Effect of O/A Ratio on Extraction Performance of Centrifugal Contactor

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The PUREX process is widely used in reprocessing plants for spent nuclear fuel. In the process, uranium and plutonium are completely separated in the partitioning stage, and this increases the risk of nuclear proliferation. Japan Atomic Energy Agency (JAEA) has constructed a co-processing process that recovers plutonium with a part of uranium in the partitioning stage. The process requires a higher O/A ratio, which indicates the flow ratio of the organic phase and the aqueous phase, as opposed to a conventional PUREX process. Additionally, JAEA discusses the application of a centrifugal contactor that separates the aqueous and organic phases from a mixed phase by using a strong centrifugal force due to the rapid rotation of the rotor for an advanced solvent extraction process. This study investigates the effects of the O/A ratio on the extraction and back extraction performances of uranium in a centrifugal contactor.

1. Introduction

The PUREX process is a widely used process in present fuel reprocessing plants; the process separates plutonium and uranium in the partitioning stage. However, plutonium isolation increases the risk of nuclear proliferation, and thus, a co-processing process modified PUREX process was developed with the co-recovery of Pu and U [1-3]. The co-processing process reprocesses fuels at a higher O/A ratio, which denotes the flow ratio of the organic phase and the aqueous phase, than the PUREX process.

JAEA has developed an annular type centrifugal contactor for solvent extraction in spent fuel reprocessing, which allows the mixing of the aqueous and organic phases in the annular area and their separation inside the rotor [4-5]. Given these characteristics, a centrifugal contactor offers attractive advantages such as a more compact design and a shorter liquid residence time, when compared to conventional contactors such as a mixer settler or a pulsed column [6-8].

In this study, the effects of O/A ratio on extraction and back extraction performances of a centrifugal contactor were investigated to appropriate the centrifugal contactor for the co-processing process.

2. Experimental

2.1 Equipment

The basic structure of the centrifugal contactor is shown in Figure 1. It comprises a motor, a driving unit, a rotor, and housing. In the study, the centrifugal contactors with a rotor 25 mm in diameter were used. The extraction and back extraction performances were studied by using single stage and four stage centrifugal contactors (Figure 2), respectively. The rotor speed was controlled at 3,500 min^{-1} across all the experiments.

