

Development of *in-situ* UV-vis technique for the molten salt electrorefining process of uranium

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1. Introduction

During the last decade, interest in the pyrometallurgical treatment of spent nuclear fuel has been drastically increased because of its relatively low processing cost as well as its proliferation resistance of the nuclear fuel cycles[1,2]. Similar but unique researches have been conducted by several institutions in various countries using their own strategies, i.e. IFR fuel cycle in ANL, DOVITA process in RIAR and OMEGA program in JAERI [3]. The Korea Atomic Energy Research Institute (KAERI) is developing an electrorefining process using PWR surrogate spent fuels. In this fuel cycle, uranium and TRU oxides are electrochemically reduced while the rare earth oxides are intact. Thus, the prepared ingot consists of metallic uranium, TRU and rare earth oxides. The main scientific and technological interests in the electrorefining process using the electrochemically reduced fuel ingot are how to effectively partition a spent fuel into Uranium, TRU and fission products (FPs). Furthermore a systematic consideration for a series of pyrochemical treatments of the spent fuel which includes not only an electrorefining but also a cathode process has not been reported. Hence in this study, we would like to report on the methodology to recycle PWR fuel for a future use and some important results in the electrorefining of the uranium and the cathode process of the deposit. Also, *in-situ* UV-vis absorption spectrometry was adopted to observe the behavior of Nd_2O_3 in molten salt encouraged by the recent results of Yamana et. al.[4-6].

2. Experimental

The electrorefining apparatus was installed in a glove box filled with high-purity Ar gas. The solid cathode with a rugged groove can be rotated during an electrodeposition to achieve a better recovery and the molten salt itself is also agitated by means of a crucial anode. The material of the anode and cathode was STS 304L and the reference electrode was iron. High purity LiCl-KCl eutectic(41.5-58.2 mol%, T_m :355 °C) and rare earth salts of a 99.9% purity were purchased from Sigma-Aldrich. The chloride of the trivalent uranium was extracted as molten LiCl-KCl by an oxidation reaction between the depleted uranium metal in the anode basket and CdCl_2 . All the chemicals were handled in a glove box in which both the oxygen and moisture contents in the argon atmosphere were

maintained at lower than 10 ppm. The SUS 304 cell with a proper insulation device was located in a stainless steel thermowell which was heated externally with an electric furnace attached to the floor of a glove

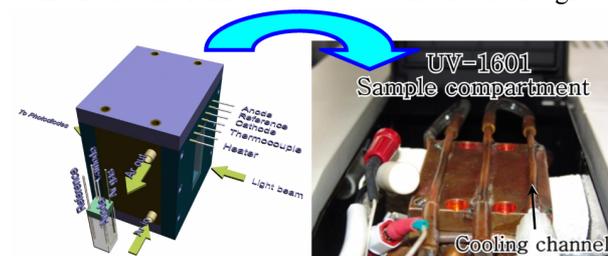


Fig. 1. *in-situ* UV-Vis spectrophotometry measurement system for molten chloride sample(cooling channel is hidden in the left hand schematic for simplicity)

box, and the temperatures were controlled at 500 °C. Electrodeposition tests were performed by the use of an Ecohemie Autolab 30 potentiostat controlled by a computer system. In the case of the partitioning experiment, LiCl-KCl eutectic salt containing uranium and three REs(Gd, Dy and Ce) or Nd_2O_3 with a 10 wt% ratio to the uranium were used on the assumption that the REs were fully reduced to a metallic form or not, respectively, during the electroreduction step. Three REs which have similar electrochemical characteristics

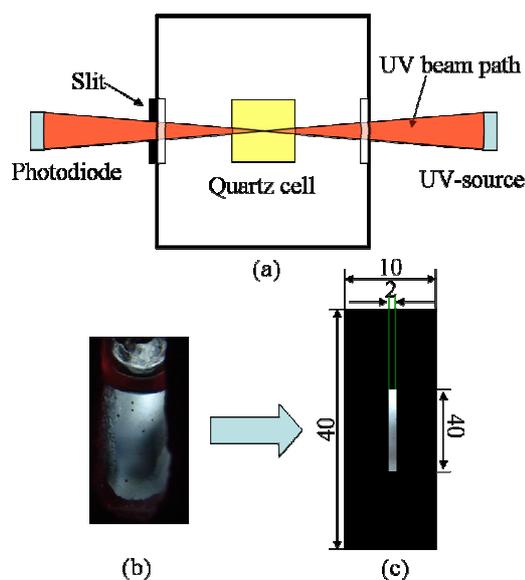


Fig. 2. Configuration of *in-situ* UV-cell(a) and before(b) and after(c) slit installation

