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ARTICLE

Thermochemical conversion of uranium oxides for pretreatment of nuclide analysis

ZhuoRan Ma [a], Yoshiya Homma [b], Kenji Konashi [b] and Tatsuya Suzuki [a*]

*[a] Department of Nuclear Technology, Graduate School of Engineering, Nagaoka University of Technology,
1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan; [b]International Research Center for Nuclear Science,
Institute of Material Science, Tohoku University, Oarai-machi, Higashi-Ibaraki-gun, Ibaraki 311-1313, Japan*

The chlorination experiments of uranium oxides, UO_2 and U_3O_8, simulated nuclear fuel debris $(U_{0.5},Zr_{0.5})O_2$ by using carbon tetrachloride, CCl_4, were carried out as the pretreatment process for the purpose of dissolution of uranium oxide contained substances. The sample powder uranium oxides packed in a Swagelok capsule made by 316ss with CCl_4 was heated. At first, CeO_2 powder was used as a simulated material of uranium oxides. Then the chlorination experiments of UO_2, U_3O_8 and $(U_{0.5},Zr_{0.5})O_2$ powder by CCl_4 at 400°C and 12h of heating times were carried out. In these experiment, the molar ratio (U:CCl_4) was adjusted 1:10. It was confirmed that $(U_{0.5},Zr_{0.5})O_2$ powder were converted to uranium chlorides or uranium chloride oxide such as UO_2Cl_2 and UCl_4 by XRD analysis. The products obtained by the thermochemical reaction were confirmed to be dissolved in 6mol/L nitric acid or hydrochloric acid aqueous solution. The dissolution rate of U confirmed by ICP-MS reached 97.7±1.0% in nitric acid and 96.5±2.0% in hydrochloric acid, respectively. In conclusion, the feasibility of the thermochemical conversion method for the dissolution of simulated nuclear fuel debris $(U_{0.5},Zr_{0.5})O_2$ which is poorly soluble in nitric acid was confirmed.

Keywords: uranium oxides; spent fuel; debris; chlorination; dissolution; actinide analysis

1. Introduction

The nuclide analysis and the actinide analysis in spent fuels and nuclear fuel debris are required for the radioactive waste managements [1,2]. For the precise and accuracy analysis, the chemical separation of nuclides is required. The almost chemical separation methods are carried out in the aqueous solution system. In addition, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Thermal Ionization Mass Spectrometer (TIMS) are strong tools for precise analysis of nuclide analysis, especially isotopic analysis [3,4]. In these studies, the aqueous solution samples are required. Thus, the spent fuels and the debris are required to be dissolved into aqueous solution for analyses. The (U, Zr)O_2 in nuclear fuel debris is known to be hardly dissolved substances in aqueous solutions [5,6]. Now we have proposed that these substitutes are chemically converted into easily soluble substitutes by thermochemical reactions. To reduce the burden and problems associated with the disposal of high-level radioactive waste, the new reprocessing technology of treating spent fuel by ion exchange proposed by our group has a new viewpoint on the treatment and disposal of high-level radioactive waste [7-10].

The new reprocessing route using hydrochloric acid (HCl) solution to dissolve spent fuel, then using pyridine resin to conduct ion exchange operations. The final target is the recovery of uranium, plutonium and high radioactive waste solution fission products in the Minor Actinide elements, especially among the Americium(Am) and Curium(Cm). Before separation by the ion exchange, the dissolution process has to be confirmed. By using the Thermochemical conversion and Chlorination conversion to make UO_2, the main composition of spent fuel or fuel debris, change into aqueous solutions or acid solutions. The behaviour of Zirconium oxide during the conversion is also needed to learn more about the disposal of the fuel debris. Nuclear Fuel Debris generated by Molten Core and Molten Core Concrete Interaction (MCCI) in Fukushima Daiichi Nuclear Power Plants accident is expected containing nuclear fuel and core structural materials, and/or concrete materials, Thus, debris are difficult to dissolved into aqueous solutions. It is speculated that uranium dioxide fuel at high temperature reacts with zirconium dioxide in the cladding to produce oxides containing other components. In addition, the reaction of cladding and steel to form alloys, or other oxides, is also worth considering. **Table 1** shows the tendency of elements in the oxide phase and metal phase after melting [11]. The metal phase is dominated by Fe-Zr alloy, and the added components of Zirconia and Steel, Ni and Sn, also exist. In the oxide phase, uranium dioxide and zirconium dioxide are the main components, and oxides of Pu, fission products

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*Corresponding author. E-mail: tasuzuki@vos.nagaokaut.ac.jp

and Minor Actinides also exist, as rare earth elements and alkaline earth metals. In the case and study results of past serious accidents, uranium zirconium solid solution (U,Zr)O_2 should be abundant in the oxide phase [12,13].

