

Selective and total dissolution method for the chemical analysis of actinides and lanthanides in the samples from pyroprocessing of spent nuclear fuel

Young-Hwan Cho*, Sang-Eun Bae, Tae-Hong Park, Jong-Yun Kim, Jei-Won Yeon
Korea Atomic Energy Research Institute, Yuseong P.O Box 105, Daejeon, Rep. of Korea

*E-mail: yhcho@kaeri.re.kr

1. Introduction

Pyroprocessing program is under development at KAERI (Korea Atomic Energy Research Institute) to develop an advanced method for treating spent nuclear fuel [1]. One of the key steps of pyroprocessing is electrolytic reduction of metal oxide fuel to 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 metallic constituents in the metal and oxide mixtures.

A general approach is to dissolve the metallic form selectively from its oxide form and analyze the dissolved contents. For the determination of uranium, a method of selective dissolution of metallic uranium by bromine-ethyl acetate has been proposed. This method of selective dissolution based on bromine-ethyl acetate solution has long history, and has been applied for various purposes [2, 3].

However, up to the present time, information on the selective dissolution of lanthanide metals is limited. And no analysis method has been validated for the use of selective dissolution of metallic lanthanides in the metal-oxide mixture samples.

Here, we report the results of thermodynamic and experimental evaluation of selective dissolution study for 7 selected metallic lanthanides and their oxides in bromine-ethyl acetate solution in an attempt to develop a method to measure the reduction yield of lanthanide metal conversion in electrolytic reduction process.

2. Experimental

The experimental procedure is similar to that of reported in the earlier literatures [2,3]. The experimental procedure is schematically shown in Figure 1. The experimental procedure consists of three parts;

(1) selective dissolution reaction in organic phase, (2) chemical stripping into aqueous phase, and (3) pretreatment for ICP analysis, sequentially. Reagent grade La, Ce, Nd, Gd, Sm, Pr, Eu metals and their oxides materials (Aldrich-Sigma Co.) were used. The bulk metal samples are cut into appropriate size for use in the experiment. All the handling and weighing of the sample before dissolution have been done under Ar atmosphere in the glove box. The O₂ and H₂O level inside the glove box were maintained to be less than 1 ppm.

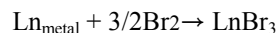
Selective dissolution of sample: It was known that bromine-ethyl acetate solution dissolves only metallic form in the presence of its oxide forms. Bromine in ethyl acetate solution reacts rapidly to form soluble Ln(III)Br₃ complexes. In order to identify the reactivity, a series of dissolution tests were performed for 7 lanthanide metals and their oxides, respectively in bromine-ethyl acetate solution. The dissolution procedure is similar to that reported elsewhere for uranium dissolution studies. Dissolution time was kept to be one and half hours to ensure complete dissolution.

Stripping into aqueous phase: After the completion of dissolution reaction, the ethyl acetate solutions containing Ln(III)Br₃ are collected. The Ln(III)Br₃ salts are easily stripped from the ethyl acetate organic phase into the aqueous phase by treating with conc. hydrochloric acid. In order to remove unreacted bromine and ethyl acetate from the Ln(III)Cl₃ solution samples are completely dried by slowly evaporating the aqueous solution.

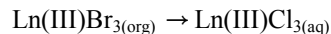
Pretreatment for ICP analysis: For ICP analysis, a preparation of homogeneous makeup solution of dried Ln(III)Cl₃ sample is necessary. Inductively coupled plasma – atomic emission spectroscopy (ICP-AES) was used to analyze the lanthanide ion concentration.

3. Results and Discussions

The dissolution reaction by the reaction of bromine and Ln metal in ethyl acetate can be written as shown below, and this reaction is exothermic, spontaneous reaction.



The metal salts (Ln⁺³Br₃⁻) are easily stripped from the ethyl acetate organic phase into aqueous phase by reacting with hydrochloric acid.



The trichlorides forms of lanthanide ions are formed. The LnCl₃ forms are more stable than those of LnB₃ forms as shown in Fig. 1.

Dissolution results by bromine-ethyl acetate method are shown in Fig. 2.

Most of the lanthanides metals are dissolved in bromine-ethyl acetate solution. However, most of their oxides are insoluble in the same conditions. Thermodynamic data explains the features of selective dissolution behavior of lanthanide metals and their oxides. The enthalpies of formation of the lanthanide tri-chlorides, tri-bromides and oxides have been

collected from the existing literature [4,5] and are presented in Fig. 1.

The other lanthanide metals not listed here also show the similar trend and values. This indicates selective dissolution method can also be applied to those lanthanide metals not tested in this paper.