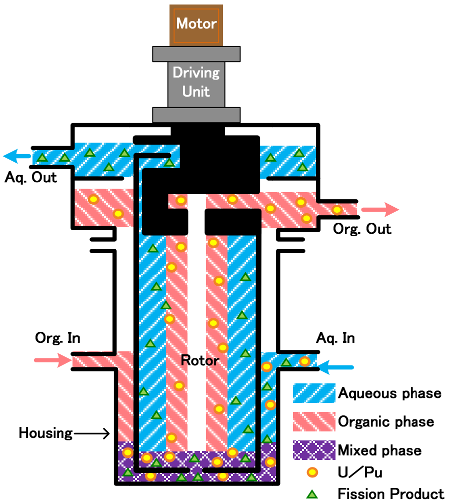

Figure 1. A schematic of the extraction process of a centrifugal contactor

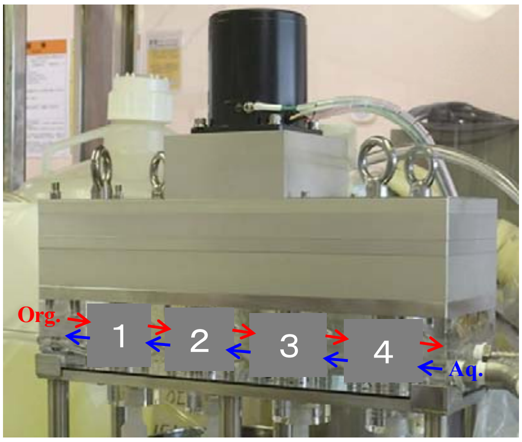

Figure 2. A four-stage centrifugal contactor

2.2 Extraction and back extraction conditions

In the extraction test, 23 g/L uranium nitrate / 3 mol/L HNO_3 solution was prepared as the aqueous phase, and 30 vol%TBP-n dodecane was prepared as the organic phase. Prior to the extraction test, the organic phase was contacted with 3 mol/L HNO_3 solution by using an O/A ratio of 1 for the HNO_3 equilibrium. In the back extraction test, a 0.02 mol/L nitric acid solution was prepared as the aqueous phase, and 30 vol% TBP-n dodecane (including 11 g/L uranium) was prepared as the organic phase. The operational conditions are shown in Table 1. The O/A ratio in the extraction test changed from 0.2 to 30, and then total flow rates were controlled at 2 L/h, 6 L/h, and 12 L/h, respectively. The O/A ratio in the back extraction test changed from 0.03 to 30 at a total flow rate corresponding to 6 L/h. The samples were regularly collected from the contactors during the extraction and back extraction tests. Uranium concentrations of the supplied and discharged solutions were measured by performing a spectroscopic analysis of V-660 (JASCO). In the back extraction test, uranium concentrations were measured at each stage to evaluate the changes in the uranium concentration profile.

Table 1. Operational conditions

Test	O/A ratio	Total Flow rates (L/h)
Extraction	0.2, 0.5, 1, 2, 5, 10, 30	2, 6, 12
Back extraction	0.03, 0.1, 0.2, 0.5, 1, 2, 5, 10, 30	6

2.3 Procedures

Prior to the extraction of uranium, 3 mol/L HNO_3 was supplied to the centrifugal contactor as the aqueous phase. Subsequently, 30 vol % TBP-n dodecane was supplied as the organic phase. After the stable operation of the centrifugal contactor, the feed of 3 mol/L HNO_3 was replaced by 23 g/L uranium nitrate solution / 3 mol/L HNO_3. The O/A ratio was changed every 10–30 min in the test. The effects of the O/A ratio in the extraction tests were evaluated by stage efficiency determined by the following equation (Murphree efficiency):

$$E = \frac{U_{Aq.feed} - U_{Aq.product}}{U_{Aq.feed} - U_{Aq.product \cdot in \cdot equilibrium \cdot exp.}} \times 100 \qquad (1)$$

where E denotes the stage efficiency, $U_{Aq.feed}$ denotes uranium concentration [g/L] in the aqueous feed solution, $U_{Aq.product}$ denotes uranium concentration [g/L] in the discharged aqueous solution, and $U_{Aq.product\ in\ equilibrium\ exp.}$ [g/L] denotes uranium concentration in the discharged aqueous solution after estimating the equilibrium by using batch-wise tests.

In the back extraction test, 30 vol% TBP-n dodecane (including 11 g/L uranium) was supplied (Figure 3 depicts the flowsheet of the back extraction test) after supplying a 0.02 mol/L nitric acid solution to the centrifugal contactor and discharging it from the centrifugal contactor through four stages. The O/A ratio was also changed every 10–30 min. The effects of the O/A ratio on the back extraction tests were evaluated by comparing it with the uranium concentration profiles calculated using MIXSET-X [9].

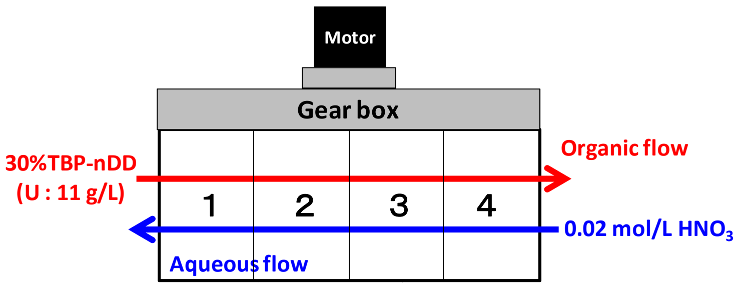

Figure 3. A flowsheet of the back extraction test

3. Results and Discussion

3.1 Extraction performance

Figure 4 depicts the changes in the flow rates and O/A ratios in the extraction test at a total flow rate of 2 L/h. During the operation, the flow rates and the O/A ratios were correctly changed as planned. Additionally, neither overflow nor entrainment was observed, and this implies that the organic and aqueous phases were separated. These results were confirmed across all the extraction tests.

