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Solubility of monoclinic and yttrium stabilized cubic ZrO₂: solution and surface thermodynamics guiding ultra-trace analytics in aqueous phase

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10

ABSTRACT. The high stability of zirconium dioxide in aqueous environments is known and 11 demonstrated, and this property is strongly used in nuclear industry to ensure the long term storage 12 13 of wastes. However, only upper limits of its aqueous solubility are known reliably and lower limits 14 linked to very well crystallized ZrO₂ are much less assessed. Indeed, the low dissolution rate of 15 zirconia makes the solubility measurements a challenging task. To overcome, high S/V ratios of 16 nanoparticles zirconia were used. This work also improved the sensitivity of analytical techniques (HR ICP-MS) and methodologies, and a reliable experimental procedure was developed to measure 17 zirconium (quantification limit $\approx 10^{-11}$ mol·L⁻¹). New Zr(IV) dioxide solubility data at pH between 0 and 18 19 2 were obtained approaching solubility from under-saturated conditions in (Na,H)Cl and (Na,H)ClO4 20 medium. Two crystalline nanoparticle structures were compared: monoclinic and yttrium stabilized cubic zirconia. Very low solubility was measured for monoclinic phase between pH 1.5 and 2: 21 between $(1.8\pm1.2)\times10^{-10}$ mol·L⁻¹ at pH 2 and $(2.3\pm1.0)\times10^{-10}$ mol·L⁻¹ at pH 1.5. The cubic zirconia 22 showed higher solubility. Integrating the effect of ionic strength, particle size and aqueous 23 speciation, solubility constants of log K_s^0 = (-8.43±0.69) for the monoclinic nanoparticles and log K_s^0 = 24 (-7.12±0.35) for the yttrium stabilized cubic nanoparticles were obtained. High-resolution techniques 25 (HR-TEM, SAXS and STEM-HAADF) were also used to assess the evolution of morphology and surface 26 27 before, during and at equilibrium. Analysis of these results shows that the morphology and surface of nanoparticles in the raw state and after reaching equilibrium in (Na,H)Cl and (Na,H)ClO₄ medium are 28 29 similar.

- 30
- 31 **KEYWORDS**: zirconia, solubility, thermodynamic, ultra-trace analyses, nanoparticles

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35 1 Introduction

ZrO₂ zirconia is a natural mineral named Baddeleyite used in various domains for its excellent 36 37 physical, chemical, and thermal properties [1–3]. Zirconia is also the corrosion product by oxidation 38 of Zr-based materials, and in nuclear fields, it is omnipresent as a tight oxidation film at surfaces of 39 nuclear fuel claddings. This oxide layer is considered as a protective layer in zirconium alloys, enhancing the corrosion resistance of the claddings in the reactor vessel as well as in the wet pool of 40 41 deactivation. It is noteworthy that this layer is exposed to several combined constraints under 42 extreme conditions such as high gradient of temperature, high pressure, mechanical stress and 43 radiolysis. The characterization of this layer show a very good stability and corrosion resistance in 44 water for temperatures as high as 400°C for many years and for high burnup [4]. The microstructure 45 of the oxide layer reveals an arrangement of small oxide grains of about 30nm, which elongate to 46 form columns of about 200nm [4]. The stability of this oxide layer is thus ensured by a dense growth 47 of nanometric size zirconia grains. However, the stability of nanoparticles strongly depends on the 48 surface energy and solubility which increases when particle size decreases [5,6]. Therefore, an 49 appropriate knowledge of the solubility of waste form constituents is required for the safety of disposal of nuclear waste in geological repository systems. 50

51 The solubility of actinide and metallic oxides confining radioactive waste has been studied in these 52 last decades using several analytical methods [7]. However, the reported solubility values are 53 contradictory with large uncertainties mostly due to changes in the characteristics of the solid 54 phases: crystallinity, composition and particle size, chemical reactions occurring on solid phases 55 during the experiment and the presence of colloids in solution. Of the tetravalent oxides, crystalline 56 zirconium dioxide is a strong refractory material leading to high corrosion resistance in acidic, neutral 57 and alkaline media. Therefore its solubility is very low ($<10^{-8}$ mol·L⁻¹) between pH 3 and 12, increasing at more acidic and alkaline pH (Figure 1). Solubility values are reported to differ by more than 6 58 59 orders of magnitude comparing results from over- and under-saturated conditions. Furthermore, 60 solubility data are influenced by the formation of polynuclear species in solution and by the 61 precipitation reaction occurring even at low pH [8]. Up to date, a wide number of zirconium dioxide solubility studies have been reported in literature as function of pH [8-19], media 62 [8,9,11,13,14,17,19], and crystallographic structure [11,14]. It appears that crystalline zirconium 63 64 dioxide is the solubility controlling phase in natural water at low temperature (T < 1420K) [20]. Solubility values are generally measured by ICP–MS [8,11,12,15,21] and by potentiometric titration 65 [8], but only few characterizations by X-ray diffraction (XRD) and Laser Induced Breakdown Detection 66 (LIBD) are available for the studied solids [8,10,12]. Reversibility of supposed solubility equilibrium 67 68 values are hardly ever tested. Difficulties in measuring reversibility are because precipitated phases

might be amorphous while the dissolved one is crystalline. A solubility constant of (log K_s^0 69 (monoclinic ZrO_2 , 298.15K) = -(7.0±1.6) (eq. (1)) was selected by Brown et al. [20] in their review 70 71 focusing on the low-temperature thermodynamics of zirconium and its compounds in aqueous 72 solution. This constant is obtained from an overall fit of hydrolysis data with a detailed review of hydrolysis of zirconium in the aqueous phase and its ionic strength dependency. The selected 73 solubility constant of the freshly precipitated amorphous hydroxides is log K⁰_s (amorphous Zr(OH)₄, 74 298.15K = $-(3.24\pm0.10)$. The lack of detailed characterization of the studied zirconium dioxide 75 76 materials may impact on the accuracy of the free energy of formation ($\Delta_f G^\circ$) of the aquo-ion Zr⁴⁺ 77 derived by Brown et al. from the equilibrium (1):

78
$$ZrO_2$$
 (monoclinic) + 4H⁺ = Zr^{4+} + 2 H₂O (eq.1)

The thermodynamic properties calculated by Brown et al. [20] vary with the degree of crystallinity of
 the zirconium oxide in equilibrium with dissolved Zr⁴⁺.