Table.1. Phase distribution of elements in nuclear fuel debris [11].

Phase	Element
Oxide	Ca,Ba,Al,Rare earth,Si,Zr,Nb,U,Th,etc
Metal	Fe,Co,Ni,Zr,Platinum metals,P,Sb,Bi,etc

Before almost analyses, the dissolution of these substances into solution is necessary for precise and accuracy analysis, and the nuclides separations and actinides separation as pretreatment of analyses. However, $U_{1-x}Zr_xO_2$ or $(U,Pu)_{1-x}Zr_xO_2$ in nuclear fuel debris becomes difficult to dissolve in nitric acid solution as the Zr amount x increases [14]. Since the accident, many researchers have proposed methods to dissolve nuclear fuel debris, such as electrolytic reduction, fluorination and vulcanization. Y.Sakamura et al. have Investigated the reduction behaviors of ZrO_2, Li_2ZrO_3 and $(U,Pu,Zr)O_2$ in a LiCl-Li_2O salt bath at 923 K to find a way for pyrochemical treatment of corium [15].The uranium in $(U,Pu,Zr)O_2$ could be reduced to the metallic form in LiCl-Li_2O. However, part of the zirconium was converted to Li_2ZrO_3 during electrolytic reduction inextricably. FLUOREX process has been studied by Thermogravimetric Differential Thermal Analysis (TG-DTA) method in the presence of fluorine (F_2) for the fuel debris treatment [16]. The ZrO_2 only showed the formation of non-volatile $ZrOF_2$ below 500 °C. The uranium rich UO_2-ZrO_2 mixture (UO_2:ZrO_2=9:1) volatilized completely by forming volatile UF_6 and ZrF_4 via oxyfluorides. However, fluorination behavior of UO_2-ZrO_2 mixture is suppressed with increasing ZrO_2 amount by the formation of stable solid solution. N. Sato et al. has carried out the study about sulfurization behavior of uranium oxides, zirconium metal and oxide and structural materials as fuel debris by the sulfurization treatment using carbon disulfide(CS_2) [17]. As a result, U_3O_8 was reduced to UO_2 by reaction with CS_2 at $T>573$ K, while UO_2 was stable in the presence of CS_2 at $T<773$ K. No reaction was observed for ZrO_2 in the presence of CS_2 at $T<773$ K. In the acid leaching experiment. The dissolution ratios were very low for uranium and plutonium and dissolution was observed for rare-earth oxysulfide and sulfide.

From the perspective of managing these insoluble radioactive wastes more safely, more research on new disposal routes is necessary. Now we have proposed that these substitutes are chemically converted into easily soluble substitutes by chlorination reactions. In order to be more conducive to the occurrence of chemical conversion reactions (increase the specific surface area), it is necessary to powderize insoluble substances containing uranium zirconium oxides. In our previous study, the non-equilibrium plasma oxidation device was used to pulverize insoluble solids containing uranium oxides, which confirmed the feasibility of thermal oxidation under milder conditions (below 200°C) to achieve pulverization [18].

