Analysis of Uranium concentration in LiCl-LiO2 salt of Electrolytic Reduction 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 is a promising technology for the qualitative or quantitative analysis of nuclear material in the pyprocessing. LIBS utilizes a laser to create a localized plasma on the surface of the sample, and optical atomic emissions are created and measured to analyze the sample composition. LIBS has characteristic such as real-time analysis, no sample preparation before the analysis, and possible in situ implementation. Most of the previous developments of LIBS are concentrated on the nuclear material analysis in electro refining process, and LIBS analysis on the electrolytic refining salt are rare. In the present work, the uranium concentration in LiCl-LiO_2 salt of the electrolytic reduction process is analyzed using LIBS.

The electrolytic reduction process is used to reduce the spent oxide fuel to metallic form in the pyroprocessing. High-heat-load fission products are dissolved into the molten LiCl-LiO_2 salt, while most of the uranium and transuranic elements are remained in the anode basket of the electrolytic reduction in normal process. If some uranium comes out of the anode basket in the off-normal process, the uranium can be contained in the LiCl-LiO_2 salt sample, which are taken from the LiCl-LiO_2 salt after stirring the salt. In the present work, the analytical characteristic of the uranium concentration in the LiCl-LiO_2 salt sample using LIBS was studied.

2. Methods and Results

At first, two LiCl-LiO_2 samples containing UO_2 were fabricated to obtain the preliminary calibration curve. One sample contained 0.5 wt% UO_2, and the other sample contained 1.0 wt% UO_2. Composition materials of the samples were placed in the glassy carbon crucible, and they were heated up to 500 ℃ to melt. The molten salt samples were slowly cooled to solid form in the furnace.

The compositions of the samples were analyzed using LIBS system, which was installed at argon filled glove box of KAERI. The laser was delivered with open path way, and the plasma emission light was collected through optical fiber. The laser was a pulsed Q-switched Nd:YAG laser with wavelength of 532 nm. Gate delay time of a delay generator was 1.5 μ s, and Q-switch delay was set at 380 μ s. The spectrometer consists of Czerny-Tunner spectrometer and Andor iXon ICCD camera. The automatic focal length adjustment system was included to the LIBS system to keep the optimized focal length < 0.01 mm during the measurement. 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.

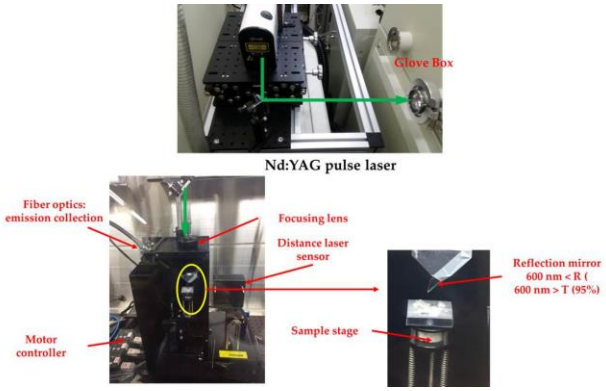

Fig. 1. LIBS system used in the present work [1]

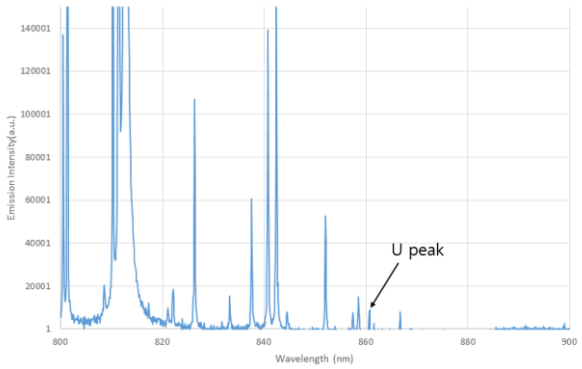

Fig. 2. Typical LIBS Spectrum. The sample of the spectrum is LiCl-LiO2 sample containing 1.0 wt% UO2.

The measured spectrum in the wavelength ranged from 690 ~ 900 nm were analyzed. The peaks from Li, Cl, and U were identified for the analysis. The relative standard deviation of Li, and Cl peak are ~ 10 %, and the relative standard deviation of UO_2 were higher due to the inhomogeneity of the U element in the sample.

Additional four LiCl-LiO_2 samples are fabricated to study the analysis characteristics of LIBS.

3. Summary

LIBS is a promising technology as the process monitoring technology applicable to the pyroprocessing safeguards. The uranium concentration in LiCl-LiO_2 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 electrolytic reduction process.

Acknowledgement

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REFERENCES

[1] B.Y. Han et al., Analysis of the applicability of LIBS to address safeguards needs with respect to pyroprocessing, KAERI/TR-6607/2016 (2016).