1–7 Toward the Recovery of Uranium from Fuel Debris
— Development of a Chlorination Method for Slightly Soluble Components —

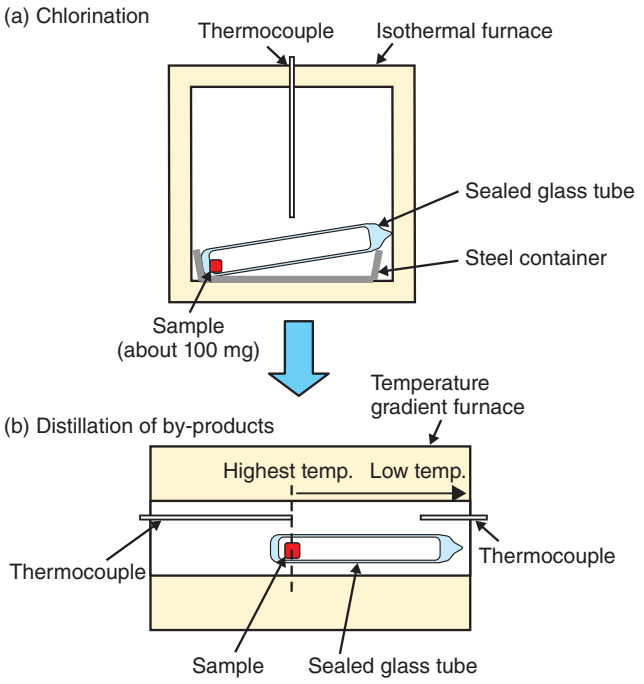

Fig.1-18 Outline of a chlorination experiment with fuel debris from $MoCl_5$
A mixture of $(U_{0.5}Zr_{0.5})O_2$ and $MoCl_5$ is sealed in a glass tube in vacuum. It is converted to chloride by homogeneous heating at 573–773 K and by-products are separated by distillation at 573 K under a temperature-gradient condition.

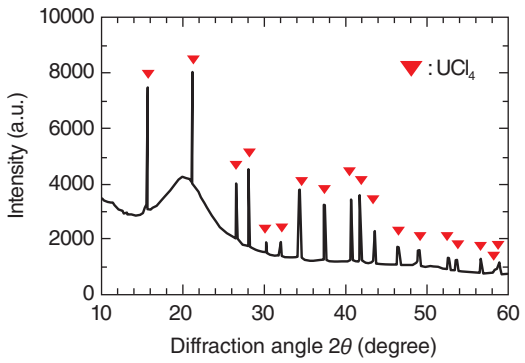

Fig.1-19 XRD profiles of the product obtained from a reaction between $(U_{0.5}Zr_{0.5})O_2$ and $MoCl_5$
Observed peaks were identified as tetragonal UCl_4 obtained by a chlorination reaction.

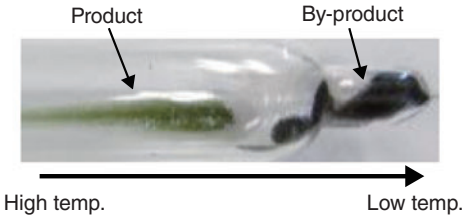

Fig.1-20 Appearance of the product after separation of by-products
By chlorination of $(U_{0.5}Zr_{0.5})O_2$, green UCl_4 was obtained as a product (left side in the figure), and $MoOCl_3$ and $ZrCl_4$ by-products were separated by distillation (right side in the figure).

As a result of the accident at the TEPCO's Fukushima Daiichi NPS, the treatment of fuel debris generated by solidification of melted fuels has been studied. One possible treatment option that has been proposed is the application of pyrochemical reprocessing technologies of spent nuclear fuels to treat fuel debris. According to the pyrochemical method, uranium and plutonium in spent fuels are separated from fission products and recovered to a cathode by electrolysis in a molten salt. A large issue with this method is the development of a pretreatment technique for converting fuel debris into chlorides.

Conventional chlorination techniques using chlorine gas over 873 K require the use of corrosion-resistant structural materials. In contrast, the chlorination technique using molybdenum pentachloride ($MoCl_5$) is expected to have advantages such as a lower reaction temperature, ease of handling the solid $MoCl_5$. By-products of this method can also be efficiently separated from chloride products by distillation.

In this study, we propose a new chlorination method of fuel debris using $MoCl_5$ and study the applicability of this method through basic experiments.

Using uranium–zirconium oxide solid solution ($(U_{0.5}Zr_{0.5})O_2$) powder and sintered pellets as simulated fuel debris, chlorination experiments with $MoCl_5$ were conducted and the reaction principle of uranium chlorination and separation of by-products by distillation (Fig.1-18) were confirmed.

Regarding the chlorination reaction, most uranium in the sample was successfully converted to uranium tetrachloride (UCl_4) at 573 K (for the powder) or 773 K (for the sintered particles) based on the following equation (Fig.1-19):

$$2(U_{0.5}Zr_{0.5})O_2 + 4MoCl_5 \rightarrow UCl_4 + ZrCl_4 + 4MoOCl_3$$

By-products of this reaction include $MoOCl_3$ and zirconium tetrachloride ($ZrCl_4$). These were successfully separated from UCl_4 by distillation at 573 K (Fig.1-20).

On the basis of these results, we proposed a new chlorination method for fuel debris using $MoCl_5$ and confirmed its applicability in principle.

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Reference

Sato, T. et al., Chlorination of UO_2 and (U, Zr)O_2 Solid Solution using $MoCl_5$, Journal of Nuclear Science and Technology, vol.52, issue 10, 2015, p.1253-1258.