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Article / Book Information

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著者(和文)	CibulaMichal
Author(English)	Michal Cibula
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

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学生氏名： Student's Name	Cibula Michal	指導教員（主）： Academic Supervisor(main)	Kenji Takeshita
		指導教員（副）： Academic Supervisor(sub)	

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In nuclear reactors, various fission products (FPs) are produced as a result of nuclear fission reaction of ^{235}U or ^{239}Pu. Among these elements, platinum group metals (PGMs) – namely Pd, Rh and Ru – are generated in significant amounts. In the closed nuclear fuel cycle, which is utilized in Japan, Plutonium Uranium Redox Extraction (PUREX) process is being applied in order to recover Uranium and Plutonium for the purpose of recycling and increasing the efficiency of energy production. The remaining elements, including fission products, minor actinides and elements coming from the construction materials of fuel assemblies, remain dissolved in concentrated nitric acid solutions known as High Level Liquid Waste (HLLW). In order to safely dispose this radioactive waste, solidification in glass matrix (vitrification) and geological disposal is commonly accepted practice. Due to the chemical and physical properties of PGMs, the high content of these metals in HLLW makes the operation of the glass melter unstable (requiring frequent maintenance) and puts some limitations on the amount of radioactive waste, which can be included in the glass matrix – vitrificate. Moreover, because of the broad industrial use and high value of PGMs, the fission platinoids can be seen as alternative resource. By reducing the concentration of PGMs prior to the vitrification process, it is possible to achieve more stable operation, higher loading percentage of waste in glass matrix, therefore reduced volume of the final product and better homogeneity of the vitrificate, leading to more efficient and safer disposal of radioactive waste. In this thesis, solvent extraction of PGMs from nitric acid solutions was studied using *N,N'*-dimethyl-*N,N'*-ditolylthiodiglycolamide (MTTDGA) and tris(*N,N*-di-*2*-ethylhexyl-ethylamide)amine (EHTAA) dissolved in toluene or chloroform in batch extraction experiments.

MTTDGA was proven to be able to quantitatively extract $Pd(NO_3)_2$ in a wide range of nitric acid concentrations (0.5 – 8 M HNO_3). It has been found that the extraction mechanism, stoichiometry of the metal-ligand complex and extraction rate strongly depend on the concentration of nitric acid. In the lower acidity region (0.5 – 1 M HNO_3), the equilibrium time for Pd(II) extraction by MTTDGA was attained within 8 hours, forming 1:1 MTTDGA:Pd(II) complexes based on loading experiments. With higher concentration of nitric acid (2 – 8 M HNO_3), the equilibrium has been attained rapidly within 30 minutes forming 2:1 MTTDGA:Pd(II) complexes. Based on the Fourier-transform infrared spectroscopy (FT-IR), it was suggested that the amide oxygen atom(s) coordinated to Pd(II) in both the 1:1 and 2:1 MTTDGA:Pd(II) complexes, but the coordination mode of the MTTDGA molecule(s) differed. It was assumed that in the 2:1 complex, two MTTDGA molecules could bind to Pd(II) in a bidentate mode (via O and S atoms), whereas for the 1:1 complex, all donor atoms (2O and S) of one MTTDGA molecule could be involved in the coordination to Pd(II) and/or other species, including H^+.

Extractability of Ru(III) was studied using MTTDGA and EHTAA independently and in mixed solutions in order to investigate a possibility of synergistic effect of these two ligands. It was found out Ru(III) could be effectively extracted (~80% extraction percentage) from 6-8 M HNO_3 by MTTDGA, while the extraction percentage was <20% for 0.5-4 M HNO_3. Synergistic effect of MTTDGA and EHTAA was not found.

In case of Rh(III) extraction, the use of mixed solutions of EHTAA and MTTDGA showed significant increase of extraction rate and extraction percentage as compared to using EHTAA and MTTDGA independently. The synergistic effect was further confirmed by varying the ratio of MTTDGA/EHTAA concentrations in organic phase and the formed complex of MTTDGA:EHTAA:Rh(III) was assumed to have stoichiometry of 1:1:1. Similarly as in case of Ru(III) extraction, the extractability of Rh(III) by mixed solutions of MTTDGA and EHTAA increased with concentration of nitric acid, reaching its maximum at 8 M HNO_3.

Based on the differences in extractabilities of Pd(II), Rh(III) and Ru(III) which were found to be dependent on concentration of nitric acid, concentration of extractants and use of mixed solutions of MTTDGA and EHTAA, a separation flow allowing the mutual separation of Pd(II), Rh(III) and Ru(III) was proposed. In the first step, Pd(II) could be quantitatively extracted by MTTDGA from 2 M HNO_3, while Rh(III) and Ru(III) remained in the aqueous phase. After the increase of the concentration of HNO_3 from 2 M to 8 M, Ru(III) could be extracted by MTTDGA while Rh(III) remained in aqueous phase. In the last step, Rh(III) could be extracted by using a mixed solution of MTTDGA and EHTAA. This separation flow was tested using multi-element solutions, including PGMs and elements such as Al, K, Fe, Co, Cs, Ba and mass balance was calculated, showing that mutual separation of PGMs from nitric acid solutions by MTTDGA and EHTAA is viable.