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ARTICLE

ZMH crystals addition to prevent ZMH encrustation in Mo-Zr-Te HNO_3 solution

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In the reprocessing process of nuclear fuel, an insoluble substance precipitates when spent nuclear fuel is dissolved in hot nitric acid and adheres to the surface of the equipment, causing a reduction in heat transfer efficiency and pipe blockage. The main substance is zirconium molybdate dihydrate (ZMH), which is produced by the reaction of zirconium, and molybdenum ions. ZMH crystals have characteristic physical properties, such as solubility and adherability, which are inversely proportional to the reaction temperature. In this study, Mo-Zr-Te-HNO_3 solution was prepared. The prepared solution was heated with pieces of metal leaf or plate at high temperature to replicate industrial conditions and to investigate the encrustation behavior. In the initial stage, an amorphous material without any particular shape and crystal structure was generated and covered the metal surface like a sheet. Encrustation formed as a result of aggregation adhering to the metal surface. Such aggregation is thought to the driving force of encrustation. Moreover, we conducted a comparative experiment by adding ZMH crystal to the reaction solution. The amount of ZMH precipitation in the solution increased, while the amount of ZMH encrustation on the metal surface decreased. This result indicates that a large reaction surface area by seed crystal allows the nucleation of Mo and Zr to form ZMH and promotes nucleation and aggregation in solution. In other words, the amount of encrustation is can be controlled by inhibiting the initial stage of the nucleation on the surface of the metal wall.

Keywords: encrustation prevention; nucleation by seed crystal; ZMH

Introduction

In industrial process plants, the occurrence of supersaturated solutions can lead to the accumulation of undissolved solids on the inner walls of pipes and vessels [1-3]. This accumulation, known as encrustation or fouling, can impair stable plant operations and lead to a decrease in overall process efficiency [2]. Not just a concern for industrial plants, encrustation also poses significant challenges for spent nuclear fuel reprocessing plants, primarily due to its impact on separation efficiency and overall operating costs [4,5]. Spent nuclear fuel, containing nuclear fission products and minor actinides resulting from fuel combustion, needs to be reprocessed for recovering U and Pu [6,7]. For example, spent nuclear fuel is sheared into pieces and dissolved in hot nitric acid. Subsequently, uranium and plutonium ions are then recovered from the solution using the Plutonium Uranium Redox Extraction (PUREX) method [8]. However, certain ions remain undissolved in the hot nitric acid due to their solubility. These ions can adhere to surfaces and accumulate around processing equipment, leading to reduced efficiency of heat transfer and causing pipe blockages [5]. The primary substance contributing to this adhesion phenomenon is zirconium molybdate hydrate ($Zr(OH)_2Mo_2O_7 \cdot 2(H_2O)$, hereinafter referred to as ZMH), which is generated by the following reaction [9,10]:

$$2HMoO_4^- + ZrO^{2+} + 2H_2O \rightarrow Zr(OH)_2Mo_2O_7 \cdot 2(H_2O) \qquad (1)$$

The ZMH crystal is characterized by physical properties such as solubility, which is inversely proportional to the acid concentration and reaction temperature [9]. The formation of ZMH is facilitated by conducting the dissolution phase at high levels of acid concentration and high temperature. Interestingly, ZMH also occurs in the storage of high-level radioactive liquid waste (henceforth HLLW) as a byproduct of liquid management [11].

Presently, the removal of ZMH encrustation involves employing high-pressure water sprays and chemical cleaning methods utilizing acids and alkalis. However, these methods increase the volume of secondary radioactive waste [9]. To mitigate the impact of ZMH encrustation on the spent nuclear fuel reprocessing process, it is vital to understand the generation of ZMH crystals and to devise an effective prevention method. Abe

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et al.[12] found that the addition of molybdenum trioxide hemihydrate (MoO_3) to the reaction solution prevented ZMH encrustation. This is achieved through the dissolution of Mo ions dissolves from the MoO_3 crystals. The dissolved Mo ion then enters a supersaturated state, leading to the promotion of preferable ZMH nucleation with surrounding Zr ions around the MoO_3 crystal. Consequently, ZMH encrustation around the wall surface is indirectly prevented by the consumption of Zr ions. However, this method is not universally applicable, as it necessitates a new duct for MoO_3 supply from a closed system.