We proposed the use of thermochemical chlorination in order to dissolve the insoluble substances consisted of uranium zirconium oxides, such as nuclear debris. In the present study, the thermochemical conversion of ceria (CeO_2, cerium is simulant element of uranium.), uranium oxides, and simulated debris $(U_{0.5}Zr_{0.5})O_2$ prepared by ammonia co-precipitation method and then sintering at 1,700°C for 3 hours, with CCl_4 were carried out, and the dissolution rates in hydrochloric acid and nitric acid solutions were evaluated. To study the chlorination conversion, the carbon tetrachloride (CCl_4) is chosen to be the chloride reagent. There is report that using $MoCl_5$ successfully make the Chlorination of $(U_{0.5}Zr_{0.5})O_2$ powders and dense pieces achieved at 573K and 773K, respectively [19]. T. Kitagaki et al investigated the chlorination behaviour of CeO_2 using the atmospheric-pressure non-thermal plasma with the chlorinating agents CCl_4. The yield of $CeCl_3$ increased with increasing irradiation time and the dissolution rate of Ce ions in pure water was significantly higher for irradiated products than for unirradiated CeO_2 [20]. Also comparing to the conventional chlorination technique of the oxide fuel using chlorine gas [21], CCl_4 is expected to have other advantages, such as high reaction rate at lower temperature and easiness of handling solution CCl_4.

2. Experimental materials and methods

2.1. Experimental materials

In order to make the chlorination reaction as completely as possible, we decided to use a closed reaction vessel to achieve a long period of heating chlorination, that is, cap and plug produced by the American company swagelok to form a closed reaction vessel, which are made by stainless steel 316, with high temperature and high-pressure resistance to chlorine gas corrosion. The appearance and the sizes are shown in **Figure 1**.

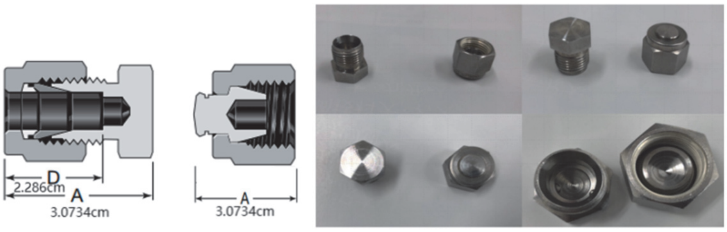

Figure 1. (right) Plug (left) and Cap (right) of Swagelok company: (left) photos of Cap and Plug.

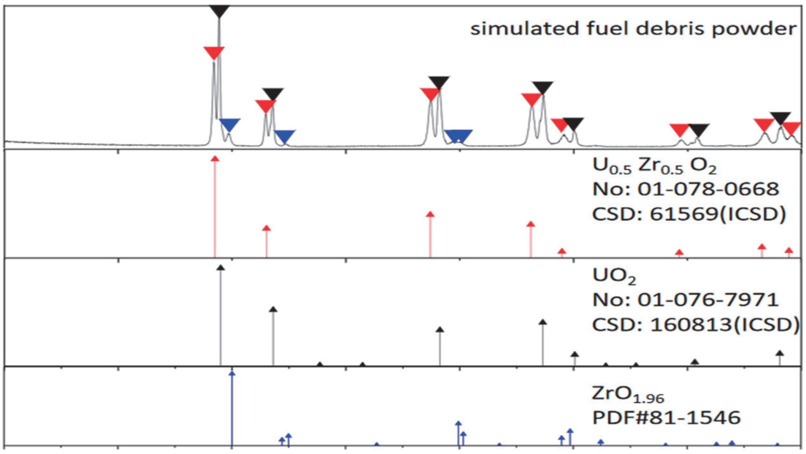

Figure 2. simulated debris prepared by Nippon Nuclear Fuel Development (NFD).

CeO_2 powder and CCl_4 solution used in the experiment were purchased commercial reagents (Wako Special Grade, FUJIFILM Wako Pure Chemical Corporation). The uranium dioxide powder used was prepared by Tohoku University through the elimination and reduction of uranyl nitrate. The triuranium octoxide powder was prepared by heating uranium dioxide powder to 600 °C for 2.5 hours in an oxygen atmosphere. The simulated nuclear fuel debris was prepared in Nippon Nuclear Fuel Development (NFD). The homogeneous precipitate powder of U, Zr was prepared by wet method, which was converted into oxide powder after reduction by heating, then sintered to prepare simulated debris pellets. **Figure 2** is the XRD data of the simulated nuclear fuel debris after being submerged and pulverized, which is the $(U_{0.5},Zr_{0.5})O_2$. The nitric and hydrochloric acid solutions used are also purchased commercial reagents (ultrapure reagent, KANTO KAGAKU).

