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Separation and recovery study of uranium from spent NaF (fillers)

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Abstract

The molten salt technique is considered to be a feasible technique applicable for the removal of uranium from the spent NaF (fillers). Simple spent NaF or NaF with NaCl, i.e. mixed salt, was used as an electrolyte and the uranium concentrations in the bath, pre-treatment condition, electrolytic temperature, current density, etc. were given as parameters in this experiment. Results from the fundamental experiments showed the potential applicability of the molten salt technique for the removal of uranium from spent NaF. © 2004 Published by Elsevier Ltd.

1. Introduction

Various kinds of chemical trap fillers such as sodium fluoride (NaF), magnesium fluoride (MgF₂), or activated alumina (Al₂O₃) are used for the removal of gaseous radionuclides, fluorine, etc. in the process off-gas of uranium conversion facility [1] or similar facilities. Gaseous uranium hexafloride (UF₆) is removed with the chemical trap charged with NaF ($3 \text{ mm}^{D} \times 3 \text{ mm}^{L}$) as adsorption fillers (adsorbent). As NaF has to be recharged when its adsorption efficiency decreases, the amount of radioactive waste increases during long-term operation of the facility. Therefore, uranium adsorbed on NaF should be separated and reused, wherever possible. A wet treatment process [2], fluoride volatility process [3], etc. are considered as feasible techniques applicable for this separation process.

The molten salt technique has been discussed as one of the promising uranium separation methods [4,5]. Results of fundamental experiments, the pre-treatment condition, electrolysis condition, composition of molten salt, etc. are presented here.

2. Experimental

2.1. Uranium compounds in spent NaF (fillers)

2.1.1. Determination of chemical compounds of uranium in fillers with X-ray diffraction analysis

The spent NaF used in this experiment was from the uranium conversion facility in Japan and was stored for several years after its 'breakthrough' due to the adsorption of gaseous UF_{6} .

As it is important to identify the characteristics of the uranium compounds adsorbed on NaF before experiment, the composition of spent NaF was investigated by X-ray diffraction analysis (XD-3AE, Shimadsu Co.). From the result, the presence of NaF, NaUF₆, Na₃UF₆ and Na₂UF₈ were confirmed but not uranyl fluoride (UO₂F₂) which was assumed to form due to reaction of UF₆ with moisture.

2.1.2. Conversion to involatile uranium compounds

 $2NaF \cdot UF_6(Na_2UF_8)$, which is formed by the adsorption of gaseous UF₆ on NaF, decompose and release gaseous UF₆

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Fig. 1. Schematic design of reduction apparatus.

again at high temperature. UF₆ is the main substance volatilized from NaF. Precaution should be taken to prevent the release of gaseous uranium compounds into the environment. One way to prevent uranium compounds from being volatilized at high temperature would be to convert them into involatile substances such as UF₄, whose vapour pressure is 650 Pa at melting point (1309 K) [6]. In this experiment, the glass retort attached to the electric heater was used as a reduction apparatus (refer to Fig. 1). The H₂ gas was supplied through the glass filter from the bottom of the retort and exhausted from the top to the off-gas line through the buffer chamber and HEPA filter. UF₆ could be reduced to UF₄ in reaction with H₂. UF₄ also forms involatile sodium uranium fluorides [7] with NaF such as NaF·UF₄ (NaUF₅), 2NaF·UF₄ (Na₂UF₆),3NaF·UF₄ (Na₃UF₇), etc.

2.2. Experimental condition of molten salt technique

A uranium separation and recovery experiment by the molten salt technique was carried out to obtain the recovery rate of uranium and the electrolytic condition for its realization. The schematic design of the apparatus used in the experiment of Run-1, 4, 5 and 6 is shown in Fig. 2. To prevent the cathode from dissolving, its material was changed from the low-carbon steel to the high purity graphite in Run-2. In Run-3, a crucible made of the high purity graphite (>99.9997%, Nippon Carbon Co., Ltd), which was ordinary graphite crucible treated at high temperature, was employed as the anode due to its wider surface area. The experimental parameters such as electrolytic temperature, current density, and uranium concentration in the bath are shown in Tables 1 and 2.



