

APPLICATION OF MODIFIED TRUEX FLOWSHEET TO MINOR ACTINIDE SEPARATION FROM HIGH LEVEL LIQUID WASTE

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ABSTRACT

Experimental studies are in progress on the application of TRUEX process to the recovery of minor actinides from the highly active waste as a part of long-term efforts to improve future nuclear fuel cycle. This paper summarizes the results obtained from the basic batch experiments to clarify the fundamental characteristics of the CMPO solvent, including distribution data for major components in the waste solution and the boundary of the third phase formation. In parallel with these batch experiments, three mixer-settler runs have been conducted using actual highly active raffinate as feed solutions. An excellent removal of minor actinides from the raffinate solution has been verified in these experimental runs. At the same time, several subjects which require further investigation or development have been identified.

INTRODUCTION

Fifty years has passed since the mankind succeeded in controlling the nuclear chain reaction. Today more than sixteen per cent of the world electricity is being generated by nuclear fission. At present, many countries are burning uranium in so-called once-through mode where the spent fuels are simply disposed of as waste. In this option, however, the utilization efficiency of uranium is extremely low, and the uranium available at modest price is projected to be used up within several decades.

As we become more aware of the finiteness of the earth and the fragility of the global environment, we have to strongly recognize it as our duty to maximize the utilization efficiency of natural resources and minimize the burden of waste so that we can share the benefit of the resources with our future descendants and assure them a healthy environment. Thus the concept of 'recycle' usage is becoming more and more important in our life today and in future. In the nuclear energy utilization, plutonium recovery by spent fuel reprocessing and its utilization in fast breeder reactor (FBR) system would best fit to this philosophy. In this 'plutonium recycle' option, the utilization efficiency of uranium becomes almost sixty times larger than in once-through option, and then the nuclear fission will become able to play an important role for many centuries as a major energy supply source. Since the nuclear waste is radioactive and requires special cares for many centuries, the utilization of the nuclear energy will be justified in the human history only when it is positively beneficial for similar time range to that of waste management. The plutonium recycle option will make it possible. In addition, it will become an important part of the solution to the dilemma of preventing global warming under increasing world energy demand, since it is enormous as energy source and produces virtually no greenhouse gases.

Considering the time length for which the nuclear energy is expected to serve, it would be appropriate to say that we are still in the very beginning portion of the nuclear era, and further developmental efforts are needed to make the nuclear technology more compatible with the human progress and the conservation of global environment. As one of such efforts, the Power Reactor and Nuclear Fuel Development Corporation (PNC) is conducting a study to recover minor actinides (TRU) from the highly active waste and burn them in FBRs

under the framework of OMEGA project in Japan. The basic concept of actinide recycle in FBR system is illustrated in Fig. 1. This option will not only provide extra energy gains but also reduce long-term hazard in high active waste. Furthermore, mixing the recovered minor actinides (plus some amount of fission products) into the fuel would significantly increase the difficulty of plutonium misuse as weapon. This paper summarizes the status of experimental studies on the TRUEX process as a method to recover minor actinides from the highly active waste.

RECOVERY OF MINOR ACTINIDES

In the spent fuel reprocessing, PUREX process has been generally applied to recover Pu and U by using tributyl phosphate (TBP) as an extractant. In the current PUREX process, neptunium is loosely controlled and distributed into both the Pu product and raffinate (1). In nitric acid media, Am and Cm are in tri-valent state which are not extractable into TBP and then become components of highly active raffinate. For minor actinide separation, both control of Np behavior and extraction of tri-valent actinides from liquid waste are required.

