Thermodynamic description of Be(II) solubility and hydrolysis in acidic to hyperalkaline NaCl and KCl solutions

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ABSTRACT

The solubility of Be(II) is investigated in carbonate-free dilute to concentrated HCl–NaCl–NaOH, KCl–KOH, NaOH and KOH solutions. Undersaturation experiments were performed under Ar atmosphere at $T = (22 \pm 2)$ °C. XRD, XPS, SEM and quantitative chemical analysis confirm that α-$Be(OH)_2$(cr) is the solid phase controlling the solubility in all evaluated systems. No transformation of α-$Be(OH)_2$(cr) to β-$Be(OH)_2$(cr) or ternary solid phases Na/K–Be(II)–OH(s) is observed in the investigated systems within the timeframe of this study ($t \leq 600$ days). An amphoteric solubility behaviour of Be(II) is observed with a solubility minimum at $pH_m \approx 9.5$ (with [Be(II)] $\approx$ $10^{\;6.8}$ M), regardless of the ionic strength. The combination of solubility data determined in acidic pH_m conditions and the hydrolysis scheme reported in the literature for cationic hydrolysis species of Be(II) is used for the determination of the solubility constant of α-$Be(OH)_2$(cr), log $^{*}K^{\circ}{}_{s,0} = (6.9 \pm 0.4)$. Slope analysis of the solubility data in alkaline to hyperalkaline conditions and ^{9}Be NMR support the predominance of the monomeric hydrolysis species $Be(OH)_2$(aq), $Be(OH)_3^-$ and $Be(OH)_4^2$ within the strongly alkaline pH_m-conditions relevant in cementitious systems. The comprehensive solubility dataset collected within this study in combination with extensive solid and aqueous phase characterization allow the development of a complete chemical, thermodynamic and (SIT) activity model for the system Be^{2+}–Na^+–K^+–H^+–Cl^-–OH^-–H_2O(l). This model provides an accurate and robust tool for the evaluation of Be(II) solubility and speciation in a diversity of geochemical conditions, including source term calculations of beryllium in the context of the nuclear waste disposal Safety Case.

1. Introduction

Beryllium is a chemotoxic, silver-gray, light weight metal with low density and a melting point of 1278 °C (Smith and Martell, 1994; Alderighi et al., 2000). Due to its low thermal neutron absorption cross section and specific chemical/structural properties, beryllium is used as neutron reflector/moderator in test and research fission reactors (Beeston, 1970; Chandler et al., 2009). The use of beryllium in fusion reactors is considered for neutron multiplication in breeding blankets and as an oxygen getter for the surfaces facing the plasma (Kawamura et al., 2004).

Substantial amounts of ^{4}He, ^{3}He and ^{3}H gases are formed in fission reactors as the result of (n, 2n) and (n, α) reactions of beryllium. The accumulation of these gases leads to the swelling of beryllium and to the alteration of its mechanical properties. For this reason, irradiated beryllium components need to be replaced and disposed of regularly (Beeston, 1970; Longhurst et al., 2003; Chandler et al., 2009).

Beryllium is the first element in the second group of the periodic table. It holds an electronic configuration [He] $2s^2$, and accordingly it is mainly found as Be(II). The $r_{Be^{2+}}$ cation is characterized by a very small ionic radii ($r_{Be^{2+}}$ 0.27 Å for a coordination number CN 4) (Shannon, 1976) compared to other elements of the alkaline-earth series (*e.g.* $r_{Mg^{2+}}$ 0.57 Å for CN 4 or $r_{Ca^{2+}}$ 1.0 Å for CN 6). This provides to beryllium remarkably different properties such as a strong hydrolysis including the formation of anionic species (*e.g.* $Be(OH)_3^-$ and $Be(OH)_4^{2-}$), and low solubility (Baes and Mesmer, 1976; Alderighi et al., 2000; Brown and Ekberg, 2016).

The hydrolysis of beryllium has been extensively studied under acidic conditions (see Table 1S, Supplementary Material), expectedly

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due to the higher solubility of $Be(OH)_2(s)$ and the insensitivity of the system to atmospheric $CO_2(g)$ (Mattock, 1954; Gilbert and Garrett, 1956; Kakihana and Sillen, 1956; Schindler and Garett, 1960; Carell and Olin, 1961, 1962; Schwarzenbach, 1962; Hietanen and Sillen, 1964; Bertin et al., 1967; Mesmer and Baes, 1967; Ohtaki, 1967; Ohtaki and Kato, 1967; Lanza and Carpéni, 1968; Pâris and Gregoire, 1968; Schwarzenbach and Wenger, 1969; Kakihana and Maeda, 1970; Tsukuda et al., 1975; Vanni et al., 1975; Baes and Mesmer, 1976; Brown et al., 1983; Bruno, 1987; Bruno et al., 1987a, 1987b; Chinea et al., 1997). On the other hand, the number of experimental studies investigating the solubility and hydrolysis of beryllium is very limited in the alkaline to hyperalkaline conditions of relevance in the context of repositories for nuclear waste disposal (Table 1S, Supplementary Material) (Gilbert and Garrett, 1956; Green and Alexander, 1963, 1965; Bruno et al., 1987a).

One of the first and most comprehensive studies on the preparation and chemical behaviour of $Be(OH)_2(s)$ in alkaline systems was conducted by Haber and Van Oordt (1904). The authors extensively investigated the effect of alkalinity, ageing and temperature on the solubility of $Be(OH)_2(s)$. These applied efforts resulted in 1909 in the international patent "*Making beryllium hydroxide*" (US Patent 822,444).

