Structural studies on trivalent lanthanide hydroxides and oxides

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Abstract Hydroxides and oxides of trivalent lanthanides (La, Eu, and Tm) aged at from 25°C to 90°C in the neutral to alkaline pH_c region were investigated by XRD, SAXS, SEM and XAFS techniques. The observed structure of the solid phases was discussed to explain their solubility behavior.

Keywords: trivalent lanthanide, hydroxides, oxides, solid phase, spectroscopic technique, solubility

1. Introduction

For the prediction of the migration behavior of trivalent actinides under nuclear waste repository conditions, it is important to establish a robust thermodynamic model for the solubility of their hydroxides and oxides. Although a number of literatures has investigated the solubility of trivalent lanthanides as analogous of trivalent actinides [1,2], detail structural features of the hydroxides and oxides, i.e. surface characteristics or particle sizes of the solid phases, which control their apparent solubility, are still not fully clarified. This study focused on the structure of lanthanide (La, Eu, and Tm) hydroxides and oxides in the neutral to alkaline pH_c regions using combined techniques of powder X-ray diffraction (XRD), small angle X-ray scattering (SAXS), scanning electron microscope (SEM), and X-ray absorption fine structure (XAFS). The obtained structures of the solid phases were discussed along with their reported solubility [2].

2. Experimental

A certain amount of crystalline lanthanide oxide powder samples (Ln_2O_3(cr) (Ln = La, Eu, Tm)) was added into sample solutions with certain pH_c ($6 < pH_c < 12$) and ionic strength (I) of 0.1 M by $NaClO_4$. The sample solutions were then aged in ovens kept at from 25 ºC to 90 ºC for given periods. The Ln solid phases were investigated by powder XRD, SAXS, SEM, and XAFS techniques to elucidate the structure of Ln solubility-limiting solid phases.

3. Results and discussion

Figure 1 shows the XRD patterns of La solid phase after aging at 25 ºC for 2 weeks, together with La_2O_3(cr) of the initial material. A clear solid phase transformation from La_2O_3(cr) to $La(OH)_3$(cr) (ICSD No. 26864) was observed. The XRD patterns of $La(OH)_3$(cr) were almost independent of pH_c, and the size of crystalline particles was calculated to be 48 nm on average based on the Scherrer equation [3], whereas that of La_2O_3(cr) was found to be larger than 100 nm. The analysis of SAXS profiles of aged $La(OH)_3$(cr) samples also suggested that the solid phases consisted of primary particles with the size of approximately 40 nm. A discussion in comparison with the solid phase structure and the solubility product for La, Eu and Tm will be presented.

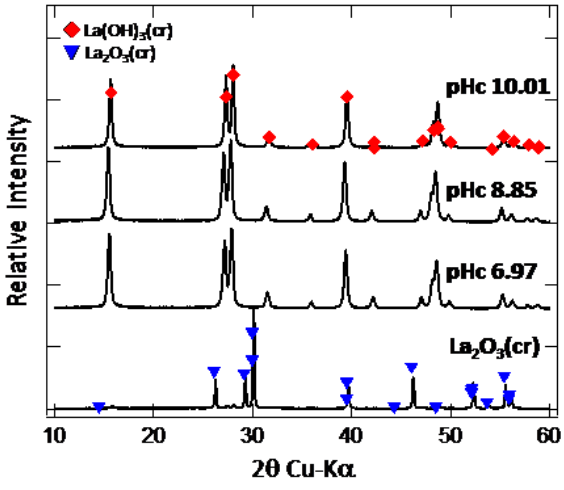

Fig. 1 XRD patterns of La solid phases after aging at 25 ºC.

References

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