

Pyrochemical Recycling of the Nitride SNF of Fast Neutron Reactors in Molten Salts as a Part of the Short-Circuited Nuclear Fuel Cycle

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Abstract. The scientific and technological aspects of the pyrochemical recycling of uranium-plutonium nitride nuclear fuel used in the circuited nuclear fuel cycle on the basis of nuclear power plant with fast neutron reactors were considered

Key Words: Pyrochemistry, uranium, UNCl, chlorination.

1. Introduction

The most interesting and promising direction in the processing of highly irradiated fuel of fast reactors is a pyrochemical method. Currently, molten chloride salt mixtures are considered the most promising media for pyrochemistry. They are the subject of intense research in a number of countries. For example, in the U.S. the works on electrochemical refining of irradiated metallic fuel are successfully developed [1]. The mixed oxide fuel is widely studied in South Korea [2]. In both cases, the anodic dissolution of spent nuclear fuel (SNF) into LiCl or the LiCl-KCl melt at moderate temperatures is considered as the initial stage of the process. In Russia the mixed uranium plutonium nitride fuel (MUPUNF) is considered as a dense fuel for fast reactors. Chemical and electrochemical interactions of irradiated MUPUNF with chloride melts have significant features as compared to the MOX and dense metal fuels. This is primarily due to the ability of uranium to form nitride-chloride (UNCl) and other stable nitrides, which are dielectrics. In electrochemical processes, for example, at irradiated MUPUNF refining, they cover part of the anode surface, which leads to substantial inefficiency of electrorefining process. To transfer the majority of the spent nuclear fuel components into the melt, a process of "soft chlorination" can be used. This process offers several advantages as compared to electrolysis. Certainly both processes are diffuse in nature, and redox potential at the surface of the nitride tablet is determined by the rate of removal of the products of the corresponding reactions.

2. Electrorefining

Direct electrolytic refining of UN tablets in the molten LiCl-KCl eutectic with simultaneous deposition of uranium on liquid cadmium cathode did not produce positive results. A considerable amount of anode material remains on the bottom of the anode basket in the form of sludge, which ultimately makes the usage of this electrochemical process meaningless. It is possible to try to minimize the formation of undesirable uranium compounds, maintaining sufficiently electronegative potential of the anode. For this purpose nitrogen should dissolve in the melt and should diffuse from the tablet surface and should not escape as a gas. Given the extremely low solubility of nitrogen, as well as its small diffusion coefficients in the LiCl-

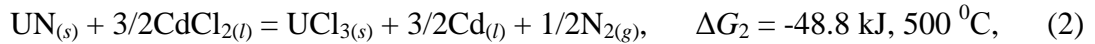
KCl eutectic (argon level), this situation is only possible at very low anode current density, just a few milliamperes per square centimeter.

3. Chlorination

Thermodynamic simulation of chlorination process depending on nitrogen and chlorine gases pressure (i.e. of the redox potential in the melt) in the presence of CdCl_2 at $500\text{ }^\circ\text{C}$ shows that UNCl is the most stable uranium compound (if the nitrogen gas pressure at the surface of the UN tablet is close to one atmosphere). Thus, reaction (1) is the most thermodynamically probable.



However in this case reaction (2) is also necessary for the nitrogen gas formation and increasing its pressure.



Since reactions (1) and (2) proceed in the molten eutectic LiCl-KCl medium, the activities of the components are lowered due to both the dilution and complexating. This significantly shifts the equilibrium of reaction (2) toward to the UCl_3 formation. Our experiments strongly support this conclusion. At the chlorination of UN with cadmium chloride in the molten LiCl-KCl medium (reaction 2), the melt color changes from colorless to purple, which definitely indicates the UCl_3 solutions formation. Fig.1 shows the changes in cadmium dichloride and uranium trichloride concentrations in the molten LiCl-KCl eutectic during the chlorination of UN tablets at the temperature $500\text{ }^\circ\text{C}$.