2.2. Experimental methods

The experimental process of chlorination heating is as follows: the material powder and carbon tetrachloride solution were mixed in the container according to the mass ratio of 1:10 (0.1g:1g). In order to reduce the volatilization of carbon tetrachloride solution, the material powder was first added. Use a wrench to completely lock the cap and plug parts of the assembly, put them into the heating furnace, start heating. Setting the heating procedure; heating at 10 °C/min to 400 °C, maintained at 400 °C for 12 hours then cooling to room temperature. The resulting products will be used to prepare XRD (X-ray diffractometer) samples and dissolution experiments.

When preparing XRD samples, in order to prevent chlorination products from absorbing moisture, the reaction vessel was opened in the assembly in the glove box under the Ar gas atmosphere without water vapor. The product was placed in a Non-reflective silicon sample holder with a cover for measurement. XRD used for the spectrogram is belong to International Research Center for Nuclear Materials Science Institute for Materials Research (IMR) Tohoku University, type RINT2500V15. The measurement conditions are as follows: incident X-ray coming from Cu, λ= 0.15418nm, voltage of X-ray tube is 40kV, current of X-ray tube is 200mA, scanning speed is 2.0 degree /min, scanning range is from 10 degree to 80 degree, scanning axis $2\theta/\theta$.

The dissolution experiment process is as follows: After opening the container in the fume hood, add ultrapure water and 1mol/L nitric acid, transfer the solution to a 50mL centrifuge tube after shaking well, and then add concentrated nitric acid/hydrochloric acid to adjust the acidity to 6 mol/L. Before pressure filtration, heat the solution with a centrifuge tube heater (80 °C, 30min), and finally filter with 0.22 mm hydrophilic filter paper. After filtration, the filter residue on the filter paper was weighed. In the dissolution experiment of simulated nuclear fuel debris, the concentration of uranium ion in the filtrate was analyzed by using an ICP-MS (7700, Agilent).

3. Results and discussion

The chosen analogue should have the same fluorite crystal structure as UO_2 (face centered cubic, space group Fm-3m). This is common in other f-block oxides, notably the rare-earth element cerium, CeO_2 and also the actinide thorium, ThO_2. The analogue must also have a microstructure similar to that of a typical UO_2 nuclear fuel: the grains should be randomly orientated and have a specific size and porosity. Both UO_2 and CeO_2 have same fluorite type structure and can be engineered to similar grain sizes and crystallographically randomly orientated grain [22,23]. Therefore, cerium oxide is used to simulate the chlorination of uranium dioxide and carbon tetrachloride. The reaction of cerium oxide with chlorine is complicated, and many side reactions exist at the same time. The conventional chlorination reaction usually takes a long time and the conversion rate is low. From the XRD results of **Figure 3**, it can be found that cerium oxide and cerium chloride are mixed in the chlorination product. As the heating time increases, the peak of CeO_2 gradually disappears, which indicate that longer heating time can better obtain chlorinated products. **Table 3** shows the dissolution results of cerium oxide chlorination products. No matter in