Fig. 2. Schematic design of electrolytic separation and recovery cell.

3. Results and discussion

3.1. Uranium separation and recovery from simple spent NaF

3.1.1. Reduction experiment of adsorbed uranium on simple spent NaF

The experiment of uranium reduction by H₂ was carried out to prevent the volatility of adsorbed uranium on NaF. 100 g of the spent NaF as sample was filled into the apparatus as shown in Fig. 1. Ar-7%H₂ gas whose volume flow rate was 200 ml/min at 773 K (the maximum reduction temperature) was used in this experiment. The chemical reaction between adsorbed uranium and H₂ is: $U^{6+} + H_2 \Rightarrow U^{4+} + 2HF$.

As the white fume of hydrogen fluoride (HF) was generated by this reduction, the progress of reaction could be observed visually. The reaction temperature was raised at every 100 K with H₂ gas being constantly and gradually fed to the glass retort charged with NaF. Although the generation of gaseous HF or UF₆ could not be observed at 373 K, reduction occurred at 473 K because white fume regarded as HF could be observed. There was no change to the NaF's colour at this stage. Then, the reaction temperature was raised to 573 K after 2 h of heating. At this point, white fume was re-generated, whereupon, NaF's colour changed into yellow green. UF₆ volatilization could not be observed at further rise of temperature from 473 to 573 K. However, when the temperature was raised from 573 to 673 K, gaseous UF₆ was generated. For the reaction temperature from 573 to 773 K, it was raised at every 50 K instead of the original 100 K, and held on for 2 h. Gaseous UF₆ could not be observed but NaF's colour changed from

Table 1

RUN no.	U concentration (before) (wt%)	Cathode size (mm)	Cathode area (cm ²)	Current density (A/cm ²)	Cell voltage (V)	U concentration (after) (wt%)
1	5.92	$10^{\text{OD}} \times 30^{\text{L}}$	9.4	0.2	approx. 1.3	4.63
2	7.5	$10^{\text{OD}} \times 30^{\text{L}}$	9.4	0.2	approx. 2.8	7.5
3	7.5	$5^{\text{OD}} \times 20^{\text{L}}$	3.1	6.4	approx. 4–12 (unstable)	7.5

Experimental conditions and results of uranium concentration in simple spent NaF at 1327 K

The measurement of current efficiency was unattainable caused by the dispropotionate reaction of uranium deposit.

Table 2 Experimental conditions and results of uranium concentration in spent NaF eutectic at 973 K

RUN no.	U concentration (before) (wt%)	Cathode size (mm)	Cathode area (cm ²)	Current density (A/cm ²)	Cell voltage (V)	U concentration (after) (wt%)	Current efficiency
4	9.47	$10^{\text{OD}} \times 30^{\text{L}}$	9.4	0.2	approx. 6	6.55	61.8
5	1.09	$15^{\text{OD}} \times 30^{\text{L}}$	14.1	0.02	approx. 7	0.007	15.2
6	0.02	$15^{\text{OD}} \times 30^{\text{L}}$	14.1	0.02	approx. 7	< 0.001	0.3

yellow green to deep green. It was found that U^{6+} adsorbed on NaF could be reduced to U^{4+} by raising the reaction temperature gradually (every 50 K) from 473 to 773 K.

