

EMULSION AND ACCUMULATION AT AQUEOUS/ORGANIC
INTERFACE OF MIXER-SETTLERS

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EMULSION AND ACCUMULATION AT AQUEOUS/ORGANIC INTERFACE OF MIXER-SETTLERS

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Abstract

The emulsion which results from Di-n-butylphosphoric acid (HDBP) and zirconium (HDBP-Zr emulsion) was studied on the formation ratio to the emulsion of nonsoluble fission product residues (nonsoluble residues emulsion) in the codecontamination cycle without solvent washing. HDBP-Zr emulsion was found three times of nonsoluble residues emulsion by one week's operation of the codecontamination cycle with the spent nuclear fuel burnt to 28,000 MWd/MTU and cooled 1,000 days. In this codecontamination cycle, 1% HDBP was salted out at the aqueous/organic interface as HDBP-Zr emulsion, and 10% HDBP dissolved in the recycling solvent stream as HDBP-U complex. It was found that HDBP-Zr emulsion accelerates the volume growth of nonsoluble residues emulsion by the emulsifying effect.

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1. INTRODUCTION

The previous study¹⁾ was carried out to investigate the origin of emulsion formation at the aqueous/organic interface of mixer-settlers by a short time solvent extraction using the irradiated fuel with the burnup of 28,000 MWd/MTU and the cooling time of 1,000 days. The main element in the emulsion was ruthenium of which most parts remain undissolved in the dissolver solution of spent nuclear fuel as the nonsoluble fission product residues. At that time, zirconium was not detected in the emulsion. As those results, it was concluded that the emulsion did not result from HDBP-Zr complex, but from the nonsoluble fission product residues under a short time solvent extraction. However, HDBP-Zr emulsion is produced together with the nonsoluble residues emulsion when carrying on the solvent extraction process with the high burnup of spent nuclear fuel, or when encountering some troubles unavoidable to stop the process for a long time, as it is. In some cases, HDBP-Zr emulsion gives rise to hydrodynamic failures in the extraction steps^{2~4)}.

The present study was carried out to determine the formation ratio of HDBP-Zr emulsion to the nonsoluble residues emulsion in a long time operation of the codecontamination cycle without solvent washing.

2. EXPERIMENTAL

Figure 1 is the flowsheet operated for the present emulsion formation and measurement. The feed solution was prepared with the dissolver solution of the spent nuclear fuel with the burnup of 28,000 MWd/MTU and the cooling time of 1,000 days. The dissolver solution was used to prepare the feed solution without clarification. The residence time of organic stream in the mixing chamber was 1 min, and that of aqueous stream was 0.7 min. These residence times are much the same as those operated usually in full-scale reprocessing plant. The uranium and plutonium loading factor of the recycling solvent was 1 ~ 70% in the extraction section and 70% in the scrubbing section at the end of the operation, RUN A. The operation of mixer-settlers were two. One was one week's operation (RUN A). The other was two weeks

operation (RUN B). The bank of the mixer-settlers used for this experiment was made of plexiglas and completely transparent. The volume of mixing chamber is 27 ml, and that of settling chamber is 110 ml. The aqueous/organic interfacial space of settling is 28 cm². The mixing was done with the four wings turbine type stirrer. The stirring rate was 1,500 rpm. All of the emulsion was recovered at every stage for the measurement of volume and gamma emitting nuclides.

3. RESULT AND DISCUSSION

The obtained results of RUN A and RUN B are shown in Table 1 and 2. A noticeable amount of ⁹⁵Zr was determined together with ¹⁰⁶Ru in the emulsion. Figure 2 shows the ⁹⁵Zr and ¹⁰⁶Ru concentration profiles of RUN A and RUN B. In each extraction stage, the emulsion was almost equal in the volume and the concentration of ¹⁰⁶Ru and ⁹⁵Zr, respectively. In the scrubbing stage, the emulsion decreased in volume and the concentration of ¹⁰⁶Ru and ⁹⁵Zr with stage. From ¹⁰⁶Ru/⁹⁵Zr of the emulsion, the total Ru/Zr ratio 1/3 was obtained roughly that agreed with the total Ru/Zr ratio of the dissolver solution employed as the feed solution. While the total Ru/Zr ratio of the spent nuclear fuel with the burnup of 28,000 MWd/MTU and the cooling time of 1,000 days is 1/1.5, the nonsoluble ruthenium is nearly 50%^{5~9)} in the dissolution of such a high burnup fuel, and the real total Ru/Zr in the feed solution is also 1/3 as equivalent as the total Ru/Zr of the emulsion. Namely, it seems that a nearly equivalent emulsifying effect is expected between ruthenium and zirconium in the finishing point of RUN A.