The aim of the present paper is to assess zirconia solubility of two crystalline polymorphs varieties, the monoclinic and the yttrium stabilized cubic zirconia phases. The purpose is also to assess the surface reactivity of the solid since the reversibility cannot be studied by comparing results of approaching solubility from under and over-saturation due to the different phases. Finally, the solubility constant (log K_s^0 (298 K)) obtained at solubility equilibrium on crystalline zirconium oxide will be discussed and compared with solubility constant values of amorphous hydrous oxide of zirconium.

88 2 Experimental

89 2.1 Solubility experiment.

90 Solubility experiments of monoclinic zirconium (IV) oxide (MZ) and cubic zirconium (IV) oxide (YSZ, 91 yttrium-stabilized zirconia up to 8 mol%) nanoparticles (Sigma-Aldrich) were performed in Teflon 92 reactor vessels with 120 mL of 10⁻² mol·L⁻¹ NaCl or NaClO₄ solutions. The ratio surface area of solid 93 over volume of solution (S/V) varied between 10^4 and 2×10^6 m⁻¹. Table 1 summarizes in detail the 94 experimental conditions. To minimize any contamination source of zirconium, sodium perchlorate, 95 sodium chloride, hydrochloric acid, perchloric acid are ultra-pure chemical solutions and prepared 96 with ultrapure water from a water purification apparatus (Milli-Q-academic, Millipore). The reactors 97 were cleaned by several washings with HNO₃, HCl and Milli-Q water at 100 °C to avoid the release of 98 Zr traces from material prior to use. Nitric acid is ultra-pure chemical and is distilled in laboratory to 99 reduce traces of zirconium. An orbital stirrer at room temperature and under atmospheric conditions 100 continuously shook the reactors.

As the dissolution rate of ZrO₂ is very slow, it may take a long time until solubility equilibrium is reached. The use of nanoparticles of high specific surface area decreases the time until equilibrium is achieved. Therefore, the S/V ratio was varied to follow the approach to equilibrium and to ensure that solid/liquid equilibrium has been reached. The determination of surface area is described in solid characterization section. Two approaches were used:

Approach of equilibrium from undersaturation: the solids dissolve slowly and it takes long time to reach constant solution concentrations. The use of a high S/V speeds up the approach of equilibrium from undersaturated conditions since at concentrations much lower than concentrations at saturation (or at solubility equilibrium), the accumulation rate of dissolved Zr in solution is proportional to the area of the dissolving surface for a given solution volume.

112 Approach of equilibrium from oversaturation: in particular in strongly acidic conditions, the dissolution rate may be fast and precipitation or growth rates slow and instead of 113 establishing equilibrium, solution concentrations increase beyond the equilibrium state. With 114 115 longer dissolution times, solution concentrations decrease again and the intervening 116 precipitation or particle growth reaction approaches equilibrium from oversaturation. The 117 use of high surface area to volume ratio allows in this case a rapid approach of equilibrium 118 since a larger surface is available to adsorb the excessively dissolved Zr providing that no new 119 particles are formed.

For the determination of solubility values, Zr concentration ([Zr]_{tot}) data are plotted as function of the product "S/V ratio" and "time", i.e. (S/V)×t. This representation allows determining zirconium solubility data for a given phase under the same pH and media conditions. For a sufficiently long experiment duration and for high S/V ratios, it becomes possible to determine a mean solubility value. The uncertainty associated corresponds to the standard deviation of the values chosen to calculate the mean solubility value.

According to the hydrolysis model, zirconium solubility can be described as the contribution of zirconium species in solution at pH [0-2] and as the function of hydrolysis constants:

128
$$[Zr]_{tot} = [Zr^{4+}] + [ZrOH^{3+}] + [Zr(OH)_2^{2+}] + [Zr(OH)_4^0(aq)] + [Zr_3(OH)_9^{3+}] + [Zr_4(OH)_8^{8+}]$$

129
$$= K_{s}[H^{+}]^{4} \left(1 + \frac{{}^{*}\beta_{1,1}}{[H^{+}]} + \frac{{}^{*}\beta_{2,1}}{[H^{+}]^{2}} + \frac{{}^{*}\beta_{4,1}}{[H^{+}]^{4}} \right) + K_{s}^{3}[H^{+}]^{3} {}^{*}\beta_{9,3} + K_{s}^{4}[H^{+}]^{8} {}^{*}\beta_{8,4}$$

where Ks represents the solubility constant and ${}^*\beta_{q,m}$ the hydrolysis constant with (q,m) referring to the general hydroxyl specie $\operatorname{Zr}_m(OH)_q^{4m-q}$ from to the zirconium hydrolysis model. The hydrolysis constants are determined according to the specific ion interaction theory SIT. The values selected