Figures 5, 6, and 7 show the effects of the O/A ratio on stage efficiencies at total flow rates corresponding to 2 L/h, 6 L/h, and 12 L/h, respectively. The stage efficiencies corresponded to approximately 100 % in any condition with the exception of the condition with low flow rate and O/A ratio. The tendencies could be caused by insufficient mixing, which was formed by less liquid volume in the mixing zone, and a few differences in the O/A ratio between the batch-wise tests and the experimental study. Therefore, a total flow rate of 12 L/h (Figure 7) with a sufficient volume for the organic phase exhibited 100% stage efficiencies in all O/A ratio conditions.

The results indicate that the centrifugal contactor exhibits sufficient extraction performance under a wide range of O/A ratios.

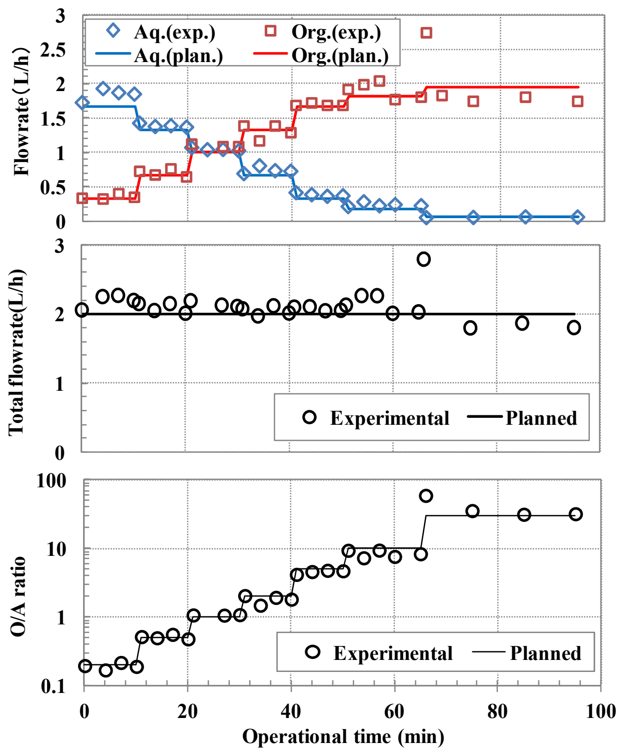

Figure 4. Changes in the flow rates and O/A ratios at a total flow rate of 2 L/h (Extraction tests)

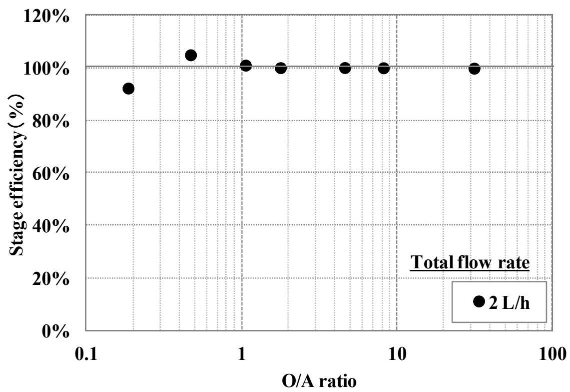

Figure 5. Effect of the O/A ratio on stage efficiency at a total flow rate of 2 L/h (Extraction tests)

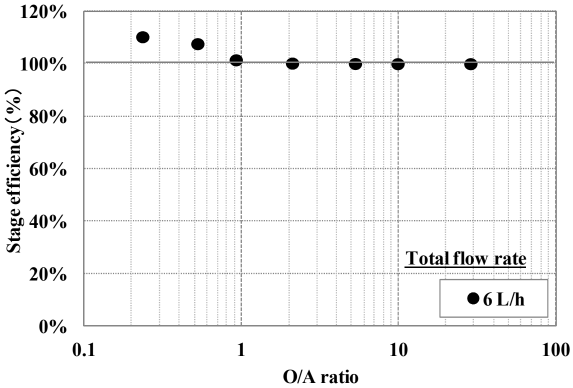

Figure 6. Effect of O/A ratio on the stage efficiency at a total flow rate of 6 L/h (Extraction tests)