3.1.2. Electrolytic separation and recovery experiment from simple spent NaF as electrolyte (RUN-1)

The reduction of U^{6+} (UF₆ and/or its double salts) to U⁴⁺ (UF₄ and/or its double salts) would be an effective method to prevent the generation of gaseous UF₆ from spent NaF during heating. The spent NaF treated by H₂ was used in the experiment from RUN-1 to RUN-3. The experimental temperature of the molten salt was 1323 K, and 0.2 A/cm² for the cathodic current density. The electrolodes were inserted into the bath approximately 7.5 min before the start of electrolysis. Then, the electrolytic decontamination was carried out with 1.88 A (0.2 A/cm² of the cathodic current density). The samplings of the bath were made every 1 h, and were analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES: Seiko Instruments Inc. SPS-7700). From the analytical results shown in Fig. 3, iron from the cathode (low-carbon steel) was found in the electrolyte together with uranium. The initial uranium concentration was approximately 6 wt% and it was 0.12 wt% for the iron concentration. Both (U and Fe) were likely to have their concentration levels reduced with a lapse of time. The condition remained relatively stable for 4 h with uranium concentration at approximately 5 wt% and approximately 0.01 wt% for iron.

The observation result of bath after experiment showed a brown layer on the electrolyte's surface. This could be due to the dissolution of the iron cathode caused by its reaction with fluorine in the electrolyte. The electrolyte was also taken out for observation of the inner crucible. It showed no corrosion which meant that the high purity graphite crucible was effectively corrosion-resistant. 3.1.3. Electrolytic separation and recovery experiment with high purity graphite anode (RUN-2)

The iron cathode was found to dissolve gradually in RUN-1. Therefore, the cathode material was changed from iron to high purity graphite for RUN-2, and the experiment was carried out under the same condition as RUN-1. The change of uranium concentration in the electrolyte and the uranium concentration in the deposit on the cathode surface are shown in Fig. 4. Here, the final uranium concentration in the deposit is approximately 16 wt%, while the rest is salt as electrolyte caught in the deposit. For all uranium existence in the deposit, uranium concentration in the bath was almost constant, i.e. approximately 8 wt%. This result was probably due to the disproportionate reaction expressed as ' $3U^{4+} + U \Rightarrow 4U^{3+}$ ' between deposited U and U⁴⁺ in the electrolyte but not due to the re-dissolution of the deposit falling off from the cathode.

3.1.4. Electrolytic separation and recovery experiment by high electrolytic current (RUN-3)

The high electrolytic current, i.e. $20 \text{ A} (6.4 \text{ A/cm}^2 \text{ for} \text{ the cathodic current density}), was employed to confirm$



Fig. 3. Change of uranium and iron concentration in electrolyte (Run-1).



Fig. 4. Change of uranium concentration in electrolyte using high purity graphite anode.



Fig. 5. Change of uranium concentration in electrolyte by high electrolytic current (Run-3).

the recovery efficiency drop by the re-dissolution of the deposit on cathode. Herein, as the vitreous carbon anode worn off vigorously, a high purity graphite crucible was made to act as the anode in order to create a stable condition for the high current density. The uranium concentration in the bath could not be reduced despite the application of higher electrolytic current as shown in Fig. 5. Extensive corrosion, however, was not obvious for the inner crucible after experiment. The above-mentioned results showed that high electrolytic current hardly contributed to the decontamination of NaF, instead it worsened the anode's condition. However, the uranium concentration in deposit did increase to approximately 25 wt% as expected.

4. Uranium separation and recovery experiments from eutectic

4.1. Eutectic point in NaF–NaCl system

The melting point of NaF (1269 K [8]) used as an electrolyte can be reduced by the use of some eutectic. Sodium chloride (NaCl) was selected because NaCl

possesses Na⁺ which is in common with NaF, and its melting point (1073.4 K) is lower than that of NaF. The lowest melting point of NaF–NaCl system is 945 K with 34 mol% NaF and 66 mol% NaCl [9]. As UF₆ in this system would form involatile compound which was found during the melting test of NaF–NaCl, UF₆ reduction by H₂ as pretreatment was not necessary for the recovery of uranium from NaF–NaCl system.

4.2. Separation and recovery experiment with high uranium concentration range (Run-4)

The mixed salt which contained 9.47 wt% of uranium was used as an electrolyte in order to confirm the possibility of the separation and recovery process of uranium using the molten salt technique. After placing the mixed salt in a high purity graphite crucible, a eutectic was formed at 973 K.