- 133 from [20] are: (i) for hydrolysis constants log ${}^{*}\beta_{1,1}^{\circ} = (0.32\pm0.22)$, log ${}^{*}\beta_{2,1}^{\circ} = (0.98\pm1.06)$, log ${}^{*}\beta_{4,1}^{\circ} = -$ 134 (2.19±1.70), log ${}^{*}\beta_{9,3}^{\circ} = (12.19\pm0.08)$, and log ${}^{*}\beta_{8,4}^{\circ} = (6.52\pm0.65)$; (ii) for ion interaction coefficients 135 $\epsilon(\operatorname{Zr}^{4+}, \operatorname{ClO}_{4}^{-}) = 0.89 \text{ kg} \cdot \operatorname{mol}^{-1}, \epsilon(\operatorname{ZrOH}^{3+}, \operatorname{ClO}_{4}^{-}) = 0.57 \text{ kg} \cdot \operatorname{mol}^{-1}, \epsilon(\operatorname{Zr}(\operatorname{OH})_{2}^{2+}, \operatorname{ClO}_{4}^{-}) = 0.62 \text{ kg} \cdot \operatorname{mol}^{-1},$ 136 $\epsilon(\operatorname{Zr}_{3}(\operatorname{OH})_{9}^{3+}, \operatorname{ClO}_{4}^{-}) = 0.93 \text{ kg} \cdot \operatorname{mol}^{-1}, \epsilon(\operatorname{Zr}_{4}(\operatorname{OH})_{8}^{8+}, \operatorname{ClO}_{4}^{-}) = 3.61 \text{ kg} \cdot \operatorname{mol}^{-1}, \epsilon(\operatorname{H}^{+}, \operatorname{ClO}_{4}^{-}) = 0.14 \text{ kg} \cdot \operatorname{mol}^{-1},$ 137 $\epsilon(\operatorname{Zr}^{4+}, \operatorname{Cl}^{-}) = 0.33 \text{ kg} \cdot \operatorname{mol}^{-1}, \text{ and } \epsilon(\operatorname{H}^{+}, \operatorname{Cl}^{-}) = 0.12 \text{ kg} \cdot \operatorname{mol}^{-1}. \epsilon(\operatorname{ZrOH}^{3+}, \operatorname{Cl}^{-}), \epsilon(\operatorname{Zr}(\operatorname{OH})_{2}^{2+}, \operatorname{Cl}^{-}),$ 138 $\epsilon(\operatorname{Zr}_{3}(\operatorname{OH})_{9}^{3+}, \operatorname{Cl}^{-}), \text{ and } \epsilon(\operatorname{Zr}_{4}(\operatorname{OH})_{8}^{8+}, \operatorname{Cl}^{-}), \text{ calculated from [20] based on Zr-hydrolysis model, give 0.16, -1.33, 1.04 \text{ and } -2.62 \text{ kg} \cdot \operatorname{mol}^{-1}, \text{ respectively.}$
- 140 In chloride media, the main reaction of zirconium occurring at pH 0-2 is $Zr^{4+} + Cl^- \leftrightarrow ZrCl^{3+}$ with 141 the hydrolysis constant log $\beta^0 = (1.59 \pm 0.06)$ [20].

142 **2.2** Solution analyzes methods

143 2.2.1 pH measurements

A combined glass pH electrode (pHC3006 Ag/AgCl, radiometer) was used to measure the pH in NaCl and NaClO₄ solutions. The pH was adjusted to either 0, 1, 1.5 or 2 by adding Zr free concentrated HCl and HClO₄ solutions to 10^{-2} mol·L⁻¹ NaCl and NaClO₄ solutions, respectively. No significant deviation from the initial pH was observed over time. The pH was constant at ±0.1. For thermodynamic calculations, the measured values were transformed to molal concentrations of protons (pmH⁺) using the known amount of acid added to a given ionic medium to obtain the selected pH (Table 1).

150 2.2.2 Solubility measurements

All solution aliquots were ultra-filtered prior to analyses at 5 kDa (Centrisart[®] I, ultrafiltration unit, Sartorius) in order to exclude the presence of colloidal particles. The aliquots are then acidified in ultra-pure and distilled HNO₃ (0.35 mol·L⁻¹) – HF (0.005 mol·L⁻¹) for inductively coupled plasma mass spectrometry (ICP-MS) analysis. For [Zr] >10⁻⁹ mol·L⁻¹ and pH [0-1], measurements were performed by quadrupole Q-ICP-MS (Xseries 2, THERMOELECTRON) with a quantification limit LQ of 10⁻¹⁰ mol·L⁻¹ ¹. For lower Zr concentrations (<10⁻⁹ mol·L⁻¹) and pH [1.5-2], measurements were performed by High Resolution HR-ICP-MS (ELAN 6100, Perkin Elmer) with a LQ of 10⁻¹¹ mol·L⁻¹.

158 2.2.3 Analytical procedure for quantitative analysis of trace levels of zirconium

159 In the present study, methods for separation between solid phase and solution are critical. Classical 160 method of filtration is not sufficiently efficient to retain the nanoparticles on the filter. Indeed, 161 depending on the separation yield of nanoparticles/solution, zirconium concentrations can vary up to 162 1 order of magnitude [12,15]. Therefore, Laser Induced Breakdown Detection (LIBD) technique was 163 used to select the most effective method of nanoparticles/solution separation for measurement of 164 aqueous zirconium. Ultrafiltration system with three pore sizes (5kDa, 10kDa and 20kDa, Sartorius) and ultracentrifugation device (49,500 g) were used. Ultra-filtrates and supernatant are compared with ultra-pure deionized water (18 M Ω ·cm⁻¹, Millipore) free of zirconia particles. For the detection, a pulsed laser beam (10 Hz, λ = 532 nm) generating plasma events (dielectric breakdowns) selectively on particles in liquid media is applied. The energy impulsion was about 10 mJ with a duration of 6 ns. The number of plasma events per number of total laser pulses and their spatial distribution in the laser focus give the colloid concentrations and the size particles. The detection limit is 5 ng·L⁻¹ or 10⁵ particles·mL⁻¹ for 10 nm colloids.

172 2.2.4 Determination of the surface site number

173 *Method of determination from continuous titration experiments.* Suspensions of $S/V = 10^6 \text{ m}^{-1}$ 174 monoclinic and cubic zirconia equilibrated for several months in $10^{-2} \text{ mol} \cdot \text{L}^{-1}$ NaCl at pH 0 and 2 were 175 titrated by NaOH solution with Titrino DMS 716 (Metrohm). The pH was measured by a combined 176 glass electrode and recorded with Tiamo software program (TiamoTM1.2. – titration and more). The 177 surface site number (DMSAP, sites per nm²) were calculated using Gran's function [22].