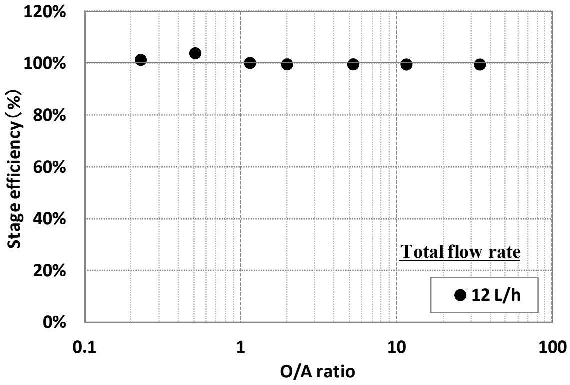

Figure 7. Effect of O/A ratio on the stage efficiency at a total flow rate of 12 L/h (Extraction tests)

3.2 Back extraction performance

Figure 8 depicts the changes in flow rates and O/A ratios in the back extraction test in which the total flow rate corresponded to 6 L/h. The flow rates and the O/A ratios were correctly changed during the operation. However, entrainment was observed at an O/A ratio of 30. It was affected by a lower difference in density between the aqueous phase and organic phase (0.17 g/cm^3) when compared with that of the extraction test (0.30 g/cm^3).

Figure 9 depicts the uranium concentration profile at an O/A ratio of 0.1. The uranium concentration in the organic phase constantly decreased from stage No.1 to stage No. 4. Additionally, uranium concentrations in stage No.3 and stage No.4 were lower than the detection limit of the spectroscopic analysis. This tendency was also confirmed in the conditions with an O/A ratio of less than 0.2.

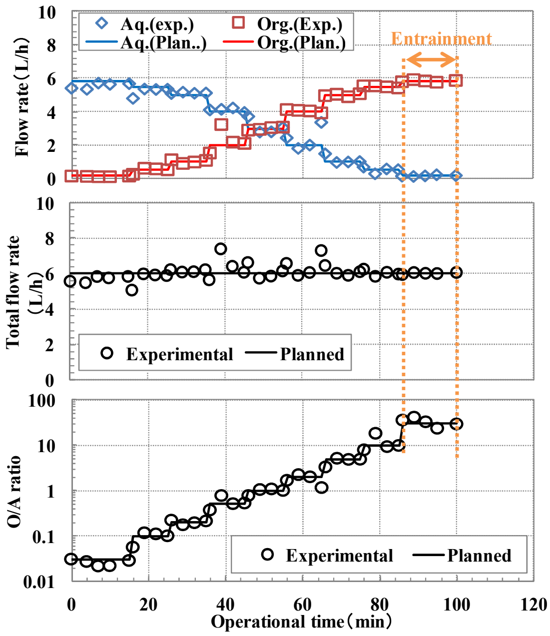

Figure 8. Changes in the flow rates and O/A ratios at a total flow rate of 6 L/h (Back extraction tests)

The O/A ratios of 0.5, 1, and 2 decreased the uranium concentration in the organic phase through the four stage centrifugal contactors (Figure 10 depicts the result at the O/A ratio of 1). With respect to an O/A ratio exceeding 5, the uranium concentration of the organic phase barely decreased through the four stage centrifugal contactors (Figure 11 shows the results for an O/A ratio of 10).

The tendencies are attributed to the transfer of NO_3^- required by the uranium transfer between the organic and aqueous phases as follows:

$$H^+{}_{(Aq.)} + NO_3^-{}_{(Aq.)} + 2TBP_{(Org.)} \Leftrightarrow HNO_3 \cdot TBP_{(Org.)} \quad (2)$$

$$UO_2^{2+}{}_{(Aq.)} + 2NO_3^-{}_{(Aq.)} + 2TBP_{(Org.)} \Leftrightarrow UO_2(NO_3)_2 \cdot 2TBP_{(Org.)} \quad (3)$$

The reaction from the left side to the right side shows the extraction process, and the reaction from the right side to the left side shows the back extraction process. As shown in the equations, HNO_3 and UO_2 were extracted by forming HNO_3-TBP and UO_2^{2+}-NO_3^--TBP complexes, respectively, in the organic phase. In the back extraction, transfer of NO_3^- from the organic phase to the aqueous phase preceded that of UO_2^{2+} due to a larger mass transfer coefficient of NO_3^- [10]. The phenomenon increased the HNO_3 concentration in the aqueous phase. The influence of the increase in HNO_3 concentration increased at a higher O/A ratio, and thus the back extraction of UO_2 was prevented.

