A1-4 SOLUBILITY AND STRUCTURAL CHARACTERIZATION OF ZR(IV) HYDROUS OXIDES

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Tetravalent metal ions (M(IV), e.g. actinides, Zr, Tc, Sn) are characterized by a strong hydrolysis and the formation of sparingly soluble amorphous hydrous oxides, MO_2(am, hyd), controlling M(IV) solubility over a broad range of pH. Ageing or exposure to elevated temperatures expectedly results in a transformation into thermodynamically more stable crystalline phases and thus in a decreased solubility in aqueous systems [1,2]. Zirconium alloys (Zircaloy) are used as cladding material for nuclear fuel, especially in water reactors. Zr-93 ($t_{1/2} = 1.53 \cdot 10^6$ a) is produced by nuclear fission of U-235 as well as by neutron activation of the cladding. ZrO_2(s) has been identified as possible solid phase controlling the solubility of Zr under repository conditions. The present study systematically investigates the impact of temperature on the crystallinity and water content of ZrO_2(s, hyd) solid phases, and further their solubility and thermodynamic properties in hyperalkaline conditions. For this purpose, freshly precipitated amorphous solids, solids aged at elevated temperatures and a commercial crystalline ZrO_2 solid are investigated with a combination of solubility batch experiments and comprehensive solid phase characterization methods. Density functional theory (DFT) calculations are performed to gain additional insights on the surface processes governing solubility phenomena. As overarching objective, this work intends to shed light on the mechanisms for the potential transformation of amorphous hydrous oxides into thermodynamically more stable crystalline phases of Zr(IV) relevant in the context of nuclear waste disposal.

The starting solid phase used in this study, ZrO_2(am, hyd, fresh), was prepared by slow titration of a ≈ 0.02 M $ZrOCl_2$ solution with 0.1 M NaOH. Independent aliquots of the starting solid phase were equilibrated at T = 80 and 22°C in 0.02 M $CaCl_2$-$Ca(OH)_2$, 0.2 M $CaCl_2$-$Ca(OH)_2$ or 0.001 M NaOH solutions at pH_m ≈ 11.0 for 4, 10 and 18 months. After cooling the sample solutions down, the solid phases were separated from the supernatant solution and washed 2–3 times with water. These samples, and for comparison also a commercial crystalline ZrO_2 solid phase, were characterized with various methods including XRD, TG-DTA, SEM-EDX, XPS, EXAFS, IR-ATR, BET, TEM, SAXS and zeta potential measurements. Experiments approaching solubility equilibrium from undersaturation conditions were performed with 5–20 mg of the fresh and aged ZrO_2(s, hyd) solid phases, equilibrated at T = 22°C with 0.02 M $CaCl_2$-$Ca(OH)_2$, 0.2 M $CaCl_2$-$Ca(OH)_2$ or 0.5 M NaCl-NaOH solutions at 10 ≤ pH_m ≤ 13.4. The concentration of Zr in the aqueous phase was quantified by ICP-MS after ultrafiltration with 3 kD filters.

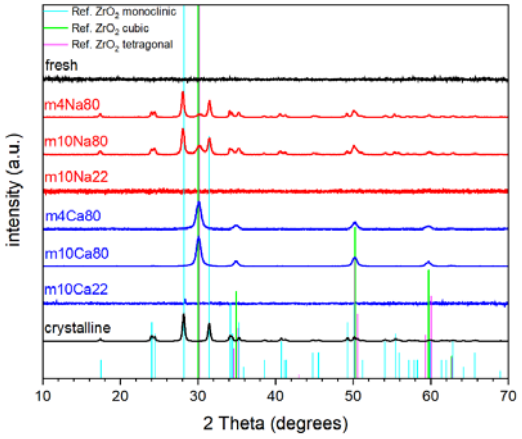

Fig. 1: *XRD patterns collected for fresh ZrO_2(s) (black) and solids aged in NaOH (red) and $CaCl_2$ (blue) at T = 80°C for 4 months (m4Na80 and m4Ca80) and 10 months (m10Na80 and m10Ca80) and at T = 22°C for 10 months (m10Na22 and m10Ca22), compared to a commercial crystalline solid (black) and reference patterns available for ZrO_2(cr) in the JCPDS database.*

XRD (Figure 1), SEM-EDX and TEM show the amorphous character of the fresh ZrO_2(am, hyd, fresh). Solid phases aged at T = 80°C in 0.001 M NaOH solutions resulted in monoclinic ZrO_2 (size of crystal domains: 23-27 nm, Scherrer analysis) with a small fraction of cubic/tetragonal ZrO_2, in agreement with XRD data reported by Kobayashi et. al. [3]. In contrast, ageing solids at T = 80°C in presence of 0.2 M or 0.02 M $CaCl_2$-$Ca(OH)_2$ results in the formation of nanocrystals with cubic/tetragonal structure and a size of 11-14 nm. The weight loss determined by TG-DTA (Figure 2) was correlated with the higher water content of the amorphous solids, qualitatively confirmed by IR spectroscopy. Rehydration experiments with amorphous solid phases after removing H_2O and OH^- by heating to T = 200 and 400°C for 2 hours show that the dehydration process is not completely reversible.

