STUDY OF APPLICABILITY OF CRYSTALLIZATION TO PUREX PROCESS

A. Shibata, Y. Koma, T. Koyama, H. Funasaka
Japan Nuclear Cycle Development Institute

Abstract

The PUREX process in the advanced fuel recycle will be simplified, in order to achieve cost reduction, waste minimization for environment and nuclear proliferation resistivity. One of applicable technologies to support the PUREX process is crystallization of uranium prior to the solvent extraction. Crystallization requires neither extracting solvent nor additional reagent. Therefore, it can contribute to reduce the volume of waste solution and the size of equipment of the reprocessing process.

First we designed the process adapted crystallization technology and the reference process simplified PUREX. Next we compared both processes in equipment and mass flow.

When the process adapted crystallization is introduced, equipment and vessels are miniaturized. Mass flow is also reduced certainly, and extra nitric acid and very low-level liquid waste is decreased largely. The PUREX with crystallization is helpful to improve the reprocessing process.

1. Introduction

The PUREX process should be simplified for the advanced fuel recycle, in order to achieve cost reduction, waste minimization for environment and nuclear proliferation resistivity. Crystallization is one of applicable technologies to support the PUREX process. Crystallization requires neither extracting solvent nor additional reagent. Therefore, it can reduce the volume of waste solution and the size of equipment.

Application of crystallization for U purification has been reported by KfK (1,2). In Japan, Tokyo Electric Power Company and Mitsubishi Materials Corporation also investigated applicability of crystallization technology to U purification process (3).

For that purpose, crystallization technology is introduced as a pre-process of the PUREX process. In this system, crystallization removes a large quantity of U from the dissolver solution. In this paper, the process flow diagram adapted crystallization technology will be described and compared with the simplified PUREX process for the advanced fuel recycle.

2. Process Development

The process adapted crystallization technology

In the KfK process (1,2), the feed solution was concentrated and adjusted to 5.8 M nitric acid and 1.5 M uranium. The first crystallization was conducted by cooling the solution from +30 to –30 °C in half an hour. The resulted UNH was dissolved and provided for the second crystallization step. The recovery of uranium was more than 90 %.

In our process, uranium nitrate crystallization is applied as pre-process for the solvent extraction. Figure 1 shows the process adapted crystallization. Feed solution is the dissolver solution. Crystallization section separates surplus uranium for FBR core fuel fabrication. The recovery of uranium is about 60 % to roughly obtain the Pu/U ratio for the core fuel. The crystallization is conducted by cooling the solution from +40 to +10 °C. Thus, high recovery of U is not needed and the process can be operated at higher temperature compared to the case of application for purification process. The residual solution is called the mother solution. The mother solution is fed to the co-decontamination section of the PUREX process.

The volume of the mother solution is smaller than that of the dissolver solution for the process without crystallization. So mass flow fed to the extraction section (extracting solvent, scrubbing solution and stripping solution) is reduced. This process strips U and Pu together and does not have Pu partitioning. This contributes to non-proliferation.

Different from the application for purification, there are many impurities in the dissolver solution. Table 1 shows the results of washing procedure experiment that was performed with simulated dissolver solution. The composition of the dissolver solution is summarized in table 2.

First the solution was cooled to 10 °C and uranium nitrate crystal was produced. Slurry of U crystal was filtrated. Next the crystal was washed with nitric acid. Washing operation was repeated for 3 times.

When Uranium crystal was not washed, DF was less than 10. Repeated washing improves decontamination of fission products (FPs). When washing was repeated three times, DF was 10-100. Decontamination for FPs in crystallization section is basically dependent on washing procedure.

Table 1 Decontamination factor of each element in crystallization using simulated dissolver solution

element	Rb	Sr	Y	Zr	Mo	Ru	Rh	Pd	Cd	Te	Cs	Ba	La

No washing	3	4	6	9	4	6	4	2	6	8	7	2	6
3 times washing	50	50	100	50	10	50	50	50	100	50	100	30	100

Table 2 Composition of the simulated dissolver solution

element	U	Rb	Sr	Y	Zr	Mo	Ru	Rh	Pd	Cd	Te	Cs	Ba	La	HNO_3
Concentration (g/L)	600	0.34	0.73	0.40	4.18	2.51	2.37	0.69	2.09	0.37	1.03	5.97	2.56	1.88	2.1 M

