of the others group was estimated for the vitrified material containing 30 wt% of oxides of fission and corrosion products. This content might be not so high for the vitrification because the others group

contains less heat generators such as Sr-90 and Cs-137. Cementation was considered for the secondary wastes such as CaHPO_4 and NaNO_3 .

Total volume of the four groups generated from the partitioning process was estimated to be 45 L which is smaller by a factor of 3.3 compared with that in the vitrification of HLLW without partitioning.

For the others group it might be possible to dispose directly into a deep underground without any long term cooling. For the cemented waste, a shallow land disposal might be suitable because alpha activities concentration is estimated to be negligible.

7. Conclusion

The four group partitioning contributes to the reduction of the high-level waste volume and the enhancement of the utilization of valuable elements or nuclides in HLLW as well as the promotion of the transmutation of long-lived nuclides which contributes to the reduction of long-term burden into natural environment.

Complete separation of TRU elements, including pentavalent Np, can be accomplished by using the DIDPA solvent. However, a chemical method using a salt-free reagent should be further developed for the back-extraction of U and Y from the DIDPA solvent to reduce the secondary waste generation and an advanced chemical method should be considered for the separation of Am and Cm from rare earths to reduce the handling liquid volume. The recovery of TRU elements, especially Pu, should be studied for the precipitate formed during the preparation step to HLLW from the TBP raffinate generated in the Purex process, long term storage of HLLW and the denitration step of HLLW.

Table 1 Volume of solid materials after partitioning for one ton of the spent fuel burned up to 33 GWd/t

Group	Main nuclides or elements	Solid form	Volume (L)
TRU	Np-237 Am-241	oxide	0.09
Tc - PGM	Tc-99 Ru, Rh, Pd	metal	0.39
Sr - Cs	Sr-90 Cs-137	calcined product	14
Others	Zr, Mo, Fe rare earths	vitrified material	31
Secondary wastes	NaNO ₃ CaHPO ₄	cemented material	330

