

Design of In-situ Measurement System of Uranium Concentration in LiCl-KCl Eutectic Electrolyte

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1. Introduction

Pyrochemical process technology of nuclear fuels using a LiCl-KCl eutectic, currently being developed in the Korea Atomic Energy Research Institute (KAERI) as promising options for future spent nuclear fuel management in Korea, has many advantages such as compactness, economy, radiation stability of the solvent, and non-proliferation [1]. In this pyrochemical process, it is essential to have in-situ information on the concentration of process material such as uranium, plutonium, and fission products as well as their chemical and physical behaviors in a high temperature molten salt medium, since the actinides and lanthanides in the molten salt play an important role for an effective actinide metal recovery during the electro-refining step. In the electro-refining step of the pyrochemical process, a small amount of UCl_3 is added to a LiCl-KCl eutectic bath to initiate electro-deposition of uranium onto a working electrode [2]. Since the concentration of uranium in the melts has a tendency to decrease after several batches of process, the concentration of uranium has to be checked continuously, especially when being transferred to the electro-winning step to collect the minor actinides such as neptunium, plutonium, americium, and curium left over in the salts.

The study of the application of a spectroscopic technique, especially absorption spectroscopy, which is known as the one of the most powerful tools to apply on-line monitoring, has been continuously increased for the investigation of the behavior of RE elements as well as actinides present in molten salt [3-5].

In this report, the applicability of UV-Vis absorption spectroscopy was studied as the on-line monitoring method for uranium concentrations in molten chloride electrolyte and a new design of UV-Vis absorption device setup was proposed for direct application to the electro-refining process.

2. Experimental

All the experiments were performed in a glovebox controlled under Ar atmosphere and equipped with a temperature controlled furnace system as shown in Fig. 1. The furnace system was specially designed for the simultaneous experiment for spectroscopic and electrochemical measurements.

The spectrometric measurement system is interfaced with an integrated glove box-furnace system. A

rectangular quartz cell (path length: 1 cm) attached to a 350-mm-long quartz tube (o.d.: 10 mm) is placed at the center of the electric furnace. The light beam (Ocean Optics Inc.) is guided into the sample chamber by using a quartz optical fiber. A suitable quartz lens and iris is used to collimate the beam path and maximize the intensity. The concentrations of uranium species were determined by ICP-AES after each experiment.

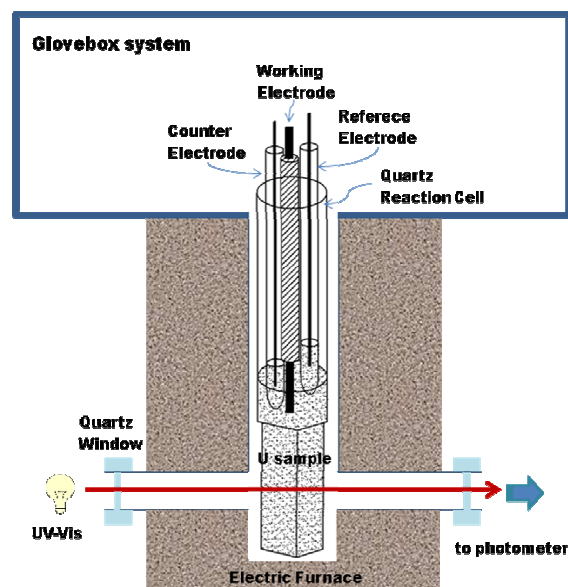


Fig. 1. Schematic view of the experimental apparatus

2. Results

Uranium(III) chloride in LiCl-KCl eutectic salt at 773K shows a deep red color as shown in Fig. 2. This is a beneficial phenomenon when using the absorption spectroscopic method for quantitative analysis, since the many possible elements present in electro-refining process such as lanthanides and minor actinides in molten salt media do not show red color as uranium.

