

論文 / 著書情報  
Article / Book Information

|                   |  |
|-------------------|--|
| 題目(和文)            | ベタインウム型イオン液体を用いた ウラン廃棄物からの 選択的ウラン分離法に関する基礎研究   |
| Title(English)    |  |
| 著者(和文)            | 森貴宏  |
| Author(English)   | Takahiro Mori  |
| 出典(和文)            | 学位:博士(工学),<br>学位授与機関:東京工業大学,<br>報告番号:甲第10372号,<br>授与年月日:2016年12月31日,<br>学位の種別:課程博士,<br>審査員:鷹尾 康一郎,竹下 健二,加藤 之貴,大貫 敏彦,塚原 剛彦  |
| Citation(English) | Degree:Doctor (Engineering),<br>Conferring organization: Tokyo Institute of Technology,<br>Report number:甲第10372号,<br>Conferred date:2016/12/31,<br>Degree Type:Course doctor,<br>Examiner:,,,,, |
| 学位種別(和文)          | 博士論文   |
| Category(English) | Doctoral Thesis  |
| 種別(和文)            | 論文要旨   |
| Type(English)     | Summary  |

## 論文要旨

### THESIS SUMMARY

|                          |       |    |  |                      |
|--------------------------|-------|----|--|----------------------|
| 専攻 :<br>Department of    | 原子核工学 | 専攻 | 申請学位 (専攻分野) :<br>Academic Degree Requested | 博士 (工学)<br>Doctor of |
| 学生氏名 :<br>Student's Name | 森 貴宏  |    | 指導教員 (主) :<br>Academic Advisor(main)       | 鷹尾康一郎                |
|                          |       |    | 指導教員 (副) :<br>Academic Advisor(sub)        | 高橋 実                 |

### 要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words )

From the start of commercial use of nuclear power, huge amount of radioactive wastes have been discharged in each stage of a nuclear fuel cycle. Especially, uranium contaminated steel materials and sludge are discharged as “uranium waste” from the frontend of the cycle. To reduce the volume of these uranium wastes and for recovery of uranium, development of decontamination methods are eagerly required. Although several decontamination methods such as solvent extraction, adsorption and precipitation have been proposed, these methods usually need to use of flammable materials (e.g. organic solvents or resins) which can be causes of conflagrations. The fundamental feasibility of an U(VI) separation and recovery method using betainium-type ionic liquid (IL) which has thermal stability, non-flammability and negligibly low vapor pressure was studied. The extraction chemistry of U(VI) by using betainium-type IL was mainly focused on since it is the most important part of the present method. This doctoral thesis consists of eight chapters as described below.

Ch. 1, the background of this thesis was introduced. The priority of chemical decontamination of the uranium wastes was mentioned by comparing with other methods. The protocol of the decontamination process using betainium-type IL was proposed. It was mentioned that the objective of this thesis is to investigate the fundamental chemical aspects in the separation and recovery method of uranium from the uranium wastes using betainium-type IL.

Ch. 2, extraction behavior of U(VI) in the [HGbet][Tf<sub>2</sub>N]–water system was investigated. The distribution ratio of U(VI) decreased with an increase in acid concentration of the aqueous phase. The formation of [UO<sub>2</sub>(Gbet)<sub>n</sub>]<sup>2+</sup> was assumed as an extractable species, which supported by optical spectroscopy and DFT calculations. The formation of [UO<sub>2</sub>(Gbet)<sub>2</sub>]<sup>2+</sup> followed by its coextraction with 3[Tf<sub>2</sub>N]<sup>-</sup> and [HGbet]<sup>+</sup> were proposed as an extraction mechanism.

