Analysis of Uranium Concentration in LiCl-KCl Salt of Electrorefining Process Using LIBS

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1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) has been developed for the effective and efficient safeguards of pyroprocessing at Korea Atomic Energy Research Institue (KAERI) [1]. LIBS analyzes based on the optical analysis of the radiation emitted by the plasma generated by concentrating a strong laser beam on the surface of the sample. LIBS has characteristic such as real-time analysis, no sample preparation before the analysis, and possible in situ implementation. In this study, U and lanthanide element in LiCl - KCl salt are measured as electrorefining process material of pyroprocessing via LIBS and the possibility of measurement of actinide (Pu, Cm) element is analyzed in the future try to. In fact, in the refining process delivered in the pyroprocessing, there are substances in the state of molten salt at 500℃. In this study, LiCl - KCl based salts $LaCl_3$, $CeCl_3$, $BaCl_2$, $PrCl_3$, $NdCl_3$, YCl_3 , $SmCl_3$ and UCl_3 were added and melted and then sampled the salt in the solid state was measured in order to reduce the measurement error.

2. Methods and Results

At first, five LiCl-KCl samples containing UCl_3 were fabricated to obtain the preliminary calibration curve. Sample contained from 1wt% to 10wt% UCl_3. Composition materials of the samples were placed in the glassy carbon crucible, and they were heated up to 650℃ to melt. The molten salt samples were slowly cooled to solid form in the furnace.

Experiments were conducted in a glove box with an atmosphere of Ar gas with moisture and oxygen content of 100 ppm or less for samples with high deliquescence. A laser beam was injected through the port of the glove box and the optical fiber cable was inserted I received it. The sample surface was somewhat irregular and the distance between the sample and the focusing lens was corrected each time the sample surface was changed by interlocking the XYZ moving sample table with a high precision distance meter to match the same focal length. A beam of Q-switched Nd: YAG pulse laser (Brilliant B, Quantel) with a wavelength of 532 nm is focused on the sample surface to generate plasma and Echelle spectroscopy with 20,000($\lambda/\Delta\lambda$) resolution to detect plasma emission line and ICCD camera was used. The emission lines of U and other emission line were selected in the wavelength region of 200 to 400 nm where spectroscopy is permitted. The number of laser pulses in the measurement was 100. After collecting of LIBS spectrum at a position, the sample was moved horizontally to obtain the scan data of the sample surface. As shown figure 1, the measured U spectrum in the wavelength 290.825 nm were analyzed. And then As shown figure 2, The relative standard deviation of K peak are ~ 10%, However, the

amount shown on the X-axis in the figure 2 is nominal amount before chemical analysis. For better analysis of the performances, multivariate calibration using a partial least squares regression [2] was employed to take into account the intensity correlations between the analyte lines and reference signal. The quality of the calibration could be improved through a multivariate analysis.

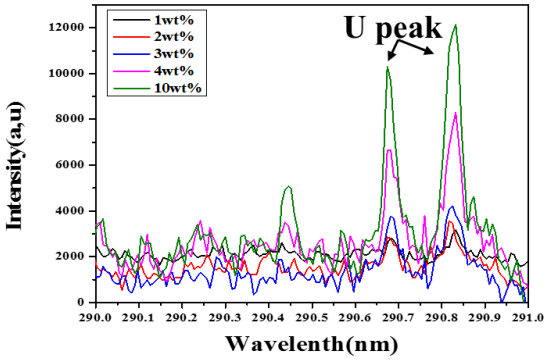

Fig. 1. U spectrum in a sample containing from 1.0wt% to 10.0wt% U in LiCl-KCl.

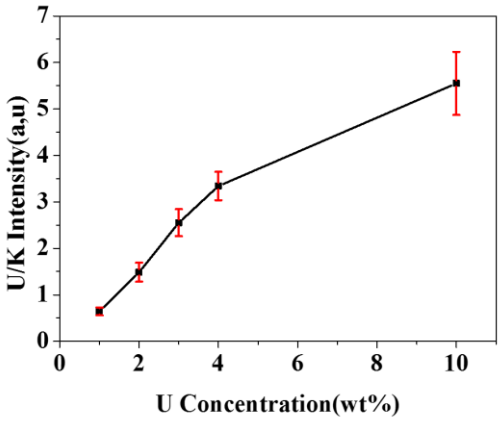

Fig. 2. The count ratio of U/K with increasing U concentration.

3. Summary

LIBS is a promising technology as the process monitoring technology applicable to the pyroprocessing safeguards. The uranium concentration in LiCl-KCl salt were measured using LIBS system, and the quantitative analysis performance of LIBS such as repeatability and Limit of Detection (LOD) are analyzed. These effort will help to assess the applicability of LIBS to the off-normal process in the electrorefining process.

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