In order to recover Am and Cm from high acidic solution, extractants which are capable of extracting tri-valent metals are required. One of the remarkable extractants to have such capability is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) which was synthesized at Argonne National Laboratory (2). The process based on this

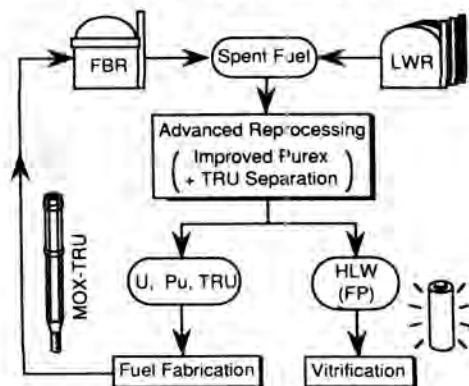


Fig. 1. FBR fuel cycle with TRU separation process.

extractant is called TRUEX process, and its fundamental characteristics and feasibility of actinide removal from real high level liquid waste (HLLW) were reported (3). Recently, N,N' -tetraalkylmalonamide (diamide) which does not contain phosphorus was reported by French researchers to have similar capability (4).

In PNC, the advanced PUREX process is being developed to improve the efficiency of removal of platinum group elements and to include the capability to recover minor actinides (5). TRUEX process was selected as a reference method for minor actinide separation because of the abundance of technical information on this process.

EXPERIMENTAL STUDIES OF ACTINIDE SEPARATION BASED ON MODIFIED TRUEX PROCESS

Basic Distribution Characteristics of Major Elements

Distribution measurements were done in both batch-wise and stage-wise experiments. The composition of solvent was 0.2 M CMPO and 1.0 M TBP diluted in *n*-dodecane. Measured distribution ratios (*D*) of typical elements were gathered and compared in Fig. 2. In 3M nitric acid solution, all the actinide ions except Np(V) showed very large *D* values. As acid concentration decreases down to 0.1M, these *D* values decrease more than one order of magnitude for most of the actinides but they remain as large as 10 for U and Pu. The *D* value of Pu(IV) measured in our experiment is somewhat lower than the value reported by Horwitz et al. which was measured with the addition of nitrous acid for stabilizing Pu(IV)(6). The *D* values for Pu(III) and Np(V) were obtained by adding excess amount of hydroxyl amine nitrate to Pu and Np solution. Observed *D* value of Pu(III) in low acidity was unexpectedly large, and one possible explanation for this would be reoxidation of Pu(III) into Pu(IV) by nitric and nitrous acid in the solvent despite the excess amount of reducing reagent in the aqueous phase. Np(IV) and Np(VI) was adjusted by adding Fe(II) and Cr(VI) respectively. The *D* value of Np without valency adjustment, Np(mix), was large enough for extraction from 3M nitric acid solution. In this case, Np is considered to be in the mixture of tetra- and hexa-valent states due to the disproportionation.

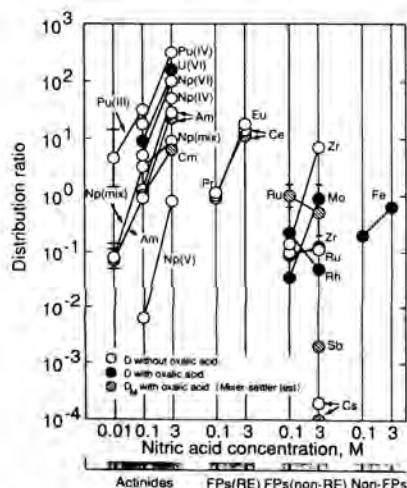


Fig. 2. Acid dependency of distribution ratios of major elements in HLLW.

Among typical fission products, lanthanide elements such as Eu, Ce and Pr behaved quite similarly to the trivalent actinide Am. Other fission products showed relatively small *D* values in general, which indicates these are not extractable with the CMPO solvent. Zr was extractable with the CMPO solvent but its *D* value was suppressed below 1 when oxalic acid was added as a complexing reagent. Ru exhibited very inconsistent behaviors depending on the test conditions and the system. The *D* value of Ru measured in the batch test was about 0.1 whereas the value measured in the counter-current test was close to 1.