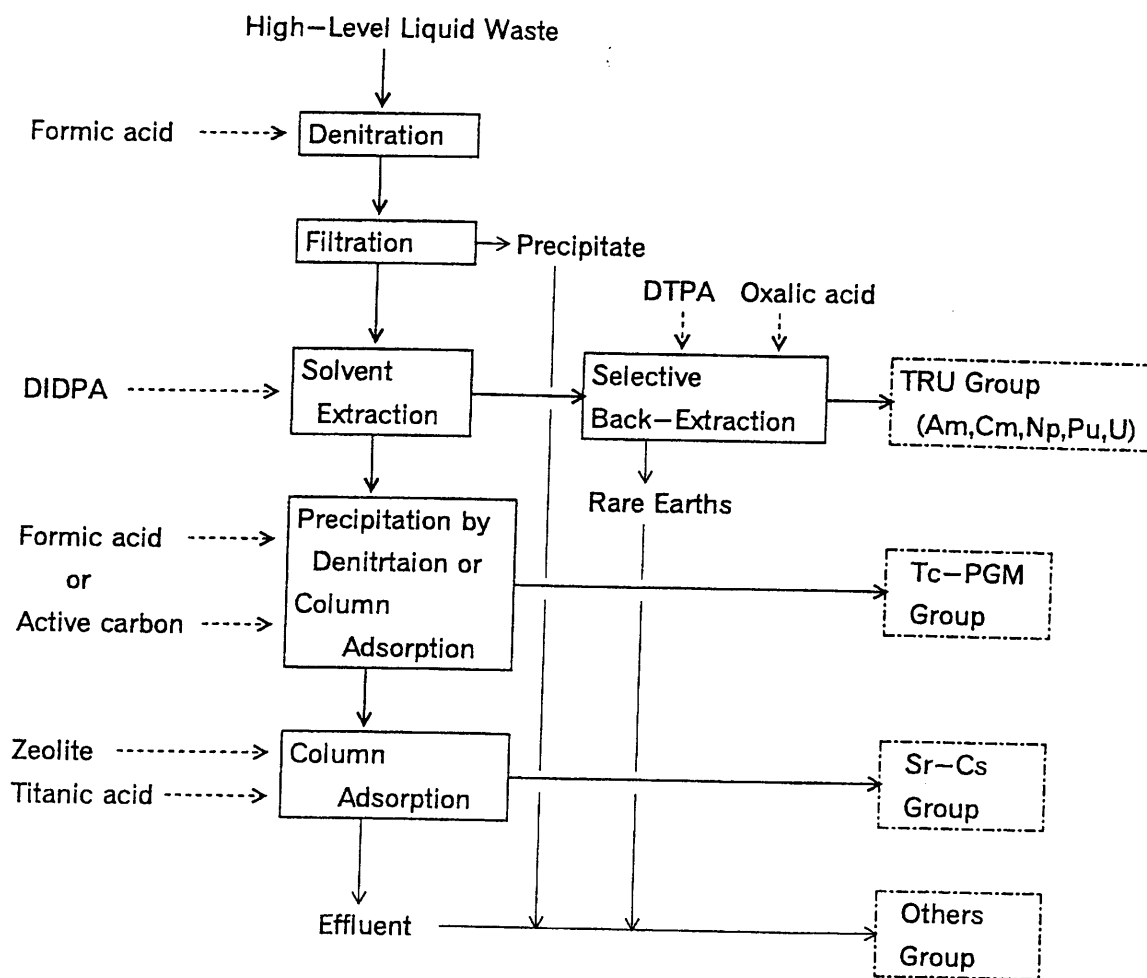


Fig. 1 The four group partitioning process

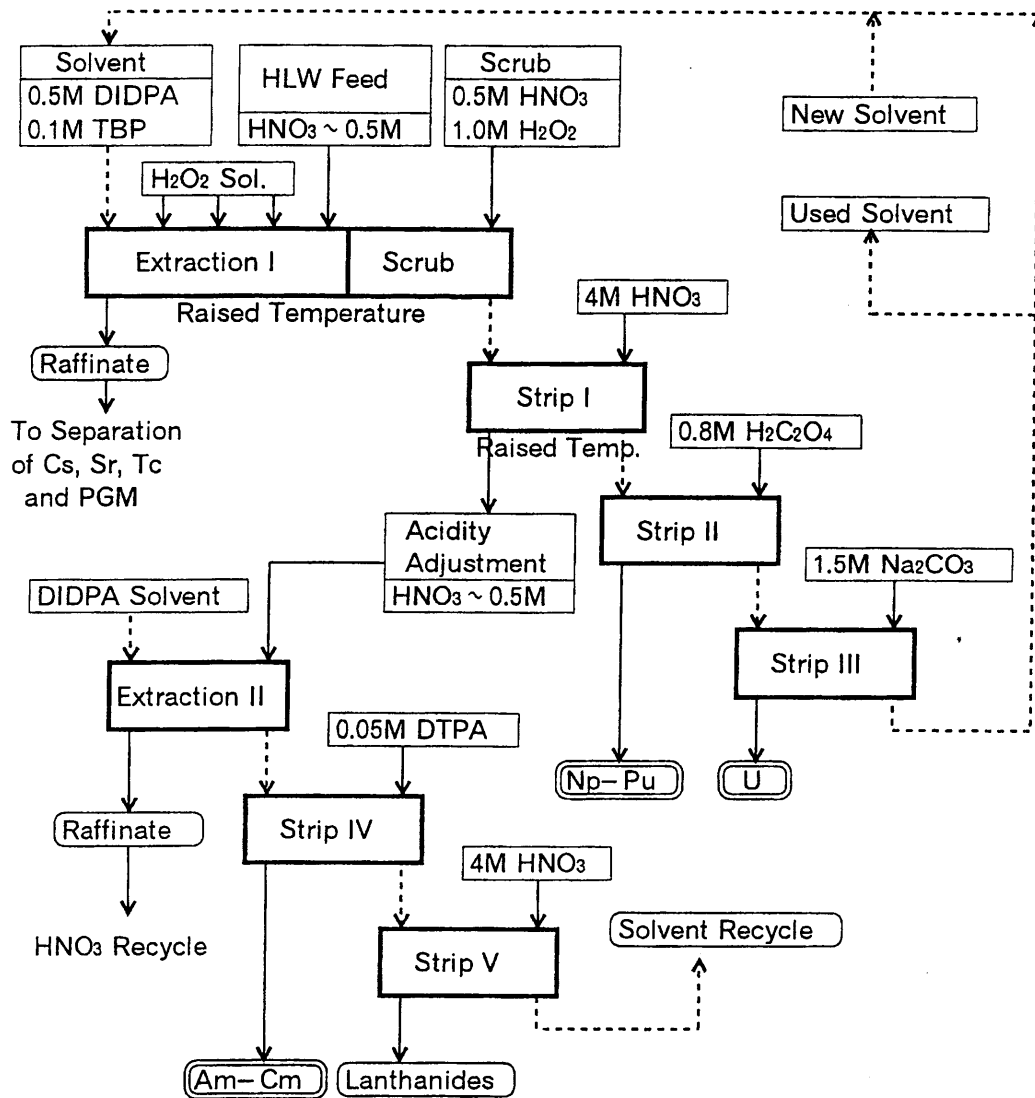


Fig. 2 The DIDPA extraction process including the separation of Am and Cm from rare earths