In this study, we examined the initial nucleation of ZMH in a reaction involving Mo and Zr ions. During the reaction, changes in their concentration and the formation of crystals were monitored. Subsequently, we investigated the anti-encrustation effect by introducing ZMH as a seed crystal. We selected ZMH due to its abundant production after the dissolution process, coupled with its potential for repeated reuse. In addition to the combination of Mo and Zr ions, Te ions also play a significant role in ZMH precipitation. Previous work by Kubota and Fukase indicated that Mo, Zr, and Te co-precipitate from a simulated waste solution containing nitric acid. Furthermore, several studies have suggested that Te influences the precipitation of Mo and Zr [12,13]. Consequently, we were keen to explore both ZMH and its tellurium adduct, investigating the anti-encrustation effect. Our investigation extended to both the Mo-Zr and Mo-Zr-Te systems, where we intoroducad ZMH crystals to assess their anti-encrustation effect.

1. Materials and methods

1.1. Substances and devices

Table 1 shows the reagents used to prepare a Mo-Zr-Te HNO_3 solution. All reagents, excluding nitric acid were dissolved in pure water. The reaction solution was stirred in a SUS304 reaction vessel (850 mm diameter × 850 mm height). SUS304 is the same type of stainless steel is identical to the type used in actual reprocessing plants [14].

Table 1. Reagents used in this study.

Material	Chemical formula	Detail
Molybdenum (VI) disodium dihydrate	$Na_2MoO_4 \cdot 2H_2O$	99.0+%
Zirconyl nitrate dihydrate	$ZrO\,(NO_3)_2 \cdot 2H_2O$	97.00%
Telluric acid	$Te\,(OH)_6$	99.0+%
Nitric acid	HNO_3, (1.38)	60%-62%

The devices used in this experiment and their respective uses are outlines as follows.

- Oil bath sets (AS ONE, OBS-200M & OBS-200AM, Japan); employed for heating the solution.
- Inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent Technologies Ltd., Agilent 5100 SVDV, USA); utilized for measuring the concentrations of Zr, Mo and Te ions. Before measuring the concentration of the solution, the solution was filtered (pore size 0.2 µm).
- Scanning electron microscopy (SEM, JEOL Ltd., IT-100LA, Japan); employed to observe the formation of crystals and encrustation.
- X-ray diffraction (XRD-Cu tube, Rigaku Co.Ltd., MiniFlex600, Japan); utilized for analyzing the crystal structure.

At a specific time intervals during heating, 1.0 mL of the solution was taken, diluted, and analyzed by ICP-OES. After the reaction, the encrusted crystals were washed with pure water, dried, and analyzed by XRD. These operations were performed at room temperature.

1.2. Prepared solution

Table 2 presents experiment conditions. The ion concentrations used are equivalent to the real HLLW solution [12]. Given that fuel dissolution typically occurs at temperatures of around 90°C -100 °C, the oil bath temperature was set to 90 °C and stirred by paddle blades for 240 min. After the reaction, the generated solids were removed by filtration, followed by a drying process, and finally crushed.

Table 2. The experiment condition preparing Mo-Zr-Te HNO_3 solution.