178
$$DMSAP = \frac{C_{NaOH} \times (V2 - V1) \times N_A}{m \times S \times 10^{18}}$$
 (eq.2)

where V1 represents the neutralization volume of the excess proton ions in the suspension by the added hydroxyl ions and V2 the neutralization volume of the excess hydroxyl ions in solution, m is the mass of solid (g), S is the specific surface area (m^2/g) and N_A is the Avogadro number.

182 It should be noted that this function is a mass balance representation of the reactions that take place 183 at the surface of the solid following the interactions of the solid with the solution. It does not 184 represent the real reactions of reaction steps at this interface. The analysis of the variation in 185 function of the added volume gives information on the reactions of the ions added to the suspension 186 (H⁺ or OH⁻) with the surface of the solid.

187 Method of determination from crystallographic calculation. The surface site number can be deduced 188 from crystallographic data of zirconia [23,24]. It is determined by dividing the number of zirconium 189 atoms of the surface of zirconia unit cell corresponding to atoms in contact with aqueous solutions, 190 by the area of zirconia unit cell.

191 **2.3 Solid phase characterization methods**

192 Specific surface area (BET). The specific surface area of monoclinic and yttrium stabilized cubic 193 zirconia samples were determined from N_2 adsorption isotherms at 77 K obtained with a 194 Micromeritics ASAP 2010 M. Prior to analyses, the samples were outgassed in vacuum overnight.

X-ray diffractometer (XRD). Rigaku MiniFlex600 diffractometer equipped with a copper rotating
 anode was used to collect XRD patterns of monoclinic and yttrium stabilized cubic zirconia samples.

Data were collected in the 2θ range from 15° to 90° with a step of 0.01° and a scan-speed of 10 °·min⁻
 ¹. The size of crystalline particles was determined from the full width at half maximum (FWHM) of
 the diffraction peaks based on the Scherrer equation.

200 Transmission Electron Microscopy (TEM). High-resolution transmission electron microscopy was 201 carried out using a JEOL ARM200F with double Cs-correctors for characterization of the morphology 202 and crystallinity. For imaging, the samples were dispersed in ethanol and deposited on a holey 203 carbon coated grid. The tomography in STEM-HAADF mode (Scanning Transmission Electron 204 Microscopy – High Angle Annular Dark Field) was performed by recording a series of images for a 3D 205 construction. The tomograms were obtained from a 0.13 nm spot size, a current density of 140 pA, 206 an acceleration voltage of 200 kV and a camera with a focal length of 8 cm. The serial acquisition of 207 inclinations (bright field – BF and high-angle annular dark field – HAADF) was carried out using the 208 plug-in of "Digital Micrograph" software, which controls step by step the tilt of the sample, the 209 defocusing and the drift of the sample. The samples were tilted within ± 75° with a 2.5° step. The 210 recorded images are aligned in space by correlating the images consecutively using the IMOD 211 software [25]. The Algebraic Reconstruction Technique (ART) method [26] implemented in the TomoJ 212 plugin [27] of the ImageJ software was used to calculate the reconstructed volumes. Finally, the final 213 volumes were visualized and analyzed using the Slicer software [28].

214 Small angle x-ray scattering (SAXS). Rigaku Smartalb equipment was used with a rotative copper 215 anticathode. The wavelength of the incident X-ray, λ , was 0.154 nm for Cu K α radiation. The power of 216 the generator was 9 kW (45mV × 200mA). The *q* domain was ranged between q=0.04 - 4.2 nm⁻¹ or 217 0.06 - 6 degrees in 20, with a step size of 0.02 degree and a rotation rate of 0.53°·min⁻¹. Note that *q*, 218 which is equal to (4 π/λ)sin 0, is the magnitude of the scattering vector.

The samples were loaded into a boron silicate capillary of 0.7 or 1.5 mm of diameter (WJM-Glas Müller GmbH). The direct beam is stopped with a lead beamstop. The diffused intensity was collected by a bi-dimensional D/tex Ultra type detector. In the analysis, the *q* dependence was attributed to the structure factor, S(q), and the form factor, $P_{sphere}(q)$, of the spherical particle with the polydispersity of the particle size [29–31]. By introducing the Gaussian distribution (F(r)) with the average radius of *R* of the solid particle and the standard deviation of σ_r , the scattering function I(q)is given by the multiple product of $P_{sphere}(q)$. The scattering function I(q) is given by:

226
$$I(q) = n\Delta B^2 P_{\text{sphere}}(q)S(q)$$
 (eq.3)

227
$$P_{\text{sphere}}(q) = \int_0^\infty V^2 \left[\frac{3(\sin qr - qr \cos qr)}{(qr)^3} \right]^2 F(r) dr$$
(eq.4)

228
$$F(r) = \exp\left[\frac{-(r-R)^2}{2\sigma_r^2}\right] / \int_0^\infty \exp\left[\frac{-(r-R)^2}{2\sigma_r^2}\right] dr$$
 (eq.5)

where n, ΔB^2 , and V are the number of particles per unit volume in the solution, the scattering contrast difference between the particle and solution, and the volume of single particle, respectively. The experimental SAXS profiles in the range of 0.07 nm⁻¹ <q <1.0 nm⁻¹ were analyzed in the leastsquare fitting analysis based on the above equations to determine the average size of solid phase particle (*R*), its standard deviation (σ_r) and constant A = $n\Delta B^2 V^2 S(q)$.

234 3 Results and Discussion

235 3.1 Morphological characterization

A detailed morphological and structural analysis of zirconia samples before and after alteration
 experiments were performed using XRD, HR-TEM, STEM-HAADF and SAXS.