Uranium chloride in LiCl-KCl eutectic salt at 773K was prepared by the oxidation reaction of uranium metal with bismuth(III) chloride. The color change that occurs during the synthesis of uranium chloride gives important information for the reactions. A pale green color indicates the presence of U(IV) ions, whereas dark red exhibits the appearance of U(III) ions in the melt.

The UV-Vis spectra of the U(III) ion consist of two main peaks in the range of 400 – 600 nm which are attributable to the $5f^3 - 5f^26d^1$ transitions. The UV-Vis spectrum contains main peaks of U(III) ion with a tiny shoulder of uranium(IV) peak around 670 nm.



Fig. 2. Photo of uranium(III) chloride in LiCl-KCl eutectic melt

The small amount of U(IV) ions that coexist with U(III) were electrochemically reduced to U(III) state. The changes in electronic absorption spectra of uranium species in high temperature molten salt media during the electrochemical reduction process were monitored on a real time basis. The electrochemical reduction reaction was processed with potential of -0.7V and the absorption spectrum was measured every 5 minutes. An increase of uranium(III) peaks in the range of 400 – 600 nm was observed until 55 minutes of the electrochemical process. The absorbance of the spectrum obtained after 55 minutes of electrochemical reaction at 450 nm was used for the quantitative analysis of uranium.

A new design of UV-Vis absorption device setup was proposed for the direct application to electro-refining process of the on-site and on-line measurement of uranium concentration in the molten salt media. Fig. 3 is the conceptual drawing of in-situ measurement system for uranium concentration. This system contains two main parts; one is a spectrophotometric detection part and another is an absorption measurement part which may be installed on the top of electro-refining process facility.

On the bottom of this transfer tube, an optical mirror is placed at an inclination of 45 degrees. The light is then passed through the molten salt of the electro-refining system to absorb the uranium and then transferred to the other light transfer tube arranged in bilateral symmetry and finally to a spectrophotometer. It is very useful to change the path length of the samples in the case of measuring unknown sample without any sample pretreatment, for instance, when the concentration is too high and dilution of sample is necessary. Therefore, one of the main advantages of

this on-site and on-line system is that an operator can adjust the path length with a motorized controlling device. In addition to that, the absorption measurement part can be controlled freely vertically to have optimum sinking depth and also horizontal way to change sampling position.

3. Conclusions

A new method was proposed for the on-line monitoring of uranium concentrations in molten chloride electrolyte using UV-Vis absorption spectrometric technique. A new design of uranium concentration measurement device setup was proposed for the direct application to electro-refining process. The path length for absorption was designed to be adjustable to avoid the absorbance saturation especially when the concentration of uranium is higher than 3 wt%.

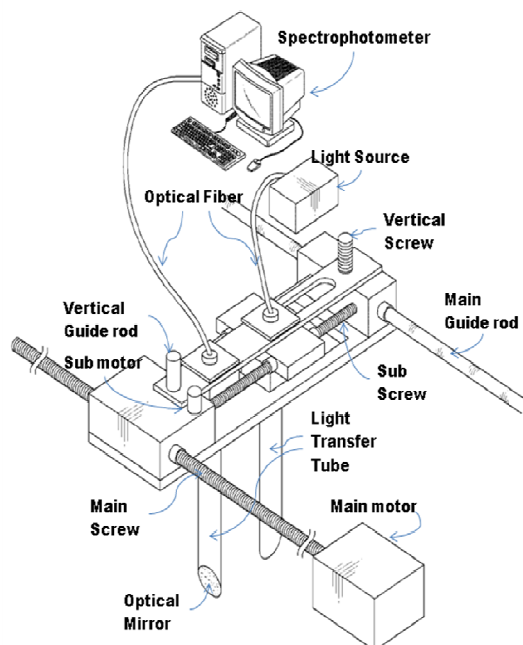


Fig. 3. Conceptual drawing of in-situ measurement system for uranium concentration

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