Soft PUREX process

The process adapted crystallization technology will be applicable to the simplified PUREX process. In the advanced fuel recycle system, the PUREX process produces U product and Pu-Np-U mixed product solutions with lower decontamination, and will be optimized to reduce the amount of waste solutions (4). The process is called as "Soft PUREX (Simplified, Optimized and Fully Trusty PUREX)" (5).
Figure 2 shows the Soft PUREX process that does not have purification sections. Because co-decontamination section can decontaminate FPs enough to make fuels adequate for the advanced fuel recycle system. Pu product is supplied to core fuel fabrication and U is supplied to blanket fuel fabrication.
This process never treats pure Pu and does not partition Pu and U thoroughly. The Pu product contains Pu, some U and a little FPs.
This simplified process is shorter than the conventional reprocessing process. Amount of the mass flow is reduced from the conventional reprocessing process. So waste solution is also reduced.

3. Process Comparison

The process that crystallization is adapted was compared with the Soft PUREX process.
First, reprocessing plants which is based on the Soft PUREX process and the process adapted crystallization were designed. The following items are premise for designing a process.
- Spent core fuel and spent blanket fuel are treated together,
- Co-recovery of Pu with U (U:Pu=3:1),
- U and Pu product is supplied to blanket fuel and core fuel fabrication, respectively,
- Plant scale is 500 kg-Heavy Metal per day,
- Plant operates 200 days per year.

Next, mass balance of each element and reagent was calculated. And the number of equipment and the volume of vessels were also calculated. These two plants were compared in the view of process simplicity, equipment and mass flow.
For convenience' sake the plant based on the process with crystallization is called plant A and the plant based on the Soft PUREX process is called plant B.
Table 3 shows the comparison of the processes. In the dissolution section, plant A needs high U and Pu concentration and high acidity. In plant A, clarification section needs to be heated, because U crystallization must be avoided before crystallization section. In plant A, crystallization section recovers 60 % of U. Extraction section co-recovers U and Pu in both plants. There is no Pu partitioning section and U stripping section in plant A.
A comparison of equipment is showed Table 4. Number of equipment in plant A is smaller than that in plant B except shape-controlled vessel. Also the volume of vessels in plant A is smaller than that in plant B. Evaporator capacity in plant B is two times as large as that in plant A.

Table 3 Comparison of the processes

Process	dissolution	clarification	crystallization	extraction
Plant A	High U/acid concentration	Heated	Recovery of 60% U	No Pu partitioning, No U stripping
Plant B	conventional	Room temperature	No	Co-recovery of Pu and U

Table 4 Comparison of equipment

Equipment	Centrifugal contactor	Shape-controlled vessel	Normal vessel	Evaporator capacity
Plant A	42 stages	21 vessels (14 m^3)	55 vessels (126 m^3)	12 m^3/d
Plant B	53 stages	17 vessels (18 m^3)	58 vessels (167 m^3)	27 m^3/d
Ratio (A/B)	0.79	1.2 (0.8)	0.95 (0.8)	0.44

Table 5 shows a comparison of mass flow. The volume of high-level liquid waste (HLW) of both plants is same, because plant scale is equal. Mass flow of nitric acid, TBP and very low-level liquid waste (VLLW) in plant A are smaller than those in plant B. Plant A strips Pu without reduction. So there is no hydroxylamine nitrate (HAN). And there is no extra nitric acid in plant A, because all nitric acid is recycled.

Table 5 Comparison of mass flow

Mass flow	Nitric acid (kg/d)	TBP (L/d)	HAN (mol/d)	HLW (m^3/y)	Extra nitric acid (t/y)	VLLW (t/y)
Plant A	782	760	0	15	0	1700
Plant B	964	1730	1080	15	50	3000
Ratio (A/B)	0.81	0.44	0	1	0	0.57

4. CONCLUSION

In this study, we evaluated the process with crystallization for the advanced fuel recycle.
When a process adapted crystallization is introduced, equipment and vessels are miniaturized. Mass flow is also reduced certainly, and extra nitric acid and VLLW is decreased greatly. And in this process Pu is not treated independently. So resistivity against Pu is enhanced. Further, reagents and solvents are decreased in the solvent extraction process. So chemical hazard from these reagents is reduced.

References

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