IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Étude fondamentale de la solubilité du Zr(IV) et des processus de surface dans les systèmes alcalins : une étude combinée sur la solubilité, la spectroscopie et la théorie.

Fundamental investigation of Zr(IV) solubility and surface processes in alkaline systems: a combined solubility, spectroscopic and theoretical study.

Laboratoire : SUBATECH

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Encadrement :

- Subatech : Bernd Grambow (directeur)
  et Tomo Suzuki-Muresan (encadrante)
- KIT : Horst Geckeis (directeur) et Xavier Gaona (encadrant)

Nom & Prénom de l'EC premier porteur du sujet, labo, adresse mail

- Tomo Suzuki, Subatech, suzuki@subatech.in2p3.fr

Nom & Prénom de l'EC deuxième porteur du sujet, labo, adresse mail

- Xavier Gaona, KIT, Xavier.Gaona@kit.edu

Mots clés en français: énergie de surface, amorphe/cristalline, taille des particules, solubilité, expérience/théorie

Mots clés en anglais : surface energy, amorphous/cristalline, particle size, solubility, experiment/theory

Contexte

The concept of solubility equilibrium of solids (*e.g.* metal oxides) in water is an integral part of the thermodynamic assessment of the behavior of nuclear waste in geological formations. Zirconium is an element relevant to the safety assessment of radioactive waste disposal, since it is produced with high yield in fission of uranium and Zr metal is used as a fuel cladding in light water reactors. Zirconium dioxide (zirconia) exists as corrosion product on used nuclear fuel rods and it may be the solubility-controlling phase for the neutron-activated product, ^{93}Zr ($t_{1/2} = 1.53 \cdot 10^6$ a). As other tetravalent metals (*e.g.* Tc, Re, U, Np, Pu, among others), saturated solutions of Zr(IV) precipitate as sparingly soluble nanoparticulate hydrous oxides. Although the transformation of these amorphous phases into ZrO_2(cr) is thermodynamically favored, the process is kinetically hindered and strongly driven by surface reactivity.

Objectifs

In this context, the overall goal of this PhD is the investigation of solubility phenomena from a fundamental perspective, looking at surface processes and energetics using a combined experimental and theoretical approach. The study will target the transition between amorphous to crystalline phases, which arises as key process in the solution chemistry of M(IV) (with M = Zr, Tc, An, …). Special efforts will be dedicated to evaluate the fundamental role of water / hydration, particle size and particle growth on solubility.

In the first part of this PhD performed at KIT, you will synthesize amorphous Zr(IV) hydroxide in the laboratory, and will thoroughly characterize the resulting material with a multi-method approach including X-ray diffraction, thermogravimetric analysis (TG-DTA), synchrotron-based techniques (e.g. XAFS, HR-XANES), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), among other techniques. You will study the solubility of this solid phase in well-defined aqueous, alkaline solutions, and will evaluate the impact of the temperature on the solubility of the aged solid phases, using the concepts of established solution thermodynamics.

In the second part of this PhD performed at SUBATECH, you will investigate the solubility of crystalline ZrO_2 under analogous conditions as in KIT, and will contribute to the improvement of specific analytical methods for the quantification of trace concentrations of Zr. Modern complementary experimental methods will be used for the characterization of the solid phases, with special focus on surface-sensitive techniques. During the second part of your PhD, you will also become acquitted with theoretical calculations looking at attachment / detachment reactions, surface energetics and eventually molecular dynamics. This will provide a fundamental understanding of the processes taking place at the interface ZrO_2-water, and thus the link between amorphous / disordered systems and crystalline phases.

Compétences requises

A strong background in materials science or inorganic chemistry, good skills in design and operation of experimental set-ups are an advantage.