238 Figure 2 shows XRD patterns of raw zirconia before alteration experiments confirming the monoclinic MZ and cubic YSZ crystallographic structures. The crystallite size determined by Scherrer equation 239 240 gives values close to 28 nm for MZ and 6 nm for YSZ. Raw monoclinic zirconia was also characterized 241 by HR-TEM showing very well crystallized particles without any amorphous phase (Figure 3-a). STEM-242 HAADF characterization reveals the presence of agglomerates of nanoparticles with a size particle of 243 (28±5) nm similar to the crystallite size (Figure 4-a). In addition, the reconstruction in 3D of the 244 aggregates of nanoparticles from the alignment of two series of BF and HAADF provides an overview 245 of the morphology and the surface state of nanoparticles. Figure 4-b and Figure 4-c show the typical 246 images extracted from the series of inclinations for the shape of MZ aggregates in equilibrium with a 247 pH 1 aqueous solution in HCl and HClO₄ media, respectively. These samples were chosen for their 248 high reactivity (low S/V ratio 10⁶ m⁻¹) among all the series of experiments. After more than 12 months 249 of dissolution, MZ particles size in HCl and HClO₄ is not modified and is within the range of the 250 measurement errors: (26±2) nm in HCl media and (32±4) nm in HClO₄ media (Figure 3-b-c). The 3D 251 reconstruction visualization and HR-TEM show that the morphology and the structure of nanoparticles in the raw state and after reaching equilibrium in acidic media are similar without any 252 253 evolution of the interfacial morphology observed during dissolution. The characterization on raw and 254 altered YSZ nanoparticles was conducted by HR-TEM. The in-depth analysis shows well-oriented 255 atomic planes in raw sample (Figure 3), confirming the strong tendency to agglomerate. The size 256 distribution of raw YSZ nanoparticles gives (7±2) nm in agreement with the crystallite size 257 determined by XRD. After alteration in acidic HCl and HClO4 media at pH 0, the nanoparticles size 258 remains stable within given uncertainties at (8±2) nm.

The micro-characterization using various techniques showed that all the alteration experiments were conducted in presence of nanoparticles close to agglomerates of crystallites. At very low pH and high surface reactivity, no modification of the morphology was observed, as well as the absence of the

formation of amorphous phase for both structures. Nevertheless, heterogeneous areas are observed at the border of some nanoparticles (Figure S4 in supplementary data). These may be attributed to the modification of atomic plans following the dissolution process of the nanoparticles. However, the occurrence of such modification was rarely observed.

266 To deepen the micro-characterization of the solids, the particle size before, during and at equilibrium 267 was determined by SAXS. The results in Figure 5 present the characteristic point on monoclinic ZrO_2 268 samples obtained at $q \approx 0.2$ nm⁻¹ corresponding to the gyration radius ($R_{\rm g}$) of the Guinier regime. The 269 average particle size of monoclinic ZrO₂ before contact with an aqueous solution was determined to 270 be (32±6) nm from the least-square fitting analysis of the SAXS profiles based on eq. (3)-(5). This 271 value is coherent with the values determined by XRD and TEM. After contacting aqueous solutions at 272 pH 2, the MZ particle size was determined to be (34±7) nm, which is almost the same as that before 273 contact with aqueous solution. The result shows the weak modification of the particle size even after 274 reaction in acidic media for 74 days. On the other hand, the particle size at pH 0 was determined to 275 be (21±4) nm after 171 days of contact with aqueous solution, slightly smaller than that of before 276 contact. For wave vector values below 0.2 nm⁻¹, intensity I(q) keeps increasing with the decrease of q. 277 For the lowest values of q, a zero slope is not observed for most spectra. This means that, in addition 278 to the presence of individual particles, the particles form aggregates larger than 90 nm, calculated 279 from the limit of the q interval (0.07 nm⁻¹ < q). For cubic ZrO_2 samples, particle size before contact 280 with an aqueous solution is (12±2) nm determined from the characteristic point at $q \approx 0.6$ nm⁻¹, 281 which is slightly higher than the values obtained by XRD and TEM. After contacting with solution (86 282 days at pH2 and 62 days at pH0), the size of particles are within the range 8-12 nm almost 283 independent of aqueous solution conditions, indicating a slight modification of the particle size after reaction in acidic media. For wave vector values below 0.6 nm⁻¹, the intensity I(q) continues to 284 285 increase with the decrease of q. This means that the particles form aggregates are larger than 90 nm, 286 calculated from the limit of the q interval (0.07 nm⁻¹ < q). Finally, the SAXS spectra analysis results for 287 both monoclinic and cubic phase show that the mean nanoparticle sizes under the different 288 conditions studied (pH 0 and 2, HCl and HClO₄ media) are comparable before and during dissolution 289 experiments, indicating that the dissolution process of ZrO₂ did not induce precipitation or the 290 formation of a new solid phase in the sample.

291 **3.2** Assessment of the ultrafiltration efficiency

The ultrafiltration efficiency was assessed using laser induced breakdown detection (LIBD) by measuring the breakdown probability (or the number of plasma events) on ultrafiltered solutions and supernatant (ultracentrifugation) as function of increasing pulse energy. 295 Figure 6-a compares the LIBD s-curves obtained by the ultrafiltration and the ultracentrifugation of 296 monoclinic zirconia nanoparticles. The LIBD s-curve of blank solution (without zirconia nanoparticles) 297 exhibits a low pulse energy threshold at 44 μ J corresponding to the presence of trace levels of 298 impurities. As the ultrafilter pore size increases (5kDa, 10 kDa and 20 kDa), the threshold in the s-299 curves at 5 kDa and 10 kDa does not significantly differ from the blank solution. Thus, the 300 ultrafiltered solutions at 5 kDa and 10 kDa could be considered to be free of nanoparticles. For the 301 ultrafilter pore size of 20 kDa, the threshold shifts to lower pulse energies (38 μ) implying the 302 presence of nanoparticles of ZrO_2 : the lower is the threshold of the pulse energy, the higher is the 303 probability of presence of nanoparticles in solution. This observation is confirmed with the last s-304 curves obtained from ultracentrifugation separation method with the lowest threshold pulse 305 energies at 12 μ J (Figure 6–b). Therefore, the results were compared from ultrafiltered solution at 5 306 kDa in contact with monoclinic zirconia at various pH. The LIBD s-curves give similar results to that of 307 blank solution. The absence of nanoparticles in the ultrafiltered solution is precious information, any 308 Zr analyzed in this solution by ICP-MS is by consequence in non-colloidal form allowing the 309 application of aqueous speciation models for solubility determination. Indeed, working with 310 nanoparticles required efficient and high-performance separation device to separate them from 311 solution. The typical filtration methods such as 0.22µm or 0.45µm filter membranes failed when 312 working with nanoparticles. The optimization of a suitable method of filtration allows decreasing the 313 uncertainties of the measurement, avoiding pitfalls reported in literature confirming the influence of 314 colloids and solid form on the solubility values.