This experiment was carried out under the condition shown in Table 2 (Run-4). Analysis showed the uranium concentration reduced to 6.55 wt% after 4 h of the experimental operation (refer to Table 2 and Fig. 6), which meant that uranium recovery was feasible in a high uranium concentration range in the eutectic, and its current efficiency was 61.8%. Meanwhile, the thickness of the alumina sheath for the anode became thinner and the dendrite with eutectic was observed on the cathode.

4.3. Recovery experiment with medium uranium concentration range (RUN-5)

The mixed salt which contained 1.09 wt% of uranium was used as an electrolyte in order to confirm the possibility of uranium separation and recovery from the spent NaF under a medium uranium concentration range. A cathode $(10 \text{ mm}^{OD} \times 30 \text{ mm}^{L})$ was applied to establish 0.05 A/cm² as a lower electrolytic current density. From Fig. 7, the uranium concentration reduced to 0.007 wt% after 5 h of the experimental operation, and its current efficiency was 15.2%. There was no change for the thickness of the anode and precipitates were observed on the cathode.



Fig. 6. Result of uranium separation under high concentration of uranium (Run-4).



Fig. 7. Result of uranium separation under medium concentration of uranium (Run-5).



Fig. 8. Result of uranium separation under high concentration of uranium (Run-6).

4.4. Separation and recovery experiment with low uranium concentration range (RUN-6)

Conducted in succession Run-5, Run-6 were carried out using the uranium concentration attained in Run 5, i.e. 0.02 wt% for confirmation of the recovery possibility of uranium from the spent NaF below a hypothetical clearance level (0.001 wt%: this value is equal to the clearance level of 0.3 Bq/g of uranium concentration by IAEA Recommendation [10]), Fig. 8 shows the result of the change of uranium concentration to the quantity of electricity. Below the clearance level, could be achieved after 8 h of experimental operation. Its decontamination factor (DF) reached above 1000 in view of 1.09 wt% as its initial concentration. However, its current efficiency of 0.3% was very low. This electric loss is mainly due to the electrolysis of NaCl.

5. Conclusion

Fundamental experiment on the molten salt technique for uranium separation and recovery from the spent NaF was carried out to investigate its possibility for the decrease in the amount of radioactive waste from the uranium conversion facility and obtained results in this experiments are summarised as below:

- (a) From the results of X-ray diffraction analysis, $NaUF_{6}$, Na_3UF_{6} , and Na_2UF_8 were identified as some of the uranium compounds adsorbed on NaF;
- (b) Volatilitization of UF_6 from spent NaF could be effectively prevented by the reduction of UF_6 to UF_4 using the reducing agent, H_2 in this experiment;
- (c) The spent NaF, after treatment by H_2 reduction, can have the uranium removed by electrolysis. There was, however, difficulty in attaining the hypothetical clearance level caused by the disproportionate reaction, i.e. U^{3+} re-dissolution into the electrolyte.
- (d) With the use of mixed salt, i.e. NaF–NaCl system as the electrolyte, uranium in the bath would likely form some involatile compounds at the experimental temperature (973 K) without the need of reduction treatment. A sufficient recovery rate of uranium could be obtained using the NaF–NaCl eutectic due to the absence of the disproportionate reaction of uranium deposit at a relatively lower temperature. However, the current efficiency decreased markedly caused by the electrolysis of NaCl after long-time operation. From the viewpoint of waste reduction, not all the electric energy are lost as some are used for the document of NaCl. The economical realization of the molten salt technique should be further pursued.
- (e) After the removal of uranium from NaF, we should look into the possible recycling of NaF into a new resource as well as its safe disposal. The stable solidification of fluorides i.e. Na₃AlF₆, etc. or oxidation (NaF⇒Na₂O) is being considered as one of the disposal methods.

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