Limit of the Third Phase Formation

There are two candidate forms of the waste solution for recovering minor actinides by applying TRUEX process; highly active raffinate or concentrated HLLW. These acidic solutions differ from each other in their metal concentration. The CMPO mixed solution is known to form the third phase more easily than TBP diluted with *n*-dodecane (7). Thus, a practical limit of aqueous metal concentration beyond which the third phase formation occurs must be determined to assure reliable operation of the actual contactor system.

The third phase formation behavior was investigated using the simulated waste. In these experiments, the effects of TBP concentration in organic phase and temperature were mainly studied. Figure 3 shows the variation of third phase volume with temperature. A very sharp cut-off temperature for the third phase annihilation was observed as well as its dependency on the TBP concentration in the mixed solvent. The simulated waste contained synthesized FP elements with the concentrations adjusted to those of the actual concentrated HLLW from the reprocessing plant, but uranium and plutonium were not contained. Although hexa-valent uranium contributes to the third phase formation more preferentially than trivalent metals, lanthanide elements are the major contributing components due to their dominant amount in the waste solution. From Fig. 3, the TBP concentration in the mixed solvent around 1.6 M or higher and the operation temperature around 40°C would be required if actinides are to be recovered directly from the concentrated HLLW. In order to use mixed solvent with lower TBP concentration without raising the operating temperature, a dilution of the

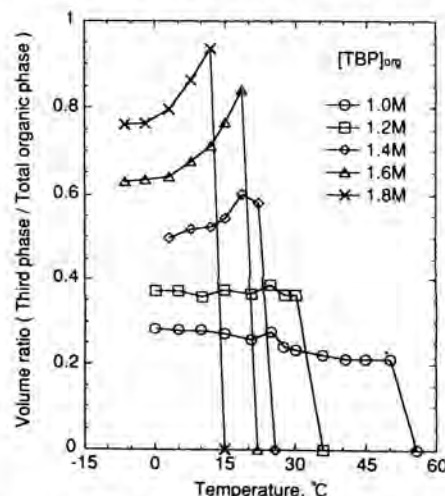


Fig. 3. Dependency of the third phase volume with temperature and TBP concentration.

HLLW would be apparently required to avoid the third phase formation. In this aspect, the application of the TRUEX process to the raffinate before concentration would be more appropriate.

Hot Experiments Using Mixer-Settlers

Three hot experiments using real active raffinate generated in FBR fuel reprocessing tests were carried out. In these experiments, mini mixer-settlers were used as contactor. Conditions of chemical flowsheet for each run are summarized in Fig. 4. The flowsheets consisted of extraction, scrubbing and stripping sections. The active raffinate was used as feed solution without any chemical treatment. In scrubbing section, oxalic acid was added to the nitric acid solution in order to suppress Zr extraction.

In the first and second experiments, stripping was done by dilute nitric acid solution without adding any reagent to see the fundamental characteristics as base cases. In the extraction section, such fission products as Cs and Sb were completely retained in the aqueous waste stream, whereas Am, Cm and Pu were well extracted and removed from the aqueous phase. However, fission product lanthanides such as Ce were also extracted into the solvent as expected from the batch test data. In addition, a certain portion of Ru was extracted into the solvent in the first experiment. Therefore, a double scrubbing method was applied to the second experiment hoping to suppress Ru retention in the solvent by feeding 7.7M nitric acid as second scrub solution. This attempt improved Ru retention problem to large extent but not completely. In the stripping section, trivalent actinides Am and Cm as well as lanthanides were back-extracted into the aqueous phase very easily, whereas Pu was not strippable by a simple dilute nitric acid solution. Ru was also hard to remove from the solvent. In these experiments, a decontamination factor for removing actinides from the highly active raffinate was about 1600. Separation factors of fission products from product americium stream were 1, 18 and $>1.4 \times 10^4$ for Ce-144, Ru-106 and Cs-137, respectively.

In the third experiment, the stripping bank was divided into four sections including a solvent washing section with sodium carbonate. In the first three sections, an attempt was made to selectively strip actinide elements by changing strip solution for each section. In the first section, trivalent actinides together with lanthanides were easily stripped by

dilute nitric acid. In the second section, HAN was added into the strip solution to recover Np by reducing it into penta-valent state, but this attempt did not seem quite successful. In the third section, oxalic acid was added aiming at the recovery of Pu but this attempt did not work either. Further investigation is necessary to clarify the reason of these results.

