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Title	Simulation study of sludge precipitation in spent fuel reprocessing
Author(s)	Takeuchi Masayuki, Aihara Haruka, Nakahara Masaumi, Tanaka Kotaro
Citation	Procedia Chemistry,21,p.182-189
Text Version	Published Journal Article
URL	https://jopss.jaea.go.jp/search/servlet/search?5055769
DOI	https://doi.org/10.1016/j.proche.2016.10.026
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5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles
Simulation study of sludge precipitation in spent fuel reprocessing

Masayuki Takeuchi^{a*}, Haruka Aihara^a, Masaumi Nakahara^a and Kohtaro Tanaka^b

^aJapan Atomic Energy Agency, 4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki, 319-1194, Japan

^bSimulation Technology Ltd. 1-1-1 Fukuura, Kanazawa-ku, Yokohama-shi, Kanagawa, 236-0004, Japan

Abstract

A simulation technology with electrolyte thermodynamic model has been developed to evaluate the precipitation behavior in reprocessing solution. In this study, we have chosen the model of OLI system Inc. which combines an excess Gibbs energy model for mixed-solvent electrolyte systems with a comprehensive treatment of chemical equilibrium. The simulation results of precipitation were compared with the experiment data from non-radioactive simulated HLLW and Pu-Zr-Mo solution, and they showed good agreement each other. Most of the precipitation species was zirconium molybdate hydrate (ZMH) from the both data. This study has shown the thermodynamic simulation model is one of the useful tools to estimate the behavior of precipitation species from the reprocessing solution.

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Peer-review under responsibility of the organizing committee of ATALANTE 2016

Keywords: Reprocessing; Insoluble sludge; Thermodynamic model; Simulation; Precipitation; Zirconium molybdate hydrate

Nomenclature

ZMH	zirconium molybdate hydrate
HLLW	high level liquid waste
G_{ex}	excess Gibbs energy
$G_{ex(LR)}$	contribution of long-range electrostatic interaction
$G_{ex(II)}$	specific ionic interactions
$G_{ex(SR)}$	short-range contribution resulting from intermolecular interaction
HKF equation	Helgeson-Kirkhan-Tanger equation

* Corresponding author. Tel.: +81-28-282-1111; fax: +81-29-282-9219.

E-mail address: takeuchi.masayuki@jaea.go.jp

1. Introduction

In an aqueous reprocessing for oxide spent fuel, various kinds of insoluble species are involved in dissolver liquor. The insoluble species is one of the potential factors to disturb a stable plant operation owing to a part of blockage in equipment, performance degradation of heat transfer devices, partial heat enhancement in equipment, or third phase formation in solvent extraction process. According to the difference of origin, it can be classified as insoluble species in fuel dissolution process named as primary sludge and precipitation species after the dissolution in nitric acid solution named as secondary sludge. The primary sludge includes mainly multi-component platinum group alloys^{1,2} and segment of cladding tube from the sharing process. Concerning the secondary sludge, on the other hand, it is reported to precipitate the insoluble species such as zirconium molybdate hydrate (ZMH)^{3,4,5} in the reprocessing solution. Most of the primary sludge can be separated from dissolved solution of spent fuel by filter system or centrifugal equipment in clarification process. On the other hand, the secondary sludge is difficult to be separated efficiently because it is formed everywhere in the reprocessing process due to change of nitric acid concentration and solution temperature. Therefore, it is significant to understand the behavior of precipitation species from dissolved fuel solution with many kinds of metal species. We have tried the experimental evaluation of the precipitation species using both real reprocessing solution and non-radioactive simulated solution in recent years, however it is not easy to get the enough information of the whole precipitation species by the experiments. We have discussed the simulation technology for the secondary sludge using thermodynamic calculation model in this study. The thermodynamic calculation was carried out using an electrolyte simulation model which is a commercial code in OLI systems Inc. In this simulation model, major thirteen elements including U, Pu and fission products were considered as metal species in the spent fuel component. The simulation results were verified by comparing with the experiment data, and the behavior of secondary sludge was discussed in this simulation work.