Parameter		Value
Initial concentration [mol L^{-1}]	Mo	0.0679
	Zr	0.0590
	Te	0.0105
	HNO_3	3.00
Total volume of the solution [mL]		300
Agitation speed [rpm]		300
Operation temperature [°C]		90

2. Results and discussion

2.1. Investigation of the initial reaction of ZMH without tellurium

Figure 1 shows the encrustation in the initial stage of the reaction. To deliberately slow down the nucleation rate, the concentration of the reaction solution was set to half of the original solution. We observed crystals on the surface of SUS304 stainless sheet at 30 minutes after the start of reaction. No crystals were observed on the surface of the SUS wafer after 5 and 10 minutes of the reaction (Figure 1 (a), (b)). Small crystals appeared for the first time after 15 minutes into the reaction (Figure 1 (c)). A large number of oval particles were observed at 20 minutes into the reaction (Figure 1 (d)). No agglomerates were confirmed at this time. Then crystals grew (Figure 1 (d)), the results of observation of the state at 30 minutes after the start of the reaction at low magnification (×1000) and high magnification (×10000) are shown in Figure 1(e) and 1(f), respectively. In Figure 1(e), aggregates of crystals adhering to each other were observed. In Figure 1 (f), a

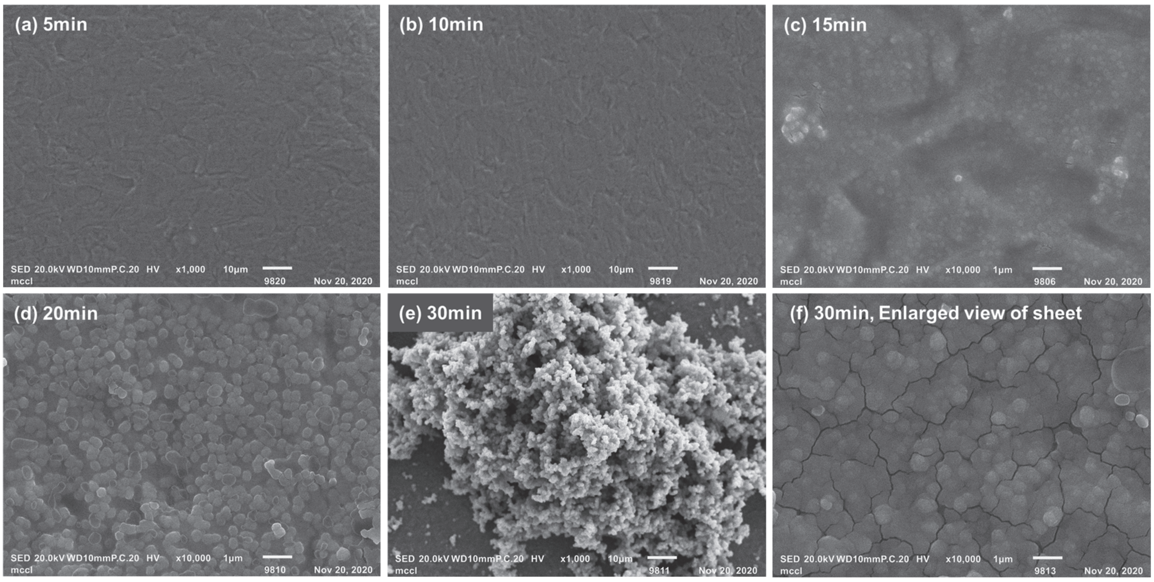

Figure 1. The SEM images of encrustation on a leaf of SUS304 in initial reaction. The agglomerates are on the sheet.

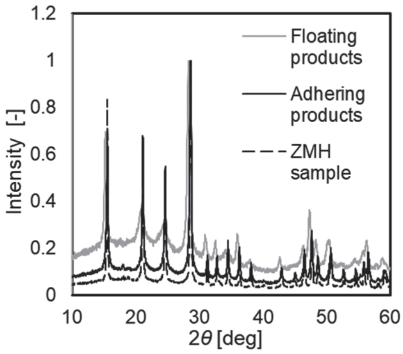

Figure 2. Diffraction patterns of the ZMH sample, floating products in the solution at 20 minutes after the reaction starts, and adhering products in the SUS wall at 240 minutes after reaction starts.