For the present emulsion measurements, 10ℓ of 30% TBP/n-dodecane was used recycling without solvent washing. About 2,000 ppm HDBP was determined in the recycling solvent of RUN A. If all the HDBP made the complex with zirconium and salted out zirconium in the emulsion, the amount of zirconium in the emulsion should reach about 4 g. But the amount of zirconium in the emulsion was calculated as 3×10^{-2} g from the volume of emulsion and the zirconium concentration in each stage of the mixer-settlers. 3×10^{-2} g zirconium is equivalent to about 1% of 4 g zirconium calculated on the assumption that all the HDBP in RUN A makes the complex with zirconium,

Zr-2HDBP. Namely, only 1% HDBP makes the complex with zirconium in RUN A. At the finishing period of operation, 0.1 g/l of uranium was found in the aqueous raffinate coming out from the mixer-settlers. HDBP still binds uranium and plutonium in the organic stream of the back extraction section. The back extraction with diluent nitric acid strips only 10% HDBP¹⁰⁾. The rest remains in the organic stream and circulates in the extraction process. The uranium bound with HDBP shows the distribution coefficient of nearly 1 at the first stage under the process condition employed for the present codecontamination cycle¹¹⁾. Therefore, the recycling solvent holds 0.1 g/l of uranium. The amount of uranium bound with HDBP is expected to be 1 g from the total volume of recycling solvent. 1 g uranium corresponds to 10% of the 10 g uranium which all the HDBP, 20 g in the recycling solvent is assumed to associate with. From these results obtained, it was understood that the recycling solvent held about 90% free HDBP.

Figure 3 shows the volume of mixed emulsions and the mean thickness calculated from the interfacial space of settler. These were found an exponential increase of the mixed emulsions in volume in RUN B. This result differs from the expectation that HDBP-Zr emulsion increases in proportion to radiated exposure of the solvent. Gamma spectrometry measured almost same ¹⁰⁶Ru concentration to that of RUN A, but lower ⁹⁵Zr concentration as shown in Fig. 2. It means that the nonsoluble residues emulsion is formed with a same residues concentration in both RUN A and RUN B. On the other hand, HDBP-Zr emulsion decreased in concentration till one-tenth of the concentration obtained in RUN A. The decrease of HDBP-Zr emulsion was caused by the tenfold volume increase of the nonsoluble residues emulsion. From these results, it appears that HDBP-Zr emulsion remains in almost formation rate in one to two weeks operation of the codecontamination cycle.

The exponential increase of nonsoluble residues emulsion can be explained on the basis of the following expectation.

- (1) HDBP-Zr emulsion has an emulsifying effect to collect a certain amount of nonsoluble residues emulsion and forms the mixed emulsion.
- (2) The formed mixed emulsion furthermore collects the nonsoluble fission product residues to increase the volume.

As to the nearly same yield of HDBP-Zr emulsion in RUN A and RUN B, there is not found out any satisfying explanation except the measurement error

derived from an analytically detectable limitation of ^{95}Zr .

The result of RUN A agreed with the result of Ochsenfeld et al⁴) that the emulsion, they call crud, is mainly composed of HDBP-Zr complexes accompanied with the fine particles of nonsoluble residues. However, the result of RUN B showed that the main part of emulsion changed from HDBP-Zr complex to the nonsoluble fission product residues by the emulsifying effect of the mixed emulsions of HDBP-Zr complex and the nonsoluble product residues.