2. Thermodynamic model

The simulation technology for the secondary sludge has been developed to understand the precipitation behavior and estimate the amount in the reprocessing process. The thermodynamic framework combines an excess Gibbs energy model for a mixed-solvent electrolyte system with a comprehensive treatment of chemical equilibrium developed at OLI system. The detail of thermodynamic model is given in some articles^{6,7,8}. The summary is described below.

The excess Gibbs energy is calculated by the following equation.

$$G_{ex}/RT = (G_{ex(LR)} + G_{ex(II)} + G_{ex(SR)}) / RT \quad (1)$$

where $G_{ex(LR)}$ shows the contribution of long-range electrostatic interaction, $G_{ex(II)}$ shows specific ionic interactions and $G_{ex(SR)}$ is a short-range contribution resulting from intermolecular interaction.

The long-range interaction contribution is calculated from the Pitzer-Debye-Hückel formula⁹ expressed in terms of mole fractions and symmetrically normalized. The short-range interaction contribution was evaluated from the UNIQUAC equation¹⁰. The specific ion-interaction contribution was calculated from an ionic strength-dependent and symmetrical second virial coefficient-type expression⁶. The specific ion-interaction contribution is by far the most important one to reproduce the properties of the solutions. While the excess Gibbs energy model is used to calculate nonideality effects on solution properties, the chemical equilibrium is governed by the chemical potentials of all species concerned with various reactions, such as precipitation, ion pairing, or complexation. The chemical potential of each ionic or neutral species was determined by its standard-state contribution and its activity coefficient.

The standard-state chemical potentials of aqueous species were calculated as functions of temperature and pressure using the Helgeson-Kirkhan-Tanger (HKF) equation of state^{11,12}. The parameters of the HKF model are available for a large number of aqueous species including ions and ion pairs. It should be noted that standard-state properties calculated from these models are based on the infinite-dilution reference state and the molar concentration scale.

The model parameters were determined using various types of thermodynamic data including activity and

osmotic coefficients, solubility of salts in water or other solvents, speciation data such as pH and dissociation constants, enthalpies of dilution or mixing, heat capacities and densities. The osmotic coefficient data constrain directly the excess Gibbs energy, whereas the solid-liquid equilibrium data can be used to constrain both the excess Gibbs energy and the properties of the solid phases that are in equilibrium with the liquid phase. The use of multiple data types is important to guarantee the accuracy of model parameters. This makes it possible to construct the reliable predictions of solubility well beyond the temperature range of experimental solubility data. The model prepares a huge database, but a part of thermodynamic data such as solubility and stability constant etc. were additively researched based on many technical articles because the unfamiliar precipitation species, for example double salt, were not available in it. In the current sludge simulation model, major thirteen elements which include uranium, plutonium, molybdenum, zirconium, ruthenium, rhodium, technetium, palladium, barium, cesium, strontium, cerium and tellurium were considered as metal species in the spent fuel component for the precipitation simulation work.