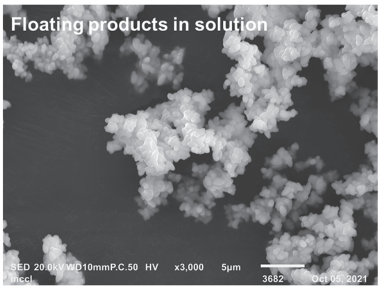

Figure 3. The SEM image of the floating products observed after 20 minutes.

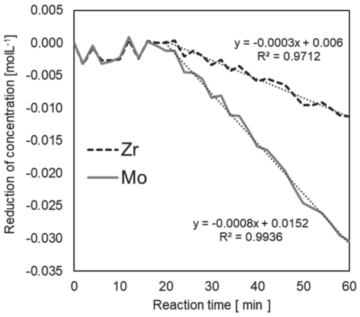

Figure 4. Concentration changes of Zr and Mo ions. The equations are linear fit of the plot of 20-60minutes after the start of the reaction.

sheet of crystal agglomerates was observed on the SUS304 sheet.

Figure 2 shows the XRD spectra of the ZMH crystal, floating products in the solution produced at 20 minutes into the reaction, and adhering products in the SUS wall at 240 minutes into the reaction. The spectral baseline for floating products is not flat, but the peaks are located similarly. Judging by this XRD spectra, we can see that products at initial reaction are ZMH crystals, including amorphous.

Figure 3 shows the SEM image of the floating products at 20 minutes into the reaction. Round crystal aggregates were obtained. However, aggregates do not adhere to the surface at this time. According to these results, crystal aggregates form in solutions and not on wall surfaces.

Figure 4 shows the changes in the concentration of Mo and Zr ions in an initial stage of the reaction. The concentrations of the solution were measured after filtering to remove small crystals from mixing in. At 0-20 minutes, the range of reduction was comparable for both ions. That is, the concentrations in the 0-20 minutes of the reaction decreased in the ratio Mo : Zr = 1 : 1. Doucet F. J and co-workers reported that the Zr : Mo ratio of amorphous sheet ZMH is approximately 1.0, which is close to the ratio of the concentration decrease for both ions in this paper. After 20 minutes, the concentration of

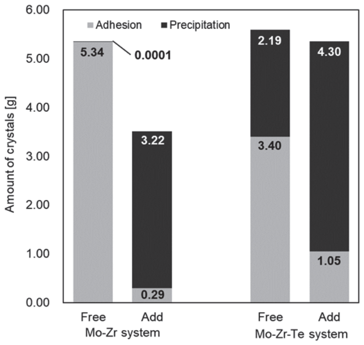

Figure 5. The adhesion and precipitation amounts in the Mo-Zr system (left) and the Mo-Zr-Te system (right).

Figure 6. The encrustation on vessels at 240 min after the reaction starts.

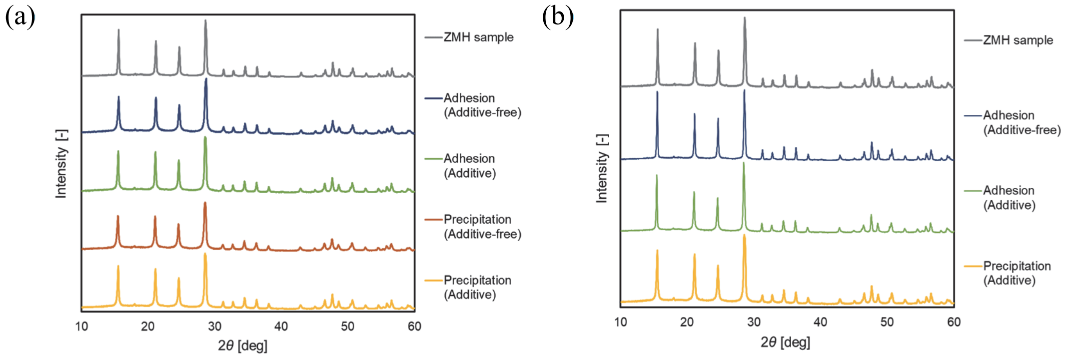

Figure 7. XRD spectra of precipitated and adhered crystals in (a) the Mo-Zr system, (b) the Mo-Zr-Te system.