4. CONCLUSION

HDBP-Zr emulsion was studied on the formation yield in the codecontamination cycle. About 1% of HDBP produced at one week's operation of the codecontamination cycle without solvent washing formed HDBP-Zr emulsion. It was found that HDBP-Zr emulsion accelerates the formation of nonsoluble residues emulsion and accumulates at the aqueous/organic interface of mixer-settlers. Ordinary codecontamination cycle has the solvent washing process and prevents HDBP from accumulating in process. Therefore, the most of emulsion formed and accumulated in ordinary codecontamination cycle is concluded to originate from the nonsoluble fission product residues that are transferred from the dissolution process and remains suspended in the feed solution to solvent extraction process.

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Table 1 Activity of Fission Products in Emulsion (RUN A)

Nuclide	Stage					
	1	5	9	10	13	15
^{241}Am	6.3×10	1.2×10^2	4.0×10	5.7	9.8×10^{-1}	4.7
^{137}Cs	6.6×10^3	7.0×10^3	3.6×10^3	6.6×10^2	9.6	6.3×10
^{125}Sb	2.3×10^2	1.6×10^2	1.3×10^2	1.0×10^1	3.6×10^{-1}	2.5
^{106}Ru	2.1×10^4	1.6×10^4	2.4×10^4	4.6×10^2	7.4×10	2.4×10^2
^{95}Zr	1.8×10	1.1×10	3.1×10	1.7	1.3	2.8×10^{-1}

Note: Burnup = 28,000 MWd/MTU
 Cooling time = 1,000 days
 Activity = mCi/l

Table 2 Activity of Fission Products in Emulsion (RUN B)

Nuclide	Stage					
	2	5	9	10	13	15
^{241}Am	1.8	—	—	1.5	2.3×10^{-1}	1.8×10^{-1}
^{137}Cs	5.2×10	7.8×10	4.0×10	1.3×10^2	1.3×10	6.4
^{125}Sb	4.3×10	1.0×10	7.4×10	9.0	1.5	1.6
^{106}Ru	7.0×10^3	2.0×10^3	2.1×10^4	1.2×10^3	4.0×10^2	4.2×10^2
^{95}Zr	2.0*	—	2.5*	4.9	1.0×10^{-1}	2.2×10^{-1}

Note: Burnup = 28,000 MWd/MTU
 Cooling time = 1,000 days
 Activity = mCi/l
 * estimated from ^{95}Nb