Ch. 3, four novel betainium-type ILs ([Tf<sub>2</sub>N]<sup>-</sup> salt of [HAbet]<sup>+</sup>, [HVBet]<sup>+</sup>, [HLbet]<sup>+</sup> and [HIBet]<sup>+</sup>) were synthesized and characterized by <sup>1</sup>H and <sup>13</sup>C NMR. Physical properties of these ILs such as viscosity, pK<sub>a</sub> and water contents were measured. The *n*-octanol / water partitioning coefficient (log *P*<sub>ow</sub>) was evaluated as the criterion of hydrophobicity. As a result, it was revealed that the order of hydrophobicity follows [Gbet][Tf<sub>2</sub>N] < [HAbet][Tf<sub>2</sub>N] < [HVBet][Tf<sub>2</sub>N] < [HLbet][Tf<sub>2</sub>N] < [HIBet][Tf<sub>2</sub>N]. Especially log *P*<sub>ow</sub> of [HLbet][Tf<sub>2</sub>N] and [HIBet][Tf<sub>2</sub>N] (1.4 and 1.8, respectively) is very high compared with that of [HGbet][Tf<sub>2</sub>N] (-0.54).

Ch. 4, extraction behavior of U(VI) in the [HGbet][Tf<sub>2</sub>N], [HAbet][Tf<sub>2</sub>N], [HVBet][Tf<sub>2</sub>N], [HLbet][Tf<sub>2</sub>N] and [HIBet][Tf<sub>2</sub>N]-water system was studied. The extraction equilibrium was found to rapidly attain except for the [HIBet][Tf<sub>2</sub>N] system, where the extractability gradually increases with the elapse of time, taking more than 2 h. Because the rate of extraction was depend on the concentration of [HXbet]<sup>+</sup> (X = G, A, V, L and I) in the aqueous phase, the rate-determining step may be complexation of [UO<sub>2</sub>(Xbet)<sub>n</sub>]<sup>2+</sup>. From the result of slope analysis of pH - log*D* plots (slope ≈ 2), extracted complex was regarded as [UO<sub>2</sub>(Xbet)<sub>2</sub>]<sup>2+</sup>.

Ch 5, selective extraction of U(VI) was tested under contamination of Na(I), Ca(II), Al(III), Fe(II), Co(II) and Ni(II). All [HXbet][Tf<sub>2</sub>N] showed high selectivity for U(VI) compared with other metal ions. [HVBet][Tf<sub>2</sub>N], [HLbet][Tf<sub>2</sub>N] and [HIBet][Tf<sub>2</sub>N] extracted 90% of U(VI) while [HGbet][Tf<sub>2</sub>N] and [HAbet][Tf<sub>2</sub>N] extracted up to 50 - 70%.

Ch 6, recovery of U(VI) from [HXbet][Tf<sub>2</sub>N] and recycle of [HXbet][Tf<sub>2</sub>N] were conducted. U(VI) was recovered from [HXbet][Tf<sub>2</sub>N] by adding 30 wt% H<sub>2</sub>O<sub>2</sub>, and the recovery ratio was more than 90% in all [HXbet][Tf<sub>2</sub>N]. To ascertain the recyclability of [HXbet][Tf<sub>2</sub>N], the extraction-recovery cycle was repeated three times in each [HXbet][Tf<sub>2</sub>N]. As a result, the higher hydrophobicity of [HXbet][Tf<sub>2</sub>N] gives the higher recyclability of themselves.

Ch. 7, the dissolution behavior of uranium oxides in the [HGbet][Tf<sub>2</sub>N] was studied. Adding HNO<sub>3</sub> or [HGbet][NO<sub>3</sub>] as an oxidant, U<sub>3</sub>O<sub>8</sub> was completely dissolved at 90°C. [HGbet][NO<sub>3</sub>] should be preferable in terms of subsequent back extraction process. Although dissolution ratio of UO<sub>2</sub> increased by adding [HGbet][NO<sub>3</sub>], it was up to 10% even at 90°C and 2h.

Ch 8, all the results were summarized. It was concluded that the novel highly hydrophobic betainium-type ILs are useful for decontamination of the uranium wastes from perspectives of thermal stability, extractability, selectivity and recyclability.

備考 : 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

注意 : 論文要旨は、東工大リサーチリポジトリ (T2R2) にてインターネット公表されますので、公表可能な範囲の内容で作成してください。

Attention: Thesis Summary will be published on Tokyo Tech Research Repository Website (T2R2).