Mo ion decreased more than that of Zr ion. The slope ratio is Mo : Zr = 2.67 : 1. A previous study reported that ZMH produces Mo : Zr = 2 : 1 [4]. Moreover, the obtained ratio is close to the reported ratio.

Therefore, the process of encrustation formation is considered to occur as follows. First, sheets of small crystals and amorphous material form on the surface of a metal wall. Simultaneously, aggregates of crystals and amorphous material also form in the solution. Then, the aggregates then adhere to the sheet and accumulate. Mo-Zr amorphous material tends to form in the initial stage, but after a certain amount of time, only crystals begin to form. Since crystal aggregates form in the reaction solution and not on the metal surface, ZMH encrustation can be controlled by preventing aggregates from adhering to the metal surface.

2.2. Prevention of ZMH encrustation adding seed crystal in the Mo-Zr and Mo-Zr-Te systems

The anti-encrustation experiment was conducted by using two types of the Mo-Zr-Te HNO_3 solutions: the Mo-Zr system and Mo-Zr-Te systems. The experimental condition is the same as listed in Table 1.

Adding crystal was produced by drying and crushing ZMH. No crystal was added to one of the solutions, while 1.0 g of ZMH crystal was added to the other solution. The reaction time was 240 minutes.

Figure 5 shows the adhesion and precipitation amounts in the Mo-Zr and Mo-Zr-Te systems. “Adhesion” means crystals encrusted to the inner wall of the vessel. “Precipitation” means crystals flow out by washing. Seed crystals were added to reduce overall encrustation and total production. On the other hand, the amount of spilled precipitate was more than the amount for the additive-free condition. In the Mo-Zr-Te system, encrustation was increased quantity than one in Te-less system. This suggests that the adhesion prevention effect is decreased by the presence of Te in conditions with additives.

Furthermore, a difference in the appearance of adhesion was observed between the two conditions in the way adhesion occured. In the additive-free condition, the accumulated layer of crystals on the wall was unable to separate from it. In the additive condition, the precipitated crystals were easily washed from the vessel. Figure 6 shows the vessels after washing, without the reaction solutions.

Figure 7(a) and **7(b)** show the XRD spectra obtained from the Mo-Zr and Mo-Zr-Te systems, respectively. The reference ZMH crystal is displayed at the top, with the adhesion and precipitation products listed below it. In the latter, the spectral patterns were nearly identical to the reference ZMH. Despite the addition of seed crystals, it was suggested that the main products were ZMH.

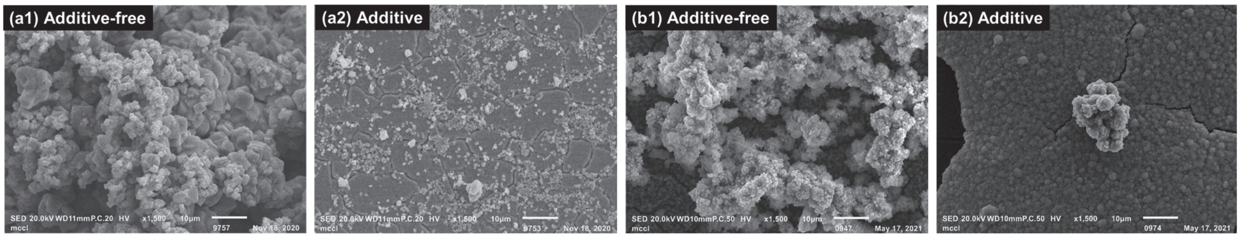

Figure 8. Crystals adhered on the surface of the SUS304 piece. (a1), (a2) in Mo-Zr system; (b1), (b2) in Mo-Zr-Te system.