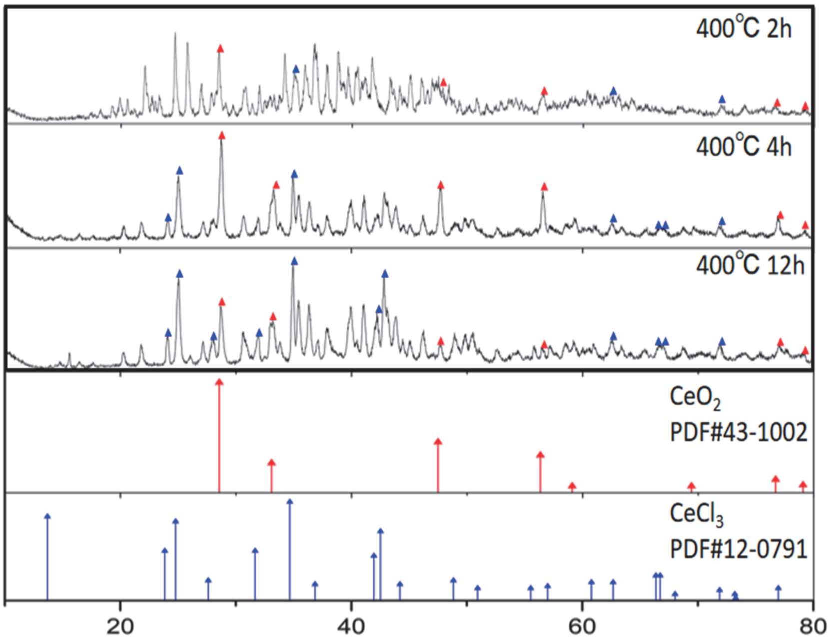

Figure 3. Chlorination products of cerium oxide

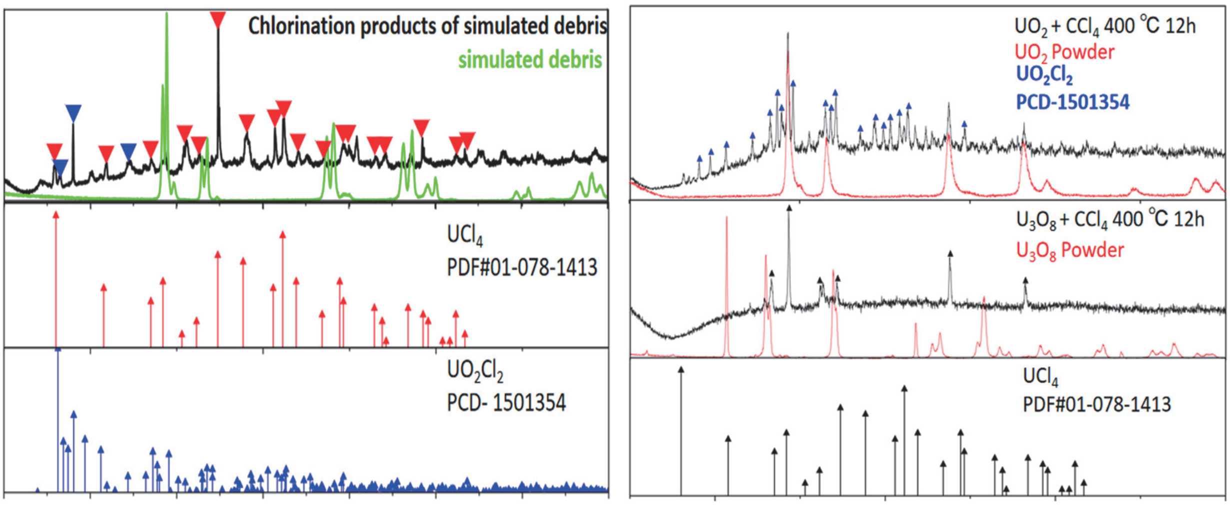

Figure 4. XRD of Chlorination products of uranium oxides (left) and simulated nuclear fuel debris (right).

hydrochloric acid or nitric acid, a high powder dissolution rate is obtained (≥90%). Under the heating time of 12h, the obtained chlorination products are almost 100% dissolved. In the uranium chloride experiment, 12h was used as the heating time.

The left side of **Figure 4** shows the XRD data of chlorinated products of UO_2 and U_3O_8. In addition to the intermediate product UO_2Cl_2, uranium dioxide remains in the chlorination products of uranium dioxide, while only chlorination products exist in the products of triuranium octoxide. As shown in the right side of Figure, unlike the chlorination results of UO_2, the chlorination products of $(U_{0.5}, Zr_{0.5})O_2$ are mainly carbon tetrachloride, with a small amount of UO_2Cl_2. and almost no $(U_{0.5}, Zr_{0.5})O_2$ indicates that the chlorination reaction has been completed relatively thoroughly.

In the description of the reaction mechanism of uranium oxides with carbon tetrachloride gas elsewhere [24], the following reaction is the principal one:

$$UO_2+CCl_4 \rightarrow UCl_4+COCl_2 \qquad (1)$$

There are also other competing reactions:

$$UOCl_2+CCl_4 \rightarrow UCl_4+COCl_2 \qquad (2)$$
$$UO_2+2COCl_2 \rightarrow UCl_4+2CO_2 \qquad (3)$$
$$COCl_2 \rightarrow CO+Cl_2 \qquad (4)$$
$$UCl_4+0.5Cl_2 \rightarrow UCl_5 \qquad (5)$$
$$UCl_4+O_2 \rightarrow UO_2Cl_2+Cl_2 \qquad (6)$$

Table 2. The dissolution results of the chlorination test for CeO_2.