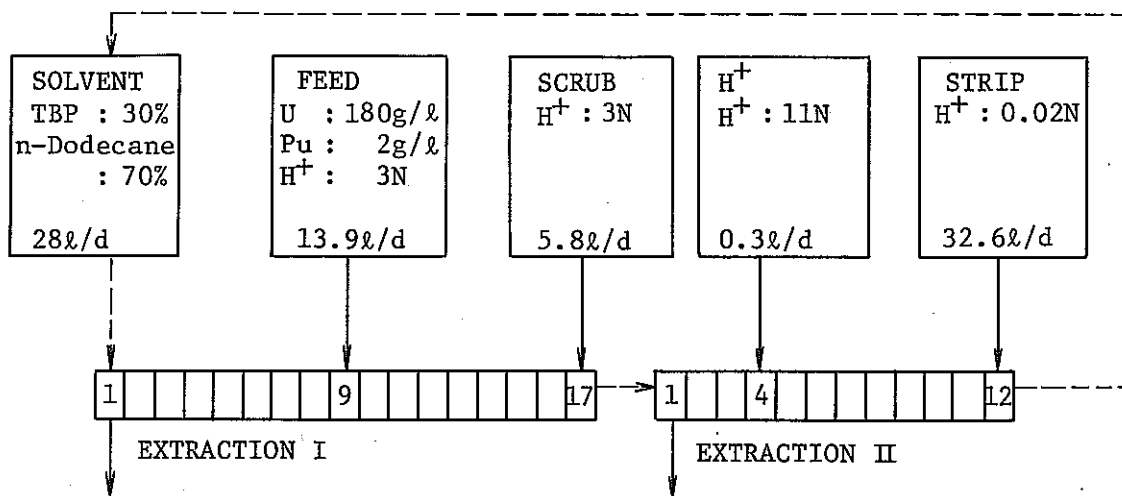


Fig. 1 Experimental flow sheet

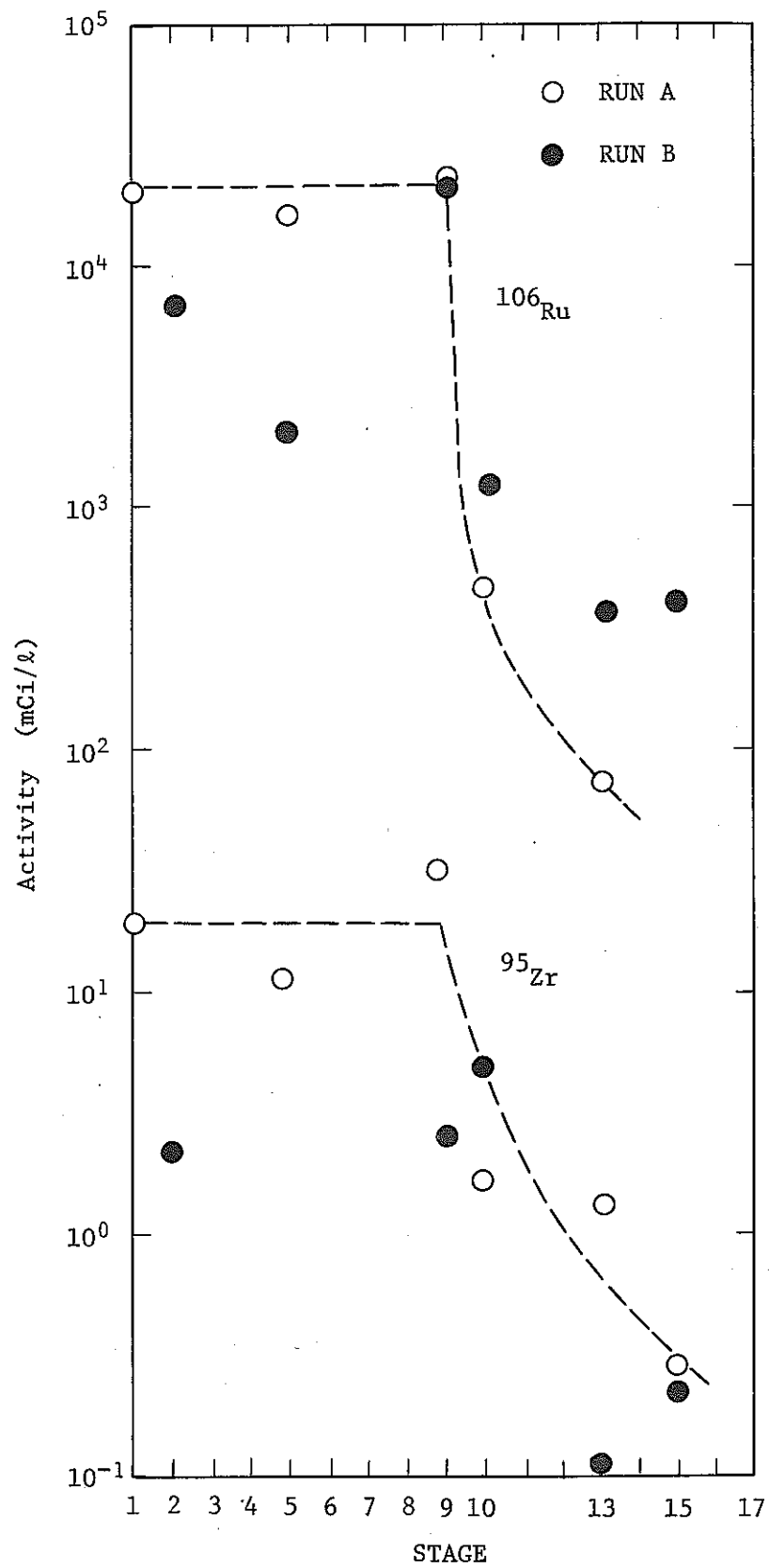


