Development of an In-Hotcell Bromine Method for the Determination of Metallic Contents of Electrolytic Reduction Products in the Pyroprocessing of Spent Nuclear Fuel

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1. Introduction

One of the key steps of pyroprocessing is electrolytic reduction of metal oxide fuel into metallic form. In this step, an appropriate analytical method is required to measure the metal conversion yield of the electrolytic reduction process product. One needs to develop a reliable analytical method to determine the metallic constituents in the metal and oxide mixtures. And system establishment for the implementation of chemical analysis of highly radioactive pyroprocessing materials has become an imminent task.

2. Chemical hot cell and shielded ICP-AES system

A shielded ICP-AES system, chemical hot cell will be used to carry out bromine method and provide chemical analysis data of highly active pyroprocessing materials. Fig. 1 shows the chemical hot cell and shielded ICP-AES system to be used for highly radioactive samples.

3. Considerations in performing bromine method in hot cell conditions

We have carried out numerous bromine methods to quantify the metallic contents from the methodology development stage to the real application to PRIDE and ACPF(cold test) samples. The samples tested comprise different physicochemical properties produced under various process operation conditions.

A standard bromine method has been established to meet the process materials for Korean concept of pyro electrolytic metal reduction process. The experience obtained from those test works enables the bromine method to be applied under the hot cell conditions in more practical ways.

3.1 Reaction time

In general, the bromine reaction with metallic component is fast and exothermic. In case of powder or porous sample, the reaction time is shorter than bulk sample. The higher the density (e.g. reduced ingot after CP, cathode process), the more time is required for the completion of bromine reaction. From our experiences 2 hr reaction time will be appropriate. During the course of bromination reaction the sample tumbles in the reaction vessel by thermal motion due to exothermic nature of the reaction. This facilitates the reaction progress. Therefore, magnetic stirring can be replaced by gentle shaking the reaction bottle by manipulator. This may help protect the electronic part of the stirring device and save the space in the hot cell. Comparative study between using magnetic stirring and gentle shaking method showed the same results.

3.2 Solid-liquid phase separation

The metallic components selectively dissolved into ethyl acetate-bromine organic liquid phase are separated from undissolved oxide solid part. A normal way of phase separation method is centrifugation. In case of hot cell with limited space, one needs to skip the installation of centrifuge device into highly radioactive hot cell condition. In that case a filtration method is a good alternative method for phase separation.

3.3 Removing U using UTEVA column for precise FP measurement

Uranium is the predominant constituent of nuclear fuel. In case of quantification of major fission product components such as TRU and lanthanides, the predominant U signal interfere significantly with weak minor element signals. Therefore for precise measurement of TRU and REEs, one needs to remove U selectively from all other chemical components. For this extraction chromatography using UTEVA column is a good method. By using ICP-MS, we measured the concentration down to 1 ppb level. For accurate reduction yield determination of TRU and REEs, removing of U is a must, not an option.

3.4 Choice of plastic lab ware materials

In the chemical operation in hot cell conditions, disposable plastic lab wares are highly recommended. Bromine is a very reactive chemical and ethyl acetate solvent may give damage to certain plastic materials. Typical plastic lab wares are severely damaged by bromine and ethyl acetate. From our experience, for chemical operations in bromine method PP (polypropylene) based plastic wares are suitable.

3.5 Validation of the test procedure

One need to check and validate the whole process of bromine test and ensure the reliability of the data. Simple way of doing this is back calculating the U recovery. Checking major element ratio such as La/Ce, La/Nd may help to diagnose the test results.

4. Conclusion

Understanding the basic underlying principles behind the bromine method and the accumulated test experiences enables the operation in hot cell conditions in effective ways.

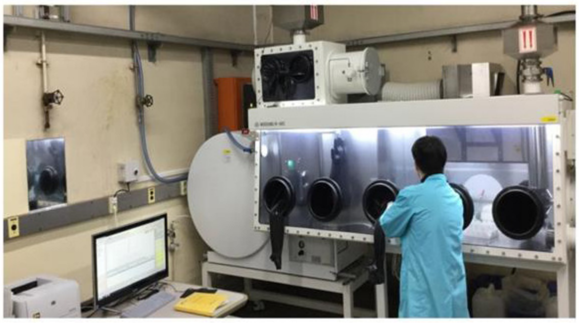

Fig. 1. Chemical hot cells (upper) and a shielded ACP-AES system (bottom).

ACKNOWLEGMENTS

This work was supported by a National Research Foundation of Korea (NRF) grant, funded by Korean government.

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