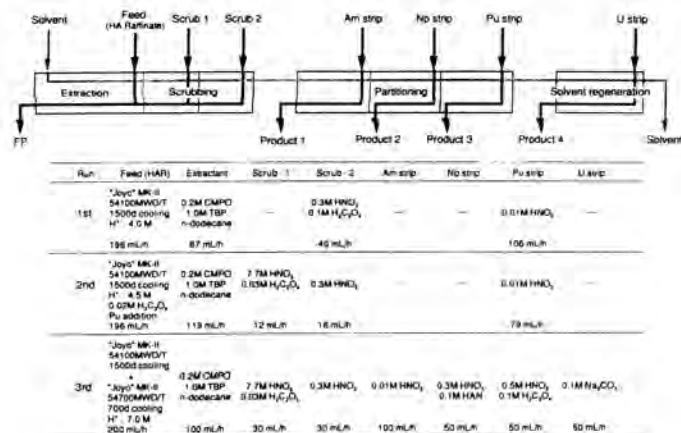


Fig. 4. Flow conditions for counter-current tests.

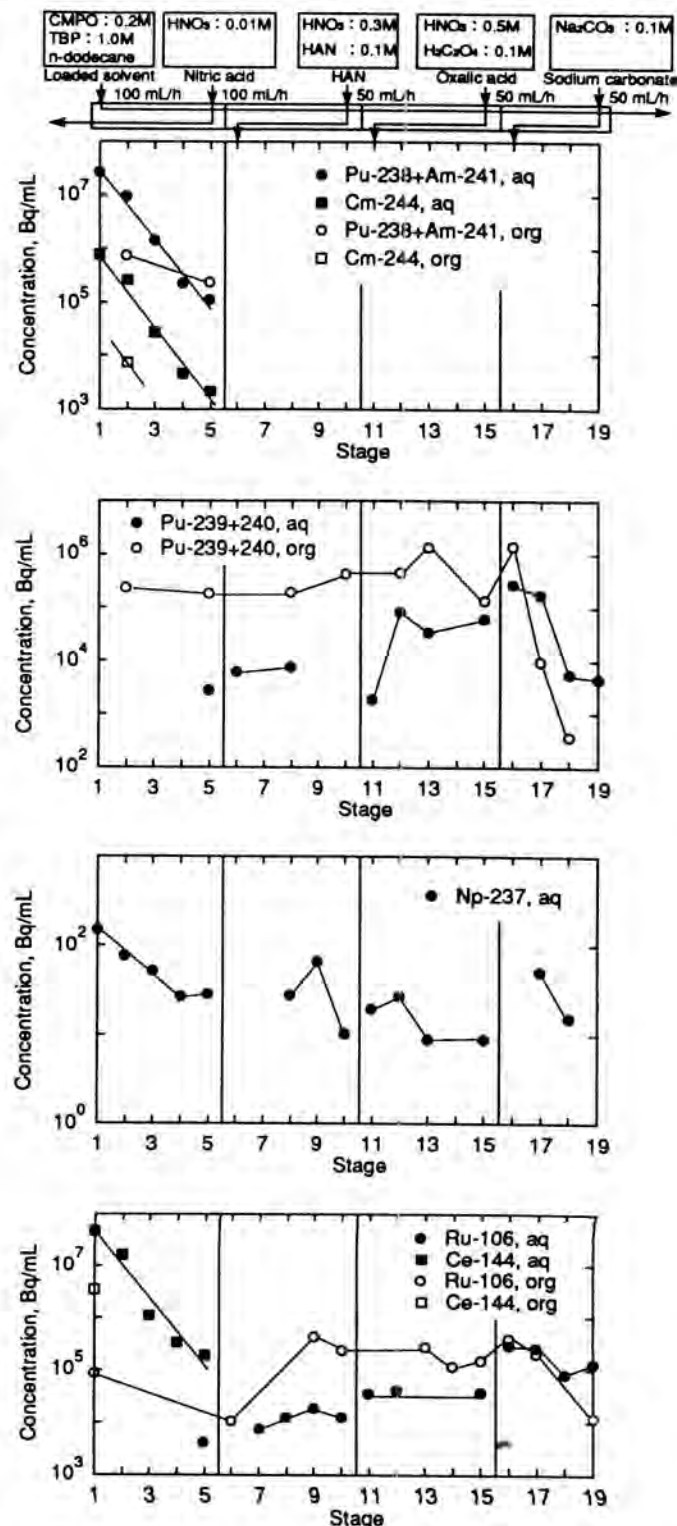


Fig. 5. The typical partitioning profiles of actinides and FPs in the third counter-current experiment.

However, Pu was efficiently removed from the solvent by washing with sodium carbonate. Even though the retention of Ru was observed in the first three sections, it was also removed by solvent washing.

Through these three runs, the third phase splitting was not observed.

Solvent Regeneration

In the PUREX Process, used solvent is washed usually with alkaline solution to remove degraded products and impurities. Because tetra- and hexa-valent metals such as U and Pu are very extractable to the CMPO solvent, stripping with dilute nitric acid solution is very difficult. One of the methods to recover loaded U and Pu would be washing with salt-free reagents such as hydrazine carbonate and hydrazine oxalate. Resulted solution could be decomposed by heating or electrolysis to recover stripped metals. To demonstrate such feasibility, a basic study on solvent cleanup was conducted using both salt-bearing and salt-free reagents.

After uranium loaded solvent was prepared, the solvent was equilibrated with 0.01M nitric acid. Uranium concentration in organic phase was about 3×10^{-3} M. Then the washing solution which contained sodium carbonate or oxalic acid were contacted with loaded solvent. Figure 6 shows the washing ratios determined in the experiment. Non of troublesome phenomena was found during washing procedure.