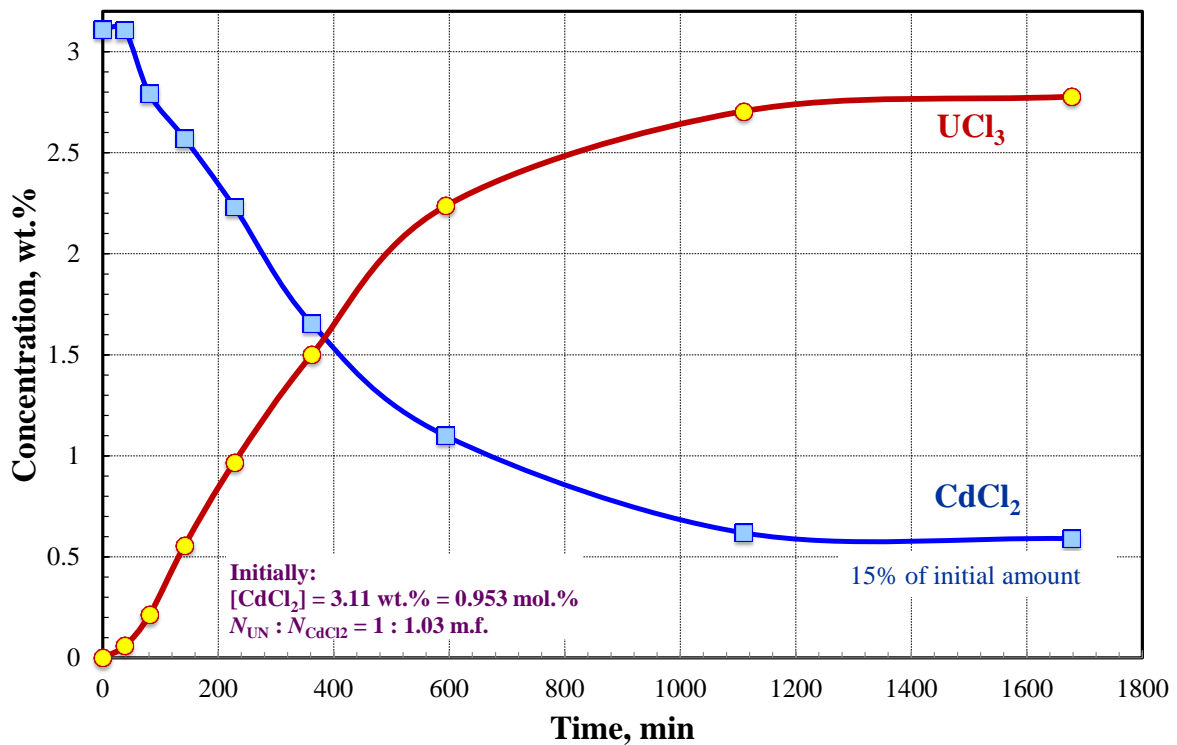


FIG. 1. Kinetics of reaction (2) in the molten LiCl-KCl medium at $500\text{ }^\circ\text{C}$.

Fig. 1 demonstrates that the concentration of uranium trichloride gradually increases and reaches a constant value. As follows from the stoichiometry of reaction (2), the mass of the UN tablet was taken with double excess with respect to cadmium dichloride. This means that the cadmium salt should be completely removed from the melt, but it does not happen. The X-ray analysis showed the presence of UNCl, U_2N_3 , UN_2 phases in the pills residues. These substances were found in comparable amounts, and UN was not detected. The conversion degree of UN into uranium trichloride by reaction (1) amounted to approximately 50%. The presence of significant quantities of UNCl confirms progress of reaction (1). Other uranium nitrides were probably formed by the reaction between UN and N_2 , evolved due to reaction (2). See for example the reaction (3):



The situation did not change significantly even if cadmium dichloride was taken in double excess (in the reaction 2).

There are two ways to increase UN conversion into UCl_3 :

1. Reduce activity of UCl_3 by replacing a salt-solvent. For example, UCl_3 activity coefficient in molten NaCl-CsCl is lower than that in the LiCl-KCl eutectic.

2. Change the temperature of interaction.

The first way can help to clarify the mechanism of interaction (reaction 2), which will help to search for positive solutions. However, in practice cesium salts can be hardly used.