315 To gain insight into the degree of zirconium losses during ultrafiltration process, the adsorption of Zr 316 on the filter was studied. Zirconium adsorption tests were conducted on the 5 kDa ultrafilters. 317 Standard zirconium solutions were prepared at pH 0, 1 and 2 (I = 0.01) and ultrafiltered for analysis 318 by Q-ICP-MS. For each standard solution, the total concentration of Zr(IV) was measured before and 319 after ultrafiltration, and the mean amounts of zirconium retention/adsorption as a function of initial 320 concentrations of standard solutions are shown in Figure 7. The amount of adsorbed zirconium is 321 constant in the [0-2] pH range: (13.7±0.3)% of dissolved zirconium is adsorbed on ultrafiltration 322 membrane. The concentration values given in the present work are corrected from the adsorption 323 coefficient.

324 3.3 Solubility data

Concentrations of Zr were followed by periodic sampling of aliquots over more than one year. Figure k displays [Zr] as function of S/V×time (S/V×t) (for more details see in supplementary information Figures S1 and S2). The experimental data show that long times and large S/V ratios both favor approach of equilibrium. For almost all experimental conditions, equilibrium is reached except for YSZ at pH0 in (Na,H)Cl showing a continuous dissolution after 466 days of contact. Table 2 reports the detailed values of solubility data, also shown in Figure 1. This work provided new solubility values, in particular at pH [1.5-2] for monoclinic phase ($\sim 2x10^{-10}$ mol·l⁻¹). These low values are explained by the efficient ultrafiltration method to remove colloids and the use of HR-ICP-MS to decrease the quantification limit. For further thermodynamic treatment, we used only data at high (S/V×t) to determine the equilibrium concentrations.

An average fraction of surface sites involved in the dissolution process was determined relating the 335 336 measured element concentration in solution to the number of crystallographic surface sites per 337 solution volume. Without considering the potential dominance of individual crystal planes in 338 surface/solution exchange, the total number of moles at the surface per solution volume may be 339 estimated from the crystallographic site density (in sites nm⁻²), the specific surface area ((36.2±0.1) $m^2 \cdot g^{-1}$ for MZ and (139.4±0.5) $m^2 \cdot g^{-1}$ for YSZ) and the mass/solution volume ratio. The 340 crystallographic site density obtained for MZ and YSZ are 7.5 and 7.6 sites.nm⁻², respectively. 341 342 Compared to these results, experimental protonable surface site density was obtained for the higher 343 S/V ratio (10⁶ m⁻¹) by acid-base titration at pH 0 and 2 (Table 3). For this S/V ratio, the number of 344 dissolved monolayers was determined at pH 0 (after 383 days of MZ alteration and 466 days of YSZ 345 alteration) and pH 2 (after reaching the equilibrium). The results show that the mass of Zr dissolved 346 to reach the observed solubility equilibrium of ZrO₂ corresponds to the dissolution of much less than 347 1 monolayer. These results are consistent with a previous study performed onto monoclinic and yttrium stabilized tetragonal $ZrO_2[32]$ and confirm the strong refractory character of the solids. 348

349 3.4 Solubility constants and Zr speciation

350 The Zr speciation in solution both for monoclinic and cubic phases was determined using the 351 Thermochemical Database of Nuclear Energy Agency NEA-TDB from Brown et al. [20], and taking into 352 account the strong effect of ionic strength on solubility at low pH values, and the hydrolysis and SIT 353 models. Polymer and monomer hydrolysis species distribution as well as chloride complexes were determined for 10⁻² mol·L⁻¹ (Na,H)Cl and (Na,H)ClO₄ solution in pH 0-2. In chloride and perchloride 354 media at pH range [0-2] the main species exist under Zr^{4+} , $ZrOH^{3+}$, $Zr(OH)^{2+}_{2}$ and $Zr(OH)_{4}$ forms. 355 Mainly monomer hydrolysis species are obtained. Dissolved polymer hydrolysis species $(Zr_3(OH)_9^{3+},$ 356 $Zr_4(OH)_8^{8+}$) are formed at very low pH and for high Zr-concentration in solution in presence of cubic 357 zirconia. Chloride complex (ZrCl³⁺) is formed at very low pH. Detailed predominance of aqueous Zr 358 359 solution species are displayed in supplementary data Figure S3.

Thus, based on the Zr-hydrolysis and SIT models [20] for aqueous speciation of dissolved zirconium and using the solubility constant K_s^0 as only fit variable, experimental solubility data are compared

with thermodynamic model data (Figure 9, Table 2). The solubility constants $\log K^0_{s}$ were calculated 362 considering either the monoclinic or the cubic ZrO₂ solid phase limiting the solubility. The obtained 363 364 log K_s^0 (298 K) value for the monoclinic phase (-7.33±0.69) is lower than the value derived by Brown 365 et al. (-7.0±1.6) as well as the uncertainty values associated [20]. Brown et al. explained the high uncertainty by the selection of solubility data from crystallized solid to amorphous hydroxides. This 366 367 work has strengthened the thermodynamic data for well-crystallized solids. Our characterizations clearly show that the solid remains crystallized even after more than 1 year of contact with solution. 368 369 For the cubic phase, a log K_s^0 (298 K) value of (-5.86±0.35) is obtained, higher than the value obtained 370 with the monoclinic phase. The obtained solubility constants of the nanoparticles are independent 371 on the ionic medium within the experimental uncertainties as expected. Solubility data are obtained from ZrO₂ nanoparticles, and to account for the effect of particle size, solubility constants have been 372 373 re-evaluated using the Schindler equation (eq. 6) [33,34]:

374
$$\ln K_s^0 = \ln K_s^0(\overline{S}_{=0}) + \frac{2\overline{\gamma}}{3RT}\overline{S}$$
 (eq.6)

with $K_s^0(\overline{S}_{=0})$ solubility constant (I=0) related to the particle size effect, $\overline{\gamma}$ the surface energy of nanoparticles (J·m⁻²), and \overline{S} the molar surface ($\overline{S}_{monoclinic} = 3302 \text{ m}^2 \cdot \text{mol}^{-1}$, $\overline{S}_{cubic} = 12717 \text{ m}^2 \cdot \text{mol}^{-1}$).