From the study on regeneration of degraded TRUEX solvents, crud formation was observed when such elements as Ru and Zr were retained in the solvent, even in the case of non-irradiated solvent. The amount of crud was apparently greater than in 30% TBP in n-dodecane. Thus, the condition of crud formation should be searched in detail to design solvent regeneration process.

CONCLUSION

As a part of the long-term efforts to improve the future nuclear fuel cycle, experimental studies are in progress on the application of TRUEX process to the recovery of minor actinides from the highly active waste. In the batch experiments, fundamental distribution behaviors with the CMPO solvent have been clarified for typical actinide elements and fission products. The boundary to avoid the third phase formation has also been experimentally established in terms of TBP concentration in the mixed solvent, temperatures, and metal concentrations. Three mixer-settler runs have been conducted using actual highly active raffinate as feed solu-

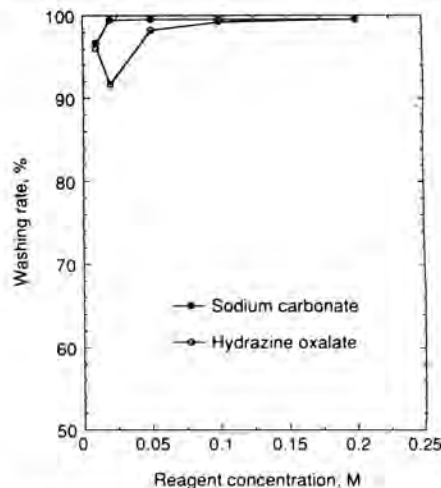


Fig. 6. The washing result of solvent containing uranium with sodium carbonate and hydrazine oxalate.

tions, and an excellent capability of the CMPO solvent has been demonstrated for actinide removal from the waste solution. However, further modification of the flowsheet is needed to improve the stripping efficiency for Pu and to decrease Ru retention as well as to add the capability to separate lanthanides from minor actinides. Aiming at these improvements, various studies are continuing.

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