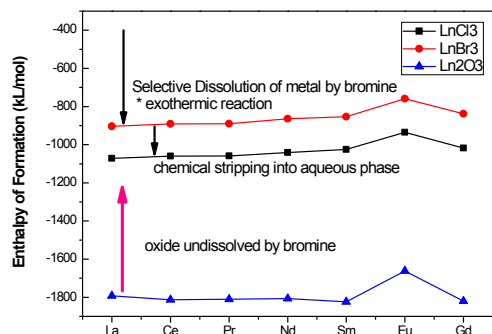


Fig.1. Thermodynamical basis of selective dissolution processes of lanthanide metals.

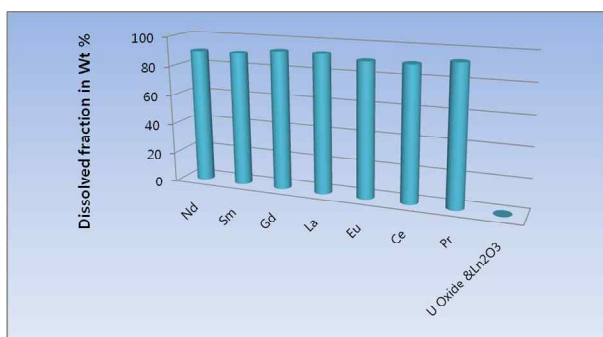


Fig.2. Dissolution results obtained using bromine-ethyl acetate method for selected lanthanide metal and their oxide samples.

It is known that metallic lanthanides are very reactive as in uranium metal. They are rapidly and easily attacked by oxygen and humidity in the open air, forming oxides surface coating and hydroxide corrosion products. This accounts for the data shown in Fig. 2. Even before experiment, some parts of metal samples are already corroded, forming surface oxide coatings. These surface coating materials are insoluble in bromine-ethyl acetate solution and is clearly seen as residue. This means that, for precise measurement of metallic conversion yield, extreme care should be made in the handling of samples under strictly controlled environment. The insoluble oxide materials are collected and completely dissolved in using nitric acid, and analyzed.

The application of bromine dissolution method for the determination of metallic conversion yield to electrolytic reduction process of spent nuclear fuel was reported by INL researchers [6]. It worked well for some actinide elements such as U, Pu and Np as

expected. However, the result was poor for lanthanide elements as well as lanthanide-like behaving actinide elements such as Am, Cm. Thermodynamic consideration support the applicability of the bromine selective dissolution method to lanthanide elements. The reason for the poor results may be due to the failure in the following pretreatment for instrumental analysis after selective dissolution step. The aqueous chemistry of pretreatment for lanthanides is quite different from that for uranium. Even within the lanthanide groups, the method for pretreatment technique exhibited big differences. Most of the problems arise from the low solubility of lanthanide compounds involved. We were able to solve this problem by using appropriate acids and H_2O_2 treatment. Use of hydrochloric acid is desirable instead of nitric acid which causes many undesirable side effects.

4. Conclusions

Most of the lanthanides metals are dissolved in bromine-ethyl acetate solution. However, most of their oxides are insoluble in the same conditions. This allows one to selectively dissolve metallic contents in the presence metal oxide mixtures. By applying selective dissolution method in bromine-ethyl acetate solution together with total dissolution technique, it will be possible to determine the metallic conversion yields of actinides and lanthanides elements in the samples of electrolytic reduction process for spent nuclear fuel.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No.2012M2A8A5025923)

REFERENCES

- [1] H.S. Lee, et al., Pyroprocessing technology development at KAERI, Nucl. Eng. Tech. 43,317-328, 2011.
- [2] R.P. Larsen, Dissolution of uranium and its alloys, Anal. Chem. 31, 545-549, 1959.
- [3] G.F. Brunzie, et. al., Selective dissolution of uranium from uranium-uranium oxide mixtures by bromine-ethyl acetate, Anal. Chem. 33, 1005-1006, 1961.
- [4] E.H.P. Cordfunke, et al., The enthalpies of formation of lanthanide compounds I. $LnCl_3$, $LnBr_3$ and LnI_3 , Thermochemica Acta 375, 17-50, 2001.
- [5] E.H.P. Cordfunke, et al., The enthalpies of formation of lanthanide compounds III. Ln_2O_3 , Thermochemica Acta 375, 65-79, 2001.
- [6] S.D. Herrmann, et al., Electrolytic reduction of spent oxide fuel, bench-scale test results, INL/CON-05-00304, 2005.