377 This relation shows that the effect of particle size is the key parameter dominating the dissolution of 378 particles with size below 100 nm [5,34–37]. Kobayashi et al. demonstrate the effect of particle size on ZrO₂ solubility: solubility decreases with increasing particle size and crystalline degree of the solid 379 (as opposed to amorphous and hydroxide phases) [5]. Using the surface energy for the hydrous 380 monoclinic phase (2.86±0.31) J·m⁻² [38] and for the hydrous cubic phase (0.85±0.07) J·m⁻² [39], the 381 solubility constant for large crystals log $K_s^0(\overline{S}_{=0})$ was calculated as (-8.43±0.69) for monoclinic phase 382 383 and (-7.12±0.35) for cubic phase. By this approach, the discrepancy in solubility constant values has been reduced. 384

385 3.5 Possible effect of Y-release on Zr-solubility values?

In dissolution experiments with YSZ cubic phase, strong release of yttrium has been observed at all 386 387 studied pH values despite very low release of Zr. The Y release after 69 days corresponds to the 388 release of (53±8)% of the Y inventory of the YSZ particles indicating a fast release of Y in solution, 389 independent on the media composition. Yttrium release from YSZ is reported in the literature [40] for 390 pH values <4. At acidic pH, the solubility of Y is high [41,42] while it decreases at neutral pH [42]. The 391 release of large quantities of Y to a depth of few nanometers implies that hydrolysis of YSZ bonds 392 occurs accompanied by diffusion of H₂O into the crystal lattice. Geochemical modelling (PHREEQC) of 393 a solid solution of La₂O₃ (homologue to Y) has shown that this composition of a solid solution of REE 394 and ZrO_2 is not stable under acid conditions and release of a large fraction (more than 99.9%) of its content of REE is expected upon equilibrating with the aqueous solution. The question is if the cubic 395 396 crystal structure in the leached surface region remains cubic after the release of its Y content. 397 Leaching studies of a mixed cubic and monoclinic Zr_{0.9} Nd_{0.1}O_{1.95} phase [43] have shown that the 398 crystal structure remains mixed cubic and monoclinic. This indicates that the cubic structure may 399 have been conserved in our experiments. On the other hand, the authors did not use a surface-400 sensitive XRD technique and it cannot be excluded that the surface region has been transformed 401 crystallographically. Our HR-TEM study clearly shows well-crystallized nanoparticles, without new 402 precipitates or amorphous phase, indicating that the cubic structure may have remained stable.

403 Zr concentrations in solution measured in the present study are much higher than that observed in 404 our experiments for the monoclinic phase. This increase of the solubility constant cannot be 405 explained by the presence of yttrium since Y has been leached from the surface region. However, the substitution of Zr by Y for stabilizing the cubic phase leads to the creation of O^{2-} vacancy sites 406 407 increasing the ionic character of Zr-O bonds and the dissolution effect [44,45]. The reactivity of the 408 vacancy site type regarding to water was assessed by Kossoy et al. on undoped and Gd-doped cerium 409 oxides in which the authors characterized by XPS that hydroxyl ions are strongly bound to oxygen 410 vacancy sites by water dissociation [46]. They also showed that this phenomenon occurs only at the 411 surface and does not involve the bulk. Moreover, in our previous study conducted on the solubility of 412 tetragonal zirconia [32], XPS characterizations were performed and revealed that hydroxyl ions are 413 dominant in the tetragonal phase of ZrO_2 compared to the monoclinic phase (Figure S5 in 414 supplementary data). Therefore, simultaneous reactions at surface with the enrichment in water 415 molecules bond to oxygen vacancy sites and the leaching of yttrium may have changed the surface energy and may have created a more open surface structure with a reduction of the average 416 417 coordination number of surface Zr atoms, leading to an easiest detachment of surface Zr atoms. 418 Therefore, the surface energy values taken from literature may not be applicable as surface energy 419 measurements are taken in neutral water, less prone to removal of Zr. Measurement of surface 420 energy of leached YSZ particles under acid conditions should be performed to study this hypothesis.

421 4 Conclusion

The present study aimed to determine the solubility of well crystallized nanoparticles of zirconia in acidic media for two crystallographic structures: monoclinic and yttrium stabilized cubic. Its high chemical stability required the development of reliable and robust analytical method to improve the detection and the quantification of zirconium at ultra-trace level. Our experimental approach has

allowed reducing the uncertainties. This was the condition of being able to distinguish clearly for the
first time between the solubility of monoclinic and Y stabilized cubic ZrO₂.

A consistent set of solubility constants derived from this work and that of Brown et al. [20] for 428 429 monoclinic and cubic ZrO_2 was obtained, indicating that nanoparticles can be used for solubility 430 assessment if extremely low quantification limits are assured and solution are carefully ultrafiltered. 431 Taking into account the ionic strength, the effect of particle size and the surface energies, the solubility constant of large crystals log $K_s^0(\overline{S}_{=0})$ was calculated to (-8.43±0.69) for the monoclinic 432 structure and (-7.12±0.35) for the cubic structure. However, in the calculation of the solubility 433 434 constant, the surface energy values were taken here from literature but no account could be taken 435 for the effect of the release of Y on surface energy of the cubic phase, in particular in acidic media 436 promoting Y and Zr release. As a perspective, the surface energies needs to be determined 437 experimentally under the same experimental conditions as those of the solubility studies.