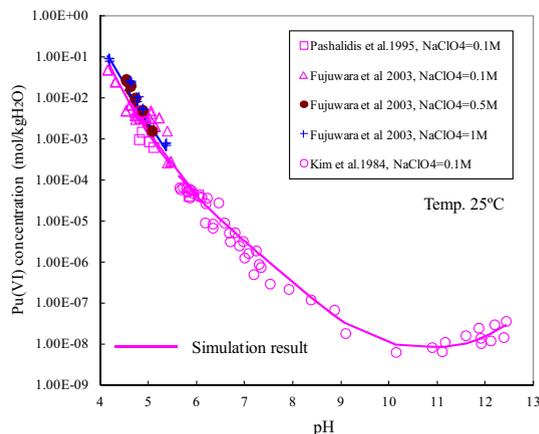


Fig. 1 Simulation of Pu(VI) solubility in pH region

In particular, the solubility is quite important to evaluate the precipitation behavior quantitatively based on the thermodynamic calculation. As examples, Fig.1 shows the verification of Pu (VI) solubility in $\text{H}_2\text{O}-\text{HNO}_3$ -Pu (VI) solution based on the experiment data from some literatures^{13,14,15}. It was verified in pH region and the ionic strength was controlled by adding NaClO_4 . The solubility curve from the thermodynamic calculation reflected well some experiment data. Fig.2 shows the verification of Zr and Mo solubility in $\text{H}_2\text{O}-\text{HNO}_3$ -Zr-Mo solution. The calculation data with the effects of nitric acid concentration and temperature gave good agreement with Esberin's experiment work¹⁶. The results showed that ZMH precipitation is promoted by lower HNO_3 concentration or higher temperature. From the verification results, the thermodynamic model showed high potential to estimate the precipitation behavior in the experiment.

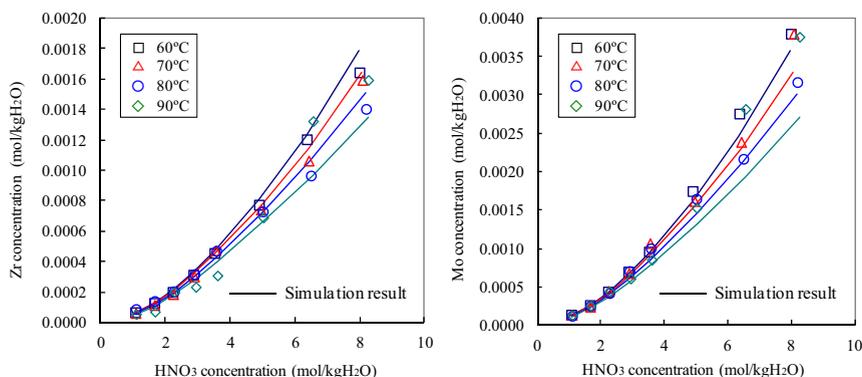


Fig. 2 Simulation of Zr and Mo solubility in nitric acid solution

3. Experimental

Some precipitation tests were performed to verify the reliability of thermodynamic model in the simulation work. The test solutions are consisted of non-radioactive simulated HLLW including ten kinds of main elements in fission products and Pu-Mo-Zr solution. The additive reagents and the target of concentration conditions for the non-radioactive simulated waste are summarized in Table 1. The test solutions include molybdenum, zirconium, ruthenium, rhodium, palladium, barium, cesium, strontium, cerium and tellurium. The three types of metal concentrations were decided based on the composition of fission products corresponding to 50, 100, 150GWd/t calculated by ORIGEN-II which is a computer code system for calculating the buildup, decay, and processing of radioactive materials. The chemicals with special grade were used for preparing the simulated waste. The appearance of three types of non-radioactive simulated waste is shown in Fig.3. The solution temperature for the precipitation tests was controlled at 95°C for 7 hrs and the solution volume was 200mL per a batch.

Table 1. Metal concentration condition for preparation of non-radioactive simulated HLLW.

Elements	Reagents	Metal concentration (g/L)		
		50 (GWD/t)	100 (GWD/t)	150 (GWD/t)
Zr	ZrO(NO ₃) ₂ ·2H ₂ O	1.34	3.20	4.87
Mo	Na ₂ MoO ₄ ·2H ₂ O	1.39	4.10	6.09
Te	H ₂ TeO ₆	0.24	0.84	1.34
Ce	Ce(NO ₃) ₃ ·6H ₂ O	2.55	7.00	10.60
Sr	Sr(NO ₃) ₂	0.31	0.54	0.80
Cs	CsNO ₃	1.79	5.36	8.27
Ba	Ba(NO ₃) ₂	0.59	1.95	2.60
Ru	Ru(NO ₃) ₃	1.07	3.70	5.66
Rh	Rh(NO ₃) ₃	0.34	1.25	1.84
Pd	Pd(NO ₃) ₂	0.61	2.67	4.22

HNO₃ conc. : 4mol/L



Fig. 3. Appearance of non-radioactive simulated waste under different burn-up conditions.