Acid	Heating time (h)	Dissolution rate ($D_{wt\%}$)	Acid	Heating time (h)	Dissolution rate ($D_{wt\%}$)
HNO_3 (6mol/L)	2	96.32%	HCl (6mol/L)	2	98.04%
	4	91.77%		4	95.24%
	12	99.52%		12	99.37%

Table 3. The dissolution results of the chlorination test for UO_2/U_3O_8 and simulated nuclear fuel debris $(U_{0.5},Zr_{0.5})O_2$.

Sample	Heating time (h)	Acid	Dissolution rate ($D_{wt\%}$)	Dissolution rate (D_{ICP-MS})	Acid	Dissolution rate ($D_{wt\%}$)	Dissolution rate (D_{ICP-MS})
UO_2	12	HNO_3 (6mol/L)	64.86%	/	HCl (6mol/L)	72.70%	/
U_3O_8			81.52%	/		79.41%	/
$(U_{0.5},Zr_{0.5})O_2$			64.72%	97.7 ± 1.0%		78.08%	96.5 ± 2.0%

In this study, no intermediate product $UOCl_2$ was found in the XRD results of the chlorination products of UO_2, U_3O_8 and uranium-zirconium solid solutions, indicating that long-term heating has completed the chlorination reaction of the substrates, and only the chlorination product of UO_2 remains. UO_2 also contains a large amount of UO_2Cl_2, and the latter two produce the corresponding chlorination product UCl_4.

Regarding the explanation of UO_2 chlorination products, this may be due to the fact that the container was not completely sealed during the experimental operation. There was not only an excess Cl_2 atmosphere, but also a large amount of air. As shown in Eq. (6), the UCl_4 partially produced was due to the presence of oxygen. And UO_2Cl_2 is generated.

There have been study [21] describing the reaction pathways during chlorination experiments on UO_2 using chlorine gas, taking into account the following reactions:

$$UO_2 + Cl_2 \rightarrow UCl_4 + O_2 \quad \Delta G = +148.9 \text{ kJ mol} \tag{7}$$

$$UO_2 + Cl_2 \rightarrow UO_2Cl_2 \quad \Delta G = -29.2 \text{ kJ mol} \tag{8}$$

The remaining uranium dioxide may not be completely chlorinated as shown in Eqs. (7) and (8), resulting in the residue of the substrate and the production of UO_2Cl_2. In the chlorination experiment of uranium-zirconium solid solution, there may be situations where the air in the container affects the chlorination reaction, but the final production of UCl_4 shows that this method should be able to complete the complete chlorination reaction of UO_2. Such effects will be further emphasized in future studies to avoid them. In addition, further prolong the reaction time and increase the amount of CCl_4 to avoid the participation of oxygen in the air during the chlorination reaction. Shaking the container during heating may promote the chlorination reaction of uranium dioxide to produce uranium tetrachloride. It has also been reported that the color of the test material changes gradually from the surface layer to the bottom layer with the increase of reaction time when chlorine is injected into the tubular furnace to chloride uranium dioxide, indicating that the chlorination reaction gradually penetrates from the surface layer to the bottom layer [25].

In this study, the chlorination product of U_3O_8 only contains UCl_4 but not $UOCl_2$ and UO_2Cl_2, indicating that it has not been affected by the air atmosphere in the container and has undergone a complete chlorination reaction. Higher dissolution rates may be possible in subsequent dissolution experiments.

Regarding the confirmation of the dissolution rate, the Weight method was used to confirm the dissolution rate in the chlorination experiments of CeO_2 and uranium oxides, and ICP-MS was also used in the chlorination experiments of simulated nuclear fuel debris.