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pH2, 74 days of contact (S1) NaCl 0.01M / HCl, (S2) NaClO₄ 0.01M / HClO₄; at pH 0, 171 days of
contact (S5) NaClO4 0.01M / HClO₄, (S6) NaCl 0.01M / HCl; (S9) raw MZ sample before alteration.
Cubic YSZ: at pH2, 86 days of contact (S3) NaClO₄ 0.01M / HClO₄, (S4) NaCl 0.01M / HCl; at pH0, 62
days of contact (S7) NaClO₄ 0.01M / HClO₄, (S8) NaCl 0.01M / HCl pH0; (S10) raw YSZ sample before



Figure 6: Breakdown probability as function of laser energy obtained by LIBD. (a) Comparison
between ultrafiltration and ultracentrifugation methods applied on the separation of ZrO₂
nanoparticles. (b) Ultrafiltration by 5 kDa at various pH of monoclinic nanoparticles.



Figure 7 : The amount of zirconium adsorbed/retained on filter membranes of standard solutions
prepared in I=0.01 (a) HClO₄ pH 2, (b) HCl pH 2, (c) HClO₄ pH 1, (d) HCl pH 1, (e) HClO₄ pH 0, (f) HCl pH
0 matrices as function of initial standard solution concentrations.



Figure 8: The total zirconium concentrations plotted against S/V×time and measured in a period of
time ranging from 7 days to 400 days of dissolution experiments of monoclinic zirconia in (a) HCl pH
0, (b) HCl pH 1 and (c) HClO₄ pH 1, and of cubic zirconia in (d) HCl pH 0.



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Figure 9: Comparison of experimental data from this work and in various ionic media from literature with NEA-TDB [20] model, only $\log K_s^0$ values were fitted.

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Table 1: Experimental conditions : pH-measured values (pH) and converted pH-measured into concentrations of protons (pmH⁺) in 10^{-2} mol·L⁻¹ NaCl and NaClO₄ media, solid phase, ratio of solid surface over volume of solution, and total duration of experiment.

Aqueous medium	рН	pmH⁺	Solid phase	(S/V)×10 ³ (m ⁻¹)	Duration (days)
	2.0	1.96	Monoclinic	10, 1000 2000	396 236
			Cubic	1000, 2000	377
	1.5	1.47	Monoclinic	10, 100	118
			Cubic	10, 100	322
(Na,H)Cl	1.0	0.94	Monoclinic	10, 50, 100	394
			Cubic	10, 50, 100	428
	0	0.15	Monoclinic	10, 50, 100 1000	383 282
			Cubic	50, 100, 1000	466
	2.0 1.94	1.04	Monoclinic	10, 1000 2000	396 236
		1.94	Cubic	1000, 2000	377
	1.5 1.46	1 46	Monoclinic	10, 100	118
		1.40	Cubic	10, 100	322
(Na,H)ClO₄	1.0	1.03	Monoclinic	10, 50, 100	394
			Cubic	10, 50, 100	428
	0	0.19	Monoclinic	10, 50, 100 1000	383 282
			Cubic	50, 100, 1000	466

Table 2: Solubility values of zirconium in presence of monoclinic and cubic zirconia. Solubility constants log K_s^0 of ZrO₂ nanoparticles determination based on Zr-hydrolysis model and ionic strength correction for each solid phase and medium, average values of log K_s^0 for a given medium for each solid phase, and solubility constant for large ZrO₂ phases log $K_s^0(\bar{S} = 0)$ calculated from Schindler equation [33]. Quantification limit (QL) $\approx 10^{-11}$ mol.L⁻¹. * Solubility constant determined from the maximum zirconium concentration obtained above the quantification limit.

Solid phase	[Zr] (mol·L ⁻¹)	$\log K_s^0$	Average of log K_s^0 for nanoparticles	$\log \mathrm{K}^0_\mathrm{S}(\overline{S}=0)$ for large ZrO ₂ phases	Media	рН
	(1.8±1.2)×10 ⁻¹⁰	-7.76±0.34	-7.33±0.69	-8.43±0.69	10 ⁻² mol·L ⁻¹ (Na,H)Cl	2±0.1
	(2.3±1.0)×10 ⁻¹⁰	-8.08±0.20				1.5±0.1
	(2.0±1.0)×10 ⁻⁸	-7.31±0.24				1±0.1
Monoclinic	(6.0±3.0)×10 ⁻⁵	-6.67±0.23				0±0.1
WONOCIIIIC	< QL				10 ⁻² mol·L ⁻¹ (Na,H)ClO4	2±0.1
	< QL	-8.07*				1.5±0.1
	(1.2±0.5)×10 ⁻⁸	-7.15±0.02				1±0.1
	(3.0±1.0)×10 ⁻⁵	-6.30±0.17				0±0.1
	(2.4±0.9)×10 ⁻⁸	-5.51±0.14	-5.86±0.36	-7.12±0.35	10 ⁻² mol·L ⁻¹ (Na,H)Cl	2±0.1
	(1.0±3.0)×10 ⁻⁸	-6.32±0.23				1.5±0.1
	(8.0±0.2)×10 ⁻⁷	-5.73±0.17				1±0.1
Cubic	(2.7±1.0)×10 ⁻⁸	-5.57±0.16			10 ⁻² mol·L ⁻¹ (Na,H)ClO4	2±0.1
	(1.4±7.0)×10 ⁻⁸	-6.38±0.12				1.5±0.1
	(4.5±0.5)×10 ⁻⁷	-5.70±0.03				1±0.1
	(1.6±0.5)×10 ⁻⁴	-5.82±0.07				0±0.1

Table 3: Number of dissolved monolayers determined from (i) DMSAP and (ii) the crystallographicdensity, for pH 0 and 2.

	рН	Number of dissolved monolayers			
Solids		based on proton exchanged (determined from DMSAP)	determined from the crystallographic site density		
Monoclinic 7rO	0	0.005	0.001		
	2	4×10 ⁻⁸	1.9×10 ⁻⁸		
Cubic 7rO	0	0.35	0.035		
	2	2.3×10 ⁻⁵	2.3×10 ⁻⁶		