Fig. 2 Concentration profiles in extraction I bank

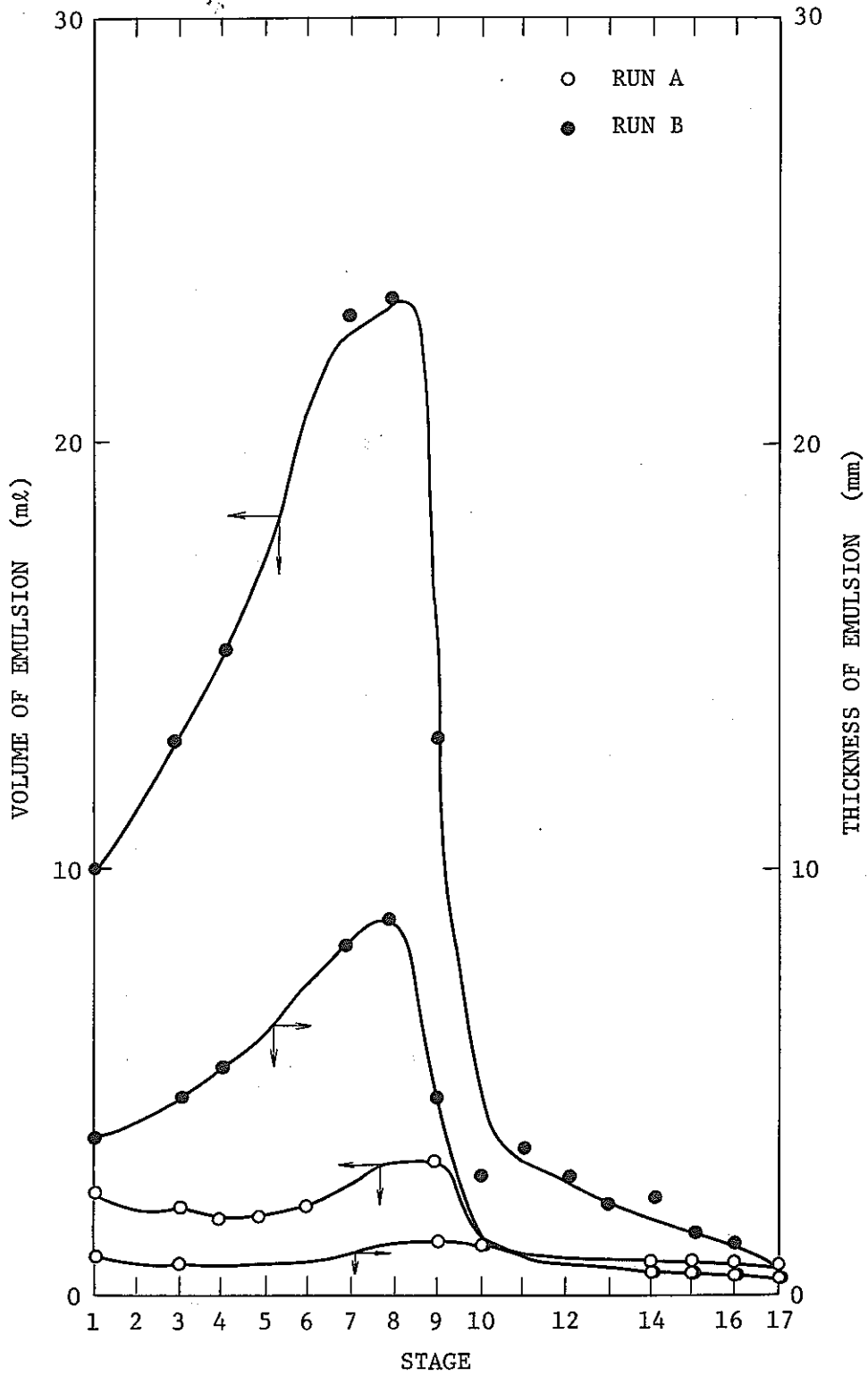


Fig. 3 Volume and thickness of emulsion in mixer-settlers