The precipitation tests using Pu-Mo-Zr solution were carried out in glove box. The volume of test solution was 50 mL per a batch and the target of metal concentration conditions from Run 1 to Run 3 are shown in Table 2. The three types of solution compositions were decided to focus the effect of plutonium concentration in Pu-Mo-Zr solution on the precipitation species and the amount. The plutonium nitrate solution separated from the dissolved solution of spent fuel by solvent extraction was used for the preparation of test solutions.

The valence of plutonium in the Pu-Mo-Zr solutions was controlled at Pu (VI) to discuss the formation of Pu(MoO₄)₂·2H₂O. The test solutions were kept at 90 °C for 4 hrs during the precipitation tests. The inconsistent conditions between the two types of the test solutions, non-radioactive simulated waste and Pu-Mo-Zr solution, were intentionally set to discuss the flexibility of the simulation model for the precipitation behavior. The schematic of equipment for the precipitation test is shown in Fig.4.

Table 2. Metal concentration conditions for precipitation test in Pu-Mo-Zr solution.

Elements	Metal concentration (g/L)		
	Run 1	Run 2	Run 3
Pu	3.6	10	22
Mo	3.6	3.6	4.0
Zr	4.8	4.5	3.7

HNO₃ conc. : 3mol/L

The precipitation reaction was promoted in the separable flask by heating the test solutions. The nitric acid vapor and mist were recovered in the flask through condenser to avoid the change of metal concentration and volume during the test. The precipitation products were separated by micro filter with pore size of less than 0.45 μ m after cooling the test solution at around 25 °C, and they were washed and dried to measure the yield. The chemical species of the precipitation products were identified by X-ray diffraction (XRD) analysis. Cs concentrations in the test solutions were determined by atomic absorption spectrometry (AAS) and the concentrations of other metals were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The metal concentrations in samples for the AAS and ICP-AES analyses were adjusted by dilute nitric acid solution at room temperature.

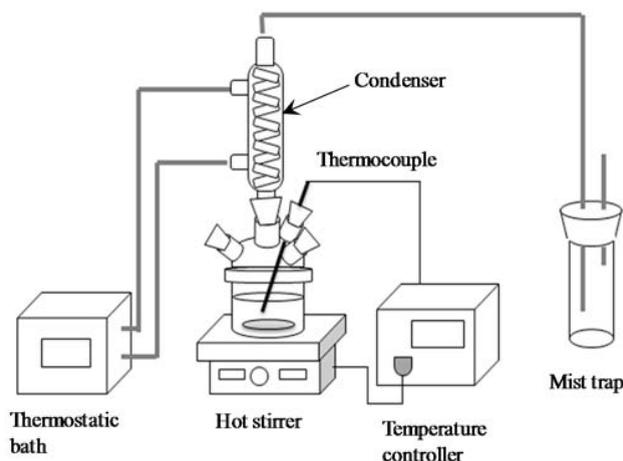


Fig. 4. Schematic of apparatus for precipitation test.

4. Results and discussion

4.1 Non-radioactive simulated HLLW

Fig.5 shows the concentrations of representative six metals in the test solution during the precipitation test at 100GWd/t condition. Mo, Zr, Te concentrations in the test solution were obviously decreased with test time and the concentrations of other elements showed almost no change. Consequently, above three elements are closely related to the composition of precipitation products. The tendency of metal concentration in the test solution was nearly same as that at 50 and 150GWd/t conditions. As an example, Fig.6 shows XRD pattern of precipitation products at 100GWd/t condition. Only ZMH was identified as the precipitation products and Te species were not included there. It is supposed the Te species were not detected by the XRD analysis because of very small amount. Fig.7 shows SEM morphology of the precipitation product at all conditions. The grain type of precipitation was very similar to that of the ZMH.