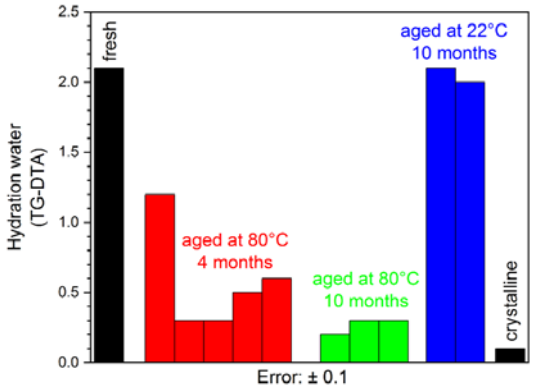

Fig. 2: *Amount of water of the ZrO_2 (s) solid phases, determined by TG-DTA assuming a stoichiometry of $ZrO_2 \cdot nH_2O$(s).*

All these observations underpin the key role of OH^- and H_2O in the ageing/ crystallization process of ZrO_2(s), which is described more accurately as $ZrOx(OH)_{4-2x} \cdot nH_2O$(s). These results highlight also the stabilization of the cubic/tetragonal structure induced by Ca at a concentration level expected in specific repository concepts.

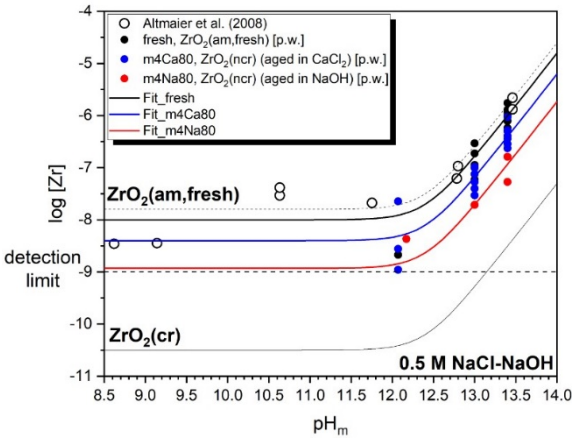

Fig. 3: *Solubility data determined for fresh and aged phases (T = 80°C, NaOH and $CaCl_2$-$Ca(OH)_2$) equilibrated at T = 22°C in 0.5 M NaCl-NaOH. Solid lines show solubility calculations for ZrO_2(am, fresh) and ZrO_2(cr) [4,5], as well as model calculations to determine the solubility product for the systems investigated in this work.*

Figure 3 exemplarily shows solubility data of Zr(IV) collected in 0.5 M NaCl-NaOH for a fresh solid (amorphous) as well as for solid phases aged in 0.2 M CaCl2-Ca(OH)2 (cubic/tetragonal) and 0.001 M NaOH (monoclinic) solutions at T = 80°C. An evaluation of the log $*K°_{s,0}$ of these solid phases was conducted for the most alkaline samples, considering the predominance of the $Zr(OH)^{2-}$ (in NaCl) and $CaxZr(OH)^{2x-2}$ (in CaCl2) aqueous complexes as reported in the NEA- TDB [4] and Altmaier et al. [5]. Log $*K°_{s,0}$ values of $-(4.5 \pm 0.4)$, $-(4.9 \pm 0.5)$ and $-(5.5 \pm 0.4)$ for the amorphous sample, the sample aged in $CaCl_2$ and the sample aged in NaOH, were determined. Further results from on-going experiments and theoretical calculations will be discussed in this contribution, also with regard to the nature of the solid/liquid interface determining solid phase solubility.

Reference

[1] Rai et al. (2000). Radiochim. Acta, 88, 297-306.

[2] Kobayashi et al. (2013). Radiochim Acta, 101, 645-651.

[3] Kobayashi et al. (2019). Langmuir, 35, 7995−8006.

[4] Brown et al. (2005). Chemical Thermodynamics of Zirconium, Elsevier

[5] Altmaier et al. (2008). Radiochim Acta, 96, 541-550.