Nanosized thoria in aqueous solutions: probing the solubility and crystallinity relationship

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In recent years, actinide (IV) oxides (AnO_2) nanoparticles have attracted great attention in the field of environmental safety control and in the development of new technological schemes. To date, the dissolution chemistry of AnO_2 is widely discussed in the literature as it is an important process that alters nanoparticle abundance and properties. Thorium dioxide (thoria, ThO_2) is an interesting object to investigate as model systems for studying actinide migration in the environment since it is non-redox sensitive and does not form non-stoichiometric oxides. Prospects for its use in the nuclear power industry are also widely debated. According to the literature sources, thoria could exist in both well-defined crystalline and X-ray amorphous states. In our previous study it was shown that by selecting the chemical precipitation and further temperature treatment conditions, well-defined nanocrystalline ThO_2 could be produced in a strictly controlled manner [1]. Later, with the use of state-of-the-art synchrotron techniques Amidani et al. reveals a mixture of ThO_2 nanoparticles and Th(IV) hexamers clusters in thoria X-ray amorphous samples [2].

The present work is focused on the solubility study of thoria samples with different crystallinity. At this work, we use a unique strategy of the solid phase and solution joint analysis. Thus obtained data will make it possible to get reliable metrical data for describing ThO_2 dissolution process in various media.

At the present study, ThO_2 samples were prepared by mixing aqueous solutions of $Th(NO_3)_4 \cdot 5H_2O$ and aqueous ammonia or NaOH of different concentrations. As-prepared samples were characterized after synthesis procedure in form of fresh precipitate. The nanoparticles size was varied using low (40-150°C) and high temperature (300-1000°C) treatment. Structure features and phase composition of thoria samples were investigated by X-ray and neutron diffraction, HRTEM, TGA/MS, Raman spectroscopy and EXAFS. The solubility experiments in aqueous solutions in a range of pH 2-7 for well-characterized crystalline ThO_2 nanoparticles of different size and X-ray amorphous precipitates were conducted. It was found that X-ray amorphous thoria samples improve their crystallinity during aging. This process depends on the pH value of the dissolution media. A thermodynamic modelling of the dissolution process of thorium dioxide samples with different particle sizes and crystallinity was carried out, as a result the solubility products were determined.

References

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[2] L. Amidani et al., *Chem. Eur. J.* **27**, 252-263, (2021).

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