Thermodynamic simulation of the temperature influence on the fullness of reaction (2) was performed. Stability diagrams were constructed for the temperature of 500 °C. According to the calculations, UN is completely converted into UCl_3 without of UNCl formation even at a nitrogen pressure close to the atmospheric one at the temperature of 750 °C or higher.

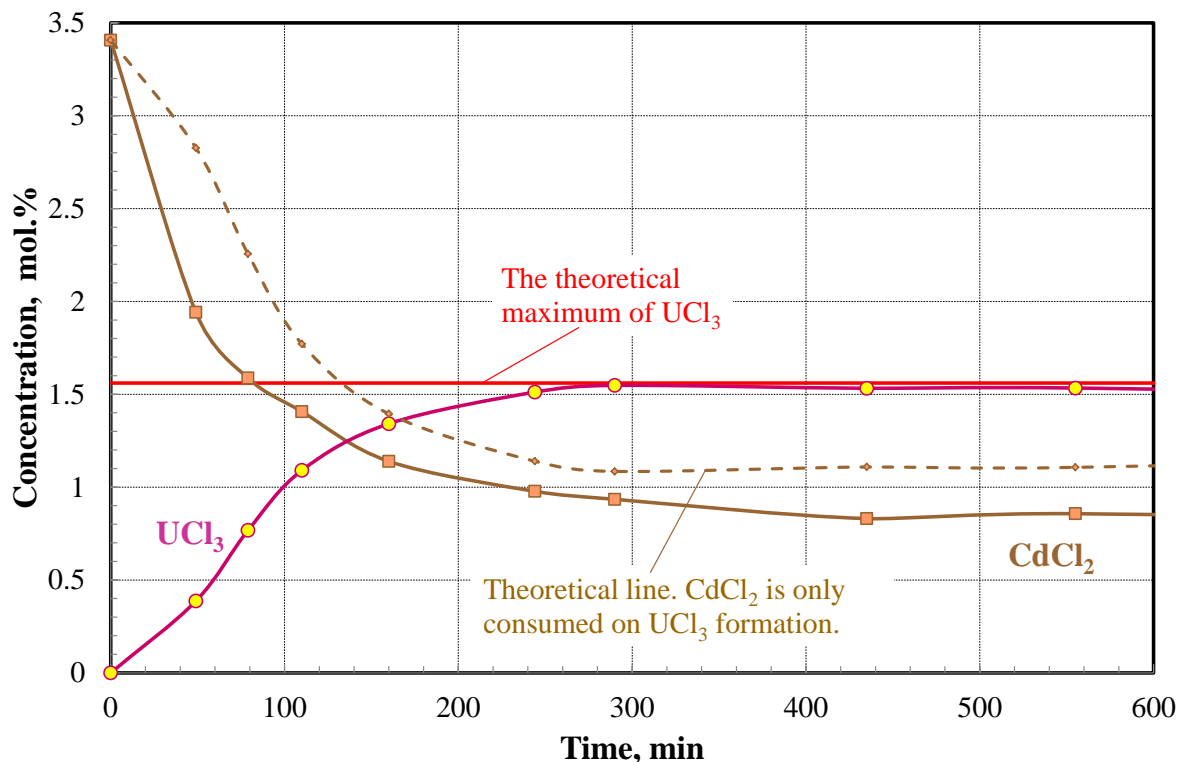


FIG. 2. Kinetics of reaction (2) in the molten LiCl-KCl medium at 750 °C. Double excess of $CdCl_2$. $t_b(Cd) = 767$ °C.

At this temperature, metallic cadmium almost boils and is completely removed from the reaction zone (it condenses at the less heated parts of the apparatus). The cadmium removal shifts additionally the equilibrium of reaction (2) to the right.

The experimental results on the “soft” chlorination of the UN tablets with cadmium chloride at 750 °C are shown in Fig. 2. As follows from the figure uranium mononitride converted entirely into UCl_3 . The amount of released cadmium and formed uranium trichloride corresponds to reaction (2) and to amount of taken UN. The additional consumption of $CdCl_2$ above stoichiometric is connected with its evaporation. In this experiment it was of the order of 9%.

Thus the increasing temperature of reaction (2) has positive effect on the efficiency of the process, and the problem may be solved by finding the optimal process parameters.

4. References

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