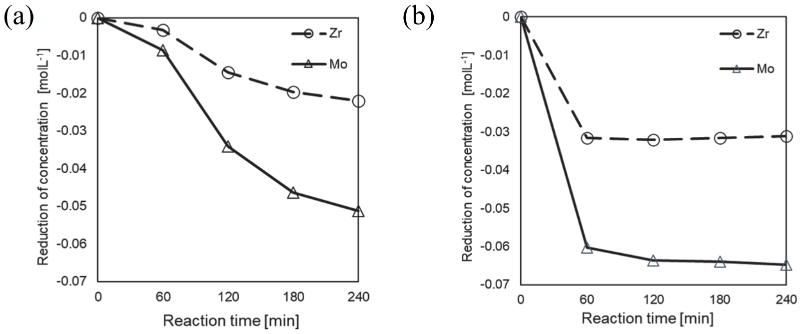

Figure 9. Concentration changes of Mo and Zr ions in the reaction solution. (a) Additive-free, (b) Additive.

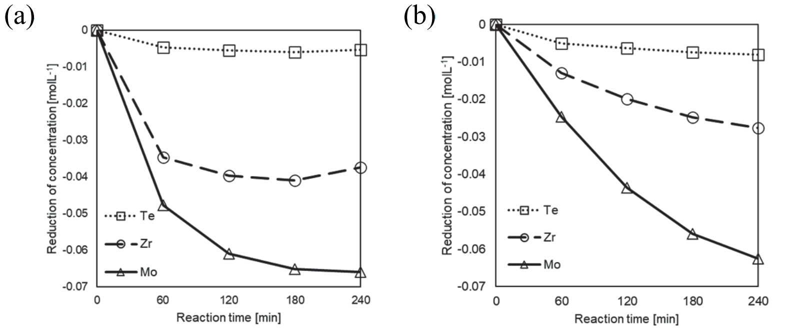

Figure 10. Concentration changes of Mo, Zr and Te ions in the reaction solution. (a) Additive-free, (b) Additive.

Therefore, we concluded to the produced material as in the present our work.

Figure 8 shows the appearance of ZMH adhesion on the SUS304 test plates. Under additive-free condition, in both systems, crystal agglomerates were formed and deposited on the surface of the SUS304 plate (Figure 8(a1) and (b1)). Under additive conditions, small crystals adhered in the Mo-Zr system (Figure 8 (a2)), a film of crystals was formed, and the crystal aggregates were also deposited on the film crystal in the Mo-Zr-Te system (Figure 8(b2)).

Figures 9 and **10** show changes in each metal ion in the reaction solution. In the Mo-Zr system, adding crystals more decreased the concentration after 4 hours. In the Mo-Zr-Te system, adding crystals had little effect on the concentration after 4 hours.

These results indicate that the addition of ZMH crystals accelerated the nucleation. Additive ZMH increased the surface area to enable nucleation. As a result, in a short time, aggregation around the seed in the solution occurred and concentrations reduced, and reaction rate improved. Concentrations were consumed in the formation of agglomerates rather than sheets of crystal and amorphous on the surface, preventing the adhesion of agglomerates to the wall. Therefore, the amount of encrustation on the wall surface decreased.

The reason for the change in the behavior of the reaction in the Mo-Zr-Te system is the adhesion of the Te compound to the additive crystals. Since previous studies reported that Zr and Te react to form Zr-Te coprecipitates materials [12,13], the attached Te compound is considered to be a Zr-Te compound. Therefore, it is considered that the surface environment of the added crystal was changed, and the adhesion inhibition effect was reduced by the presence of Te. Further research is needed to fully understand the intricate mutual relationships between Te, Zr, and Mo ions.