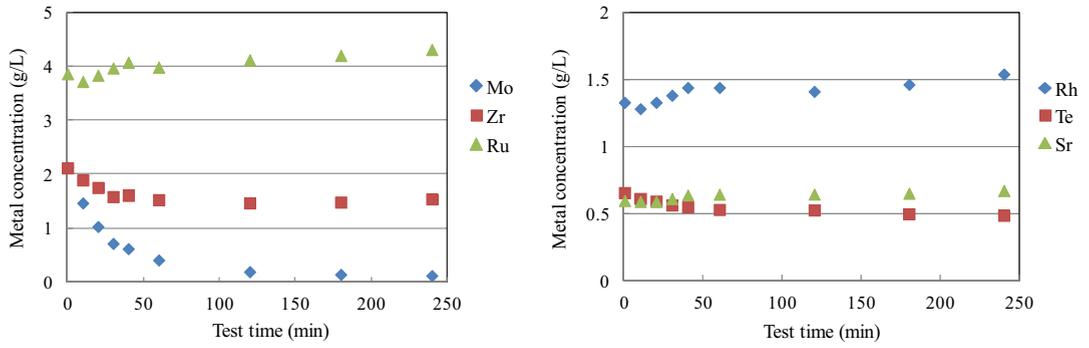


Fig. 5. Variation of metal concentrations in test solution during precipitation test at 100GWd/t condition.

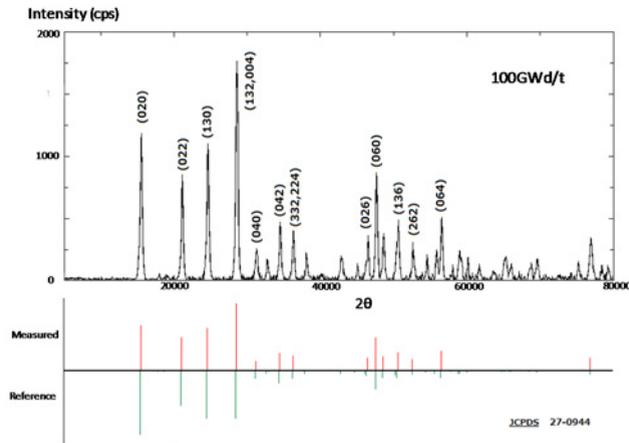


Fig. 6. XRD pattern of precipitation product at 100GWd/t condition

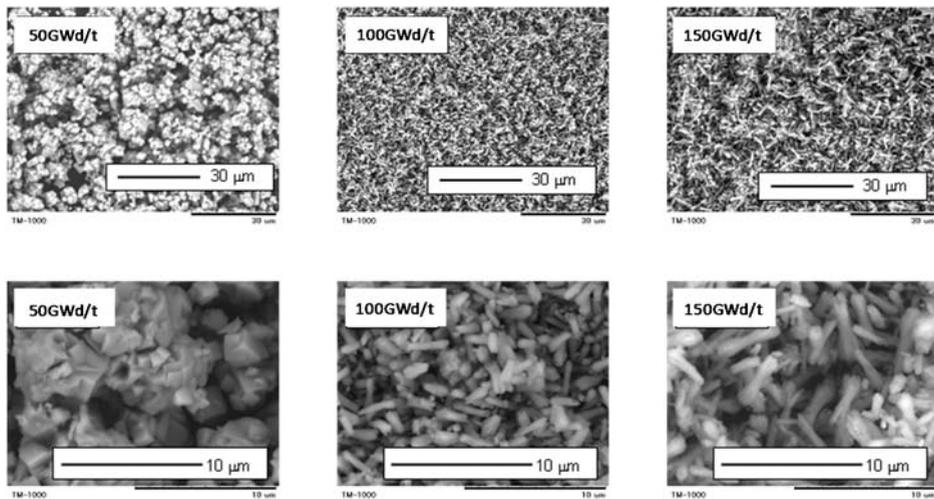


Fig.7. SEM morphology of precipitation at all conditions.