with TRU were formulated as the spent fuel surrogate, since there are difficulties in a handling of the TRU in Korea. In the case of Nd_2O_3 , it was added to the anode basket as a sintered pellet to observe the dissolution behavior during an electrorefining. The concentration of the uranium and REs in the molten salt and the deposits were determined by ICP-AES. Also, in-situ UV-vis absorption spectrometry was used to directly observe the behavior of Nd_2O_3 in the molten salt at a high temperature as shown in Fig. 1. Unlike Yamana's optical fiber system, we introduced a specially designed electrolysis cell into the UV-vis sample compartment. The overexposure originated from the heating element was removed by the installation of a slit in front of photodiode as shown in Fig. 2. The morphologies of the micro deposits were analyzed by a Scanning Electron Microscope (Philips XL30) after removing the attached salt from them.

3. Results and discussion

In order to estimate the rare earth oxide contamination for the deposit, the concentrations of Nd_2O_3 put into the anode basket were measured according to the current density. Significant dissolution of Nd_2O_3 to an electrolyte was observed, while the

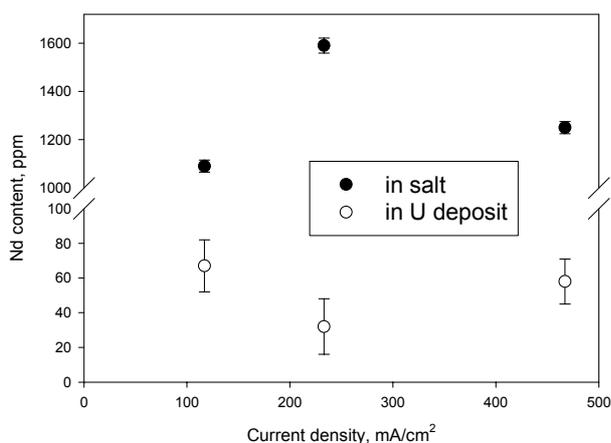
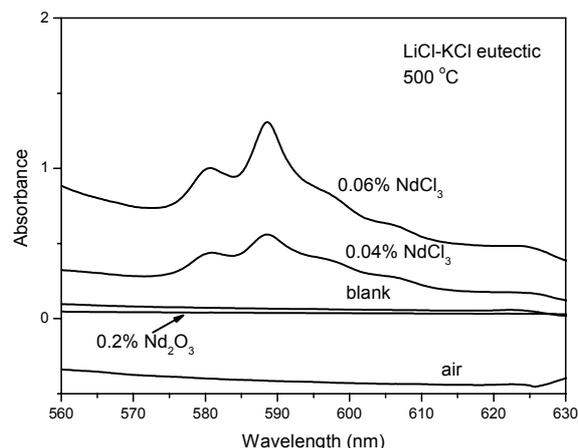


Fig. 3. Variation of Nd content in salt and uranium deposit according to current density at 500 °C and 9wt% of initial U concentration.

concentration in the U deposit was negligible as shown in Fig. 3. From the result of the irregularity of the Nd content with the current density, Nd_2O_3 might not be deposited electrochemically into the cathode deposit but physically incorporated into the uranium dendrite during a crystal growth. It was reported that dissolved NdCl_3 shows intensive hypersensitive absorption peaks at 580 and 589 nm of a wave length. In this research, absorption peaks were also observed at the same places as shown in Fig. 4. In contrast to the NdCl_3 , there is no evidence of a dissolution of Nd_2O_3 from the UV-vis absorption spectra. Hence, RE oxide powders should be removed prior to electrorefining step in order to



minimize a contamination to the U deposit through the

Fig. 4. Absorption Spectra of NdCl_3 and Nd_2O_3 at 500 °C in LiCl-KCl eutectic molten salt according to its concentration.

molten salt.

4. Conclusions

Nd(III) in molten LiCl-KCl was successfully detected by the *in-situ* UV-vis system with the help of a slit. The solubility of Nd_2O_3 was found to be negligible. It was found that the partitioning behavior of the elemental REs(Gd, Nd and Ce) are similar to each other according to the applied voltage or current and the REs can be successfully portioned, provided the initial UCl_3 concentration is more than ~6 wt%.

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