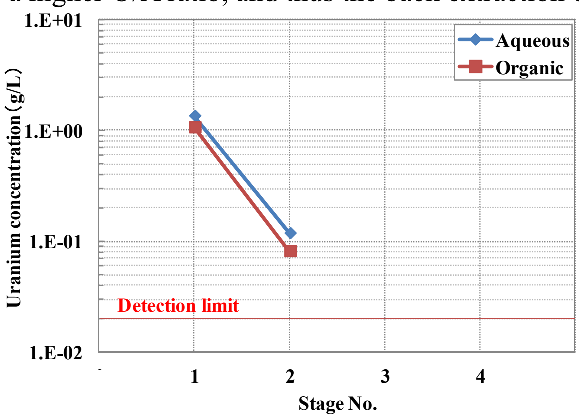

Figure 9. Profile of uranium concentration at a O/A ratio of 0.1
(Back extraction tests)

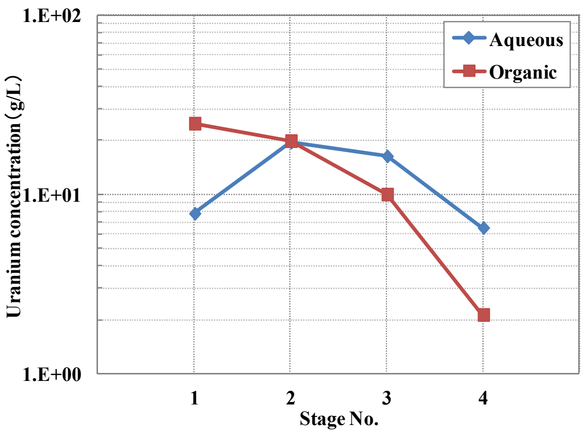

Figure 10. Profile of uranium concentration at a O/A ratio of 1
(Back extraction tests)

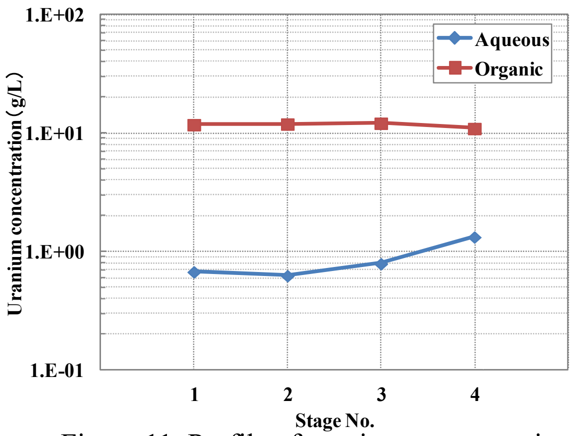

Figure 11. Profile of uranium concentration at a O/A ratio of 10
(Back extraction tests)

The experimental results of uranium profiles were also compared with the MIXSET-X calculation results. It was confirmed that the uranium concentration profiles in the tests at an O/A ratio of less than 2 were in agreement with those calculated by MIXSET-X with 90%–100% stage efficiency (Figure 12 depicts the result at an O/A ratio of 0.1). The tendency was also observed in experiments involving a higher size of the centrifugal contactor such as an 80 mm rotor [5]. In contrast, at an O/A ratio exceeding 5, stage efficiencies were indicated over 100% (Figure 13 shows the result for the O/A ratio of 10). The concentration profiles of HNO_3 at O/A ratios of 0.1 and 10 are shown in the Figures 14 and 15, respectively. The concentration profile of HNO_3 at the O/A ratio of 0.1 was in agreement with that calculated by MIXSET-X with a stage efficiency of 100% (Figure 14). However, at the O/A ratio of 10, the concentration profile of HNO_3 was in agreement with the calculation result with a stage efficiency of approximately 60% (Figure 15). This implies that the transfer of HNO_3 from the organic phase to the aqueous phase was insufficient. This tendency was influenced by a shorter residence time of the centrifugal contactor when compared with the MIXSET-X calculation results.