Table 3 shows the simulation and experimental results of precipitation species in the simulated HLLW with ten elements. The thermodynamic calculation was performed at 25 °C because the solid species were separated from the simulated waste at the temperature after the precipitation tests. The simulation results showed ZMH and $ZrTe_3O_8$ were thermodynamically precipitated under this solution condition. The total amount of precipitation species based on the thermodynamic simulation was similar to that from the experiment. The amount of precipitation from the calculation was nearly 0.1g higher than that from the experiment at all conditions. It is mainly due to the incomplete recovery of adhesive precipitation inside the flask after the test.

The variation of Te concentrations in the test solution during the precipitation test was similar to that of Zr as shown in Fig.5, however Zr-Te species was not identified in the precipitation product by XRD analysis. Probably, it was too low content to identify it, so it is considered that very small amount of $ZrTe_3O_8$ was actually precipitated during the test. It will be verified based on some experiments in future work.

Table 3. Simulation and experimental results of precipitation species from non-radioactive waste.

Burn-up conditions	Calculated values of precipitation species at 25°C			Experimental value (g)
	ZMH(g)	$ZrTe_3O_8$ (g)	Total (g)	
50GWd/t	0.61	0.07	0.69	0.59
100GWd/t	1.93	0.26	2.20	2.11
150GWd/t	2.90	0.42	3.32	3.21

4.2 Pu-Mo-Zr solution

The effect of Pu concentration in the test solution on the composition and chemical form of the precipitation products was mainly focused in the experiment using Pu-Mo-Zr solution. The white precipitation product recovered at Run 1 is shown in Fig. 8. The appearance of precipitation product at other conditions was similar to that at Run 1. The chemical species was identified as ZMH by XRD analysis in all conditions. The Pu species could not be identified in the products at any conditions however 0.1-0.2 wt% Pu was included in the precipitation.

Table 4 shows the simulation and experimental results of precipitation weight. The simulation results showed that the precipitation product is only ZMH and similar amount to the experimental data. Thus, the result of thermodynamic simulation reflected well the precipitation behavior in the experiment. The Pu concentration in Pu-Mo-Zr solution did not influence the amount and chemical species of precipitation product within these test conditions because ZMH is thermodynamically much easier to precipitate than Pu-Mo species. In addition, the simulation results showed that $Pu(MoO_4)_2 \cdot 2H_2O$ should be precipitated in Pu-Mo solution without Zr. In previous study, it was reported $Pu(MoO_4)_2 \cdot 2H_2O$ was identified by XRD analysis as precipitation products from Pu-Mo-Zr solution¹⁷. However, the precipitation conditions including the ratio of metal concentrations etc. are quite different from that in this study. The difference might be related to the precipitation time. The relationship between Zr concentration in Pu-Mo-Zr solution and formation of $Pu(MoO_4)_2 \cdot 2H_2O$ should be discussed.

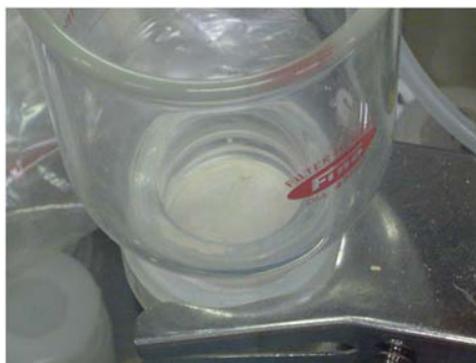


Fig. 8. Appearance of precipitation product at Run 1.

Table 4. Calculation of precipitation species in Pu-Mo-Zr solution.

Run No.	Calculated value (25°C)	Experimental value (g)
	ZMH(g)	
Run 1	0.46	0.44
Run 2	0.46	0.43
Run 3	0.46	0.45

5. Conclusions

The simulation model has been developed to estimate the precipitation behavior in reprocessing solution. In this study, it was demonstrated that the chemical species and amount of the precipitation calculated by thermodynamic model reflected well experiment results using non-radioactive simulated HLLW and Pu-Mo-Zr solution. The thermodynamic simulation technique in this study is one of useful tools to estimate the precipitation behavior in the reprocessing solution. The reliability of the model will keep being improved further due to the addition of new information on relevant chemical speciation and thermodynamic property data.

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