3. Conclusions

This study is focused on ZMH formation and the ZMH crystals addition effect to prevent ZMH encrustation on the metal wall in the Mo-Zr-Te -HNO_3 solution. Encrustation state was observed with elapsed time to show that Mo and Zr crystals and amorphous substances formed on surfaces as sheets in the initial stage of the reaction, after that aggregates were observed in the solution. These aggregates adhered to and accumulated on the sheets, forming encrustations. Based on encrustation process, we conducted ZMH crystals addition experiments, in which 1.0 g of ZMH crystals was added to the reaction solution. Comparing results with and without ZMH added crystals, the results revealed that the amount of encrustation on the wall surface reduced significantly when ZMH crystals were present. We hypothesized that the reduction effect on the encrustation amount is due to the added crystals providing larger nucleation sites, thereby promoting nucleation in solution, and inhibiting the formation of small crystals and amorphous sheets on the surface. Since this method could reuse a major precipitate ZMH as adding ZMH crystals, to eliminates the need for new additive materials. Additionally, ZMH crystals used as seed crystals can control nucleation by creating a new nucleation field in the ZMH reaction system. Future research should measure the nucleation rate when of seed crystals are present.

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References

[1] Z. Amjad, Mineral Scale Formation and Inhibition, (2011).

[2] A.L. Kavitha, T. Vasudevan and H.G. Prabu, Evaluation of synthesized antiscalants for cooling water system application, *Desalination* 268 (2011), pp. 38-45.

[3] F. Rahman, Calcium sulfate precipitation studies with scale inhibitors for reverse osmosis desalination, *Desalination* 319 (2013), pp. 79-84.

[4] F.J. Doucet, D.T. Goddard, C.M. Taylor, I.S. Denniss, S.M. Hutchison and N.D. Bryan, The formation of hydrated zirconium molybdate in simulated spent nuclear fuel reprocessing solutions, *Physical Chemistry Chemical Physics*, 4 (2002), pp. 3491-3499.

[5] A. Magnaldo, M. Masson and R.Champion, Nucleation and crystal growth of zirconium molybdate hydrate in nitric acid, *Chemical Engineering Science* 62 (2007), pp. 766-774.

[6] Broeders C. H. M., Kessler, G. (2007) "Fuel cycle options for the production and utilization of denatured plutonium." Nuclear science and engineering 156.1(2007): 1-23.

[7] A.P. Paiva and P. Malik, Recent advances on the chemistry of solvent extraction applied to the reprocessing of spent nuclear fuels and radioactive wastes, *Journal of Radioanalytical and Nuclear Chemistry* 261 (2004), pp. 485-496.

[8] R.S. Herbst, P. Baron and M. Nilsson, Standard and advanced separation: PUREX processes for nuclear fuel reprocessing, *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment* 2 (2011), pp. 141-175.

[9] L. Zhang, M. Takeuchi, T. Koizumi and I. Hirasawa, Evaluation of precipitation behavior of zirconium molybdate hydrate, *Frontiers of Chemical Science and Engineering* 7 (2013), pp. 65-71.

[10] T. Arai, D. Ito, I. Hirasawa, Y. Miyazaki and M. Takeuchi, Encrustation Prevention of Zirconium Molybdate Hydrate, *Chemical Engineering and Technology* 41 (2018), pp. 1199-1204.

[11] M. Kubota and T. Fukase, Formation of precipitate in high-level liquid waste from nuclear fuel reprocessing, *Journal of Nuclear Science and Technology* 17 (1980), pp. 783-790.

[12] R. Abe, I. Hirasawa, Y. Miyazaki and M. Takeuchi, Effect of Anti-Encrustation Additives on Zirconium Molybdate Hydrate, *Chemical Engineering and Technology* 43 (2020), pp. 1059-1064.

[13] Y. Kondo and M. Kubota, Formation and filtration characteristics of solids generated in a high level liquid waste treatment process, *Journal of Radioanalytical and Nuclear Chemistry* 221 (1997), pp. 45-52.

[14] F. Ueno, C. Kato, T. Motooka, S. Ichikawa and M. Yamamoto, Intergranular corrosion mechanism of ultra-low carbon type 304 stainless steel in a nuclear reprocessing plant, (2007), pp. 1389-1393.