The results indicate that the centrifugal contactor normally performs the back extraction of uranium with an O/A ratio of less than 2. In this condition, the behavior of uranium is evaluated by MIXSET-X with 90%–100% stage efficiency.

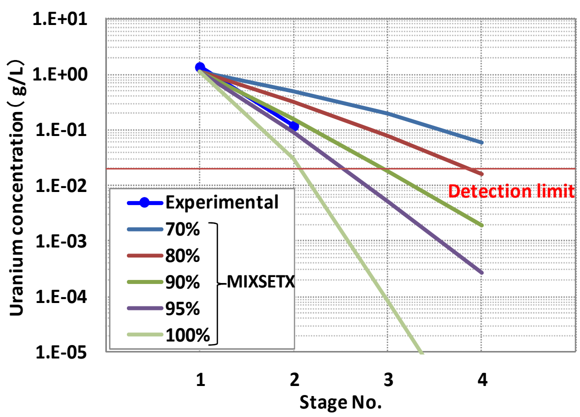

Figure 12. A comparison of uranium concentration in the aqueous phase at a O/A ratio of 0.1 (Back extraction tests)

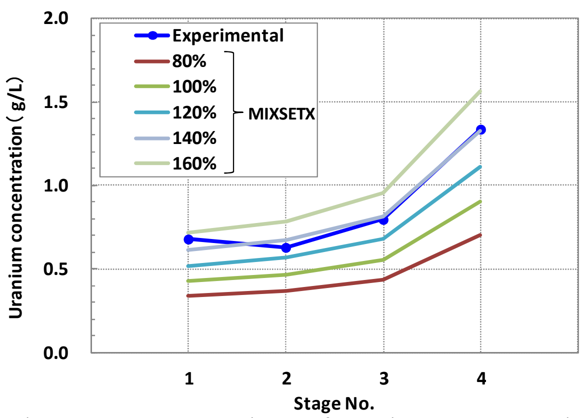

Figure 13. A comparison of uranium concentration in the aqueous phase at a O/A ratio of 10 (Back extraction tests)

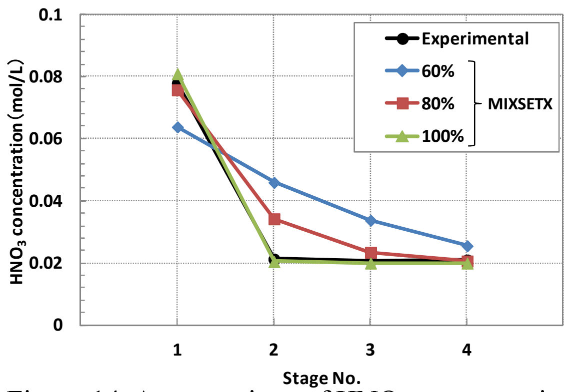

Figure 14. A comparison of HNO_3 concentration in the aqueous phase at a O/A ratio of 0.1 (Back extraction tests)

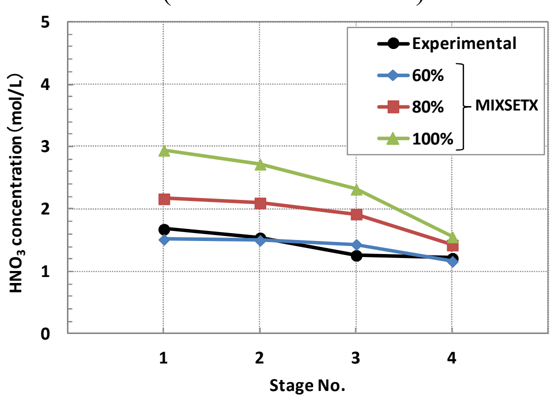

Figure 15. A comparison of HNO_3 concentration in the aqueous phase at a O/A ratio of 10 (Back extraction tests)

4. Conclusion

In this study, the effects of O/A ratio on extraction and back extraction performances of uranium in the centrifugal contactor were investigated to apply the same to the co-processing process. The centrifugal contactor was applied to the uranium extraction process with a high stage efficiency in conditions with a wide range of O/A ratios. The back extraction of uranium was achieved at an O/A ratio of less than 2 by the centrifugal contactor. In this condition, the behavior of uranium was evaluated by MIXSET-X with 90%–100% stage efficiency.

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