The dissolution rate evaluated by weighing method was calculated as follows:

$$D_{wt\%} = \frac{[m_{p\,(U/Ce)} - m_{r\,(U/Ce)}]}{m_{p\,(U/Ce)}} \times 100 \tag{9}$$

Where $D_{wt\%}$ indicates that the dissolution rate is obtained by Weight method, and the unit is percentage (%), $m_{p(U/Ce)}$, $m_{r(U/Ce)}$ are the original mass of U (or Ce) in uranium oxides (or CeO_2) and the mass of U (or Ce) in residues, respectively.

The dissolution rate evaluated by ICP-MS method was calculated as follows:

$$D_{ICP\text{-}MS} = \frac{m_{f\,(U/Ce)}}{m_{p\,(U/Ce)}} \times 100 \tag{10}$$

Where $D_{ICP\text{-}MS}$ indicates that the dissolution rate is obtained by ICP-MS method, and the unit is percentage(%), $m_{f(U/Ce)}$ and $m_{p(U/Ce)}$ are the U/Ce mass in the filtrate and the original mass of U(or Ce) in uranium oxides (or CeO_2), respectively. **Tables 2** and **3** are the results of the dissolution experiments. It can be seen in Table 2 that the chlorination product of CeO_2 has reached a higher solubility ≥90% in 6 mol/l nitric acid and hydrochloric acid, and with the increase of heating time, the powder dissolution rate of 12h has reached 99%. Table 3 shows the dissolution results of uranium oxides. The powder dissolution rate of U_3O_8 chlorination products in 6mol/L nitric acid and hydrochloric acid both reached about 80%, while UO_2 showed a lower powder dissolution rate. U_3O_8 is less susceptible to chlorination than uranium dioxide in thermodynamics, but the actual reaction product is completely transformed from black uranium trioxide powder to green uranium chloride. The data of $(U_{0.5}Zr_{0.5})O_2$ in Table 3 shows that the corresponding $D_{wt\%}$ values of the nitric acid group and the hydrochloric acid group are very close to the $D_{wt\%}$ value of uranium oxide, but the $D_{ICP\text{-}MS}$ obtained by ICP-MS shows that both the nitric acid group and the hydrochloric acid group are dissolved almost all uranium (≥95%). This is consistent with the XRD results after the chlorination experiment of $(U_{0.5}Zr_{0.5})O_2$. There is almost no raw material $(U_{0.5}Zr_{0.5})O_2$ in the chlorination product.

4. Conclusion

The conclusions of the simulated nuclear fuel debris chlorination experiments and dissolution experiments has been added to the conclusion. The revised conclusion is shown in red text below:

The chlorination experiments of CeO_2, UO_2 and U_3O_8, simulated nuclear fuel debris $(U_{0.5},Zr_{0.5})O_2$ were carried out and also the dissolution experiments of chlorination products in nitric acid and hydrochloric acid (6mol/L). The feasibility of this pretreatment process to chlorinate and dissolve uranium from uranium dioxide, triuranium octoxide and $(U,Zr)O_2$ has been confirmed.

In the chlorination experiment of CeO_2, XRD pattern shows that with the increase of heating time, the chlorination reaction is more complete (2h, 4h, 12h). In the chlorination product heated at 400°C for 12 h, a mixture of $CeCl_3$ and CeO_2 was confirmed. In the dissolution experiment, both nitric acid and hydrochloric acid have reached a high dissolution rate (≥90%).

In the chlorination experiment of UO_2 and U_3O_8, UO_2Cl_2 and UO_2 were identified in the chlorination products of uranium dioxide, while only UCl_4 was identified in the chlorination products of U_3O_8. The $D_{wt\%}$ of the chlorinated products of U_3O_8 was higher than that of UO_2 in both HNO_3 and HCl (6mol/L).

In the chlorination experiment of simulated nuclear fuel debris $(U_{0.5},Zr_{0.5})O_2$, UCl_4 and UO_2Cl_2 were identified in the chlorination products. The $D_{ICP\text{-}MS}$ reaches a high rate (≥95%) in HNO_3 and HCl (6mol/L) respectively.

In conclusion, considering the difference of reactivity between uranium dioxide (UO_2) and triuranium octoxide (U_3O_8), it is suggested to oxidize the nuclear fuel debris before the chlorination experiment to achieve better experimental results. But further analysis is still needed for the composition of the filtrate and filter residue.

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