Most of the experimental studies investigating the hydrolysis of Be(II) are based on potentiometric titrations, which allow the thermodynamic characterization of monomeric and polyatomic species but are limited in terms of metal concentration to the sub-milimolar range. Kakihana and Sillen (1956) investigated the hydrolysis of Be(II) in 3.0 M $NaClO_4$ solutions with $1 \cdot 10^{-3}$ M $\leq [Be]_{tot} \leq 0.05$ M and $2.0 < -\log [H^+] < 6.0$ using potentiometric titrations. In this pH-range, the authors reported the predominance of $Be_3(OH)_3^{3+}$ and the presence of the minor contribution of $Be_2(OH)^{3+}$ and $Be(OH)_2(aq)$ species. Gilbert and Garrett (1956) studied the solubility of α-$Be(OH)_2(cr)$ in acidic ($5 \cdot 10^{-4}$–0.120 m $HCl/HClO_4$) and hyperalkaline (0.02–0.71 m NaOH) pH conditions. The samples were equilibrated for 7–14 days under air (acid systems) or in N_2-filled vessels (alkaline systems). Assuming the predominance of the species Be^{2+} and $Be_3(OH)_3^{3+}$ in acidic conditions, the authors determined the solubility product $\log {}^*K^{\circ}_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\}$ and the hydrolysis constant $\log {}^*\beta^{\circ}_{(3,3)}$ for the species $Be_3(OH)_3^{3+}$. Solubility data collected in NaOH solutions were interpreted with the formation of $Be(OH)_3^-$ and $Be(OH)_4^{2-}$, for which the authors provided the corresponding hydrolysis constants, $\log {}^*\beta^{\circ}_{(1,3)}$ and $\log {}^*\beta^{\circ}_{(1,4)}$. Carell and Olin (1961, 1962) conducted potentiometric and enthalpy titrations in 3.0 M $NaClO_4$ solutions with 0.01 M $\leq [Be]_{tot} \leq 1.0$ M and $1.0 < -\log [H^+] < 4.0$. The authors confirmed the speciation previously proposed by Kakihana and Sillen (1956), and reported equilibrium constants and enthalpy values for the hydrolysis reactions of $Be_3(OH)_3^{3+}$ and $Be_2(OH)^{3+}$. The hydrolysis scheme reported in Kakihana and Sillen (1956) was later refined by Hietanen and Sillen (1964) using the LETAGROP program. Besides confirming the main species reported in their previous study, the authors proposed the formation of $BeOH^+$ and provided an upper limit for $\log {}^*\beta^{\circ}_{(1,1)}$. Green and Alexander (1963, 1965) investigated the hydrolysis of Be(II) using a solvent extraction method with cyclohexane/acetylacetone and toluene/*N*-n-butylsalicylideneimin. This is a relevant study because it provided a new perspective for a system so far only investigated by potentiometric and solubility methods. Extraction experiments were performed within $5 \leq pH \leq 13$ and using ^7Be ($t_{1/2}$ 53.12 days), which was quantified in the organic and aqueous phases by γ-spectroscopy. The authors interpreted their extraction data with the formation of $Be(OH)_2(aq)$ and $Be(OH)_3^-$, although acknowledging that the decrease in the distribution coefficients observed at pH > 9 (assigned to the formation of $Be(OH)_3^-$) could be attributed also to the decomposition of *N*-n-butylsalicylideneimine. The value of $\log {}^*\beta^{\circ}_{(1,3)}$ reported by Green and Alexander is in line with the one determined by Gilbert and Garrett (1956), whereas a very large discrepancy is observed between $\log {}^*\beta^{\circ}_{(1,2)}$ determined in this solvent extraction study and the values reported for this hydrolysis species in all potentiometric studies. Mesmer and Baes (1967) investigated by potentiometric titrations the hydrolysis of Be(II) in 1 m NaCl solutions with $2 \cdot 10^{-3}$ m $\leq [Be]_{tot} \leq 0.05$ m, $2.0 < pH < 7.0$ and T 0, 25 and 60 °C. The model proposed by the authors included $Be_2(OH)^{3+}$ and $Be_3(OH)_3^{3+}$, but disregarded the formation of the neutral species $Be(OH)_2(aq)$. Instead, the authors proposed the formation of $Be_5(OH)_7^{3+}$ under slightly acidic conditions, which however was substituted by $Be_6(OH)_8^{4+}$ in an updated model by the same authors (Baes and Mesmer, 1976). Brown et al. (1983) performed a very accurate potentiometric study investigating the hydrolysis of Be(II). Experiments were performed in 0.1 M KNO_3 solutions with $3.6 \cdot 10^{-4}$ M $\leq [Be]_{tot} \leq 2.7 \cdot 10^{-3}$ M and $4.2 < pH < 5.3$. The authors clearly confirmed the predominance of the species $Be_3(OH)_3^{3+}$ and $Be_2(OH)^{3+}$, and argued that the quality of the fit clearly improved when including $Be(OH)_2(aq)$. We note however that the latter species never represented more than 10% of the total beryllium concentration in the conditions of their experiments. The authors also advised that beyond this pH and Be concentration, the formation of $Be(OH)_2(s)$ would be expected.

Bruno (1987) and Bruno et al. (1987a, 1987b) performed the most comprehensive investigation available to date on the system Be(II)–H_2O–$CO_2(g)$ and covering acidic to weakly alkaline pH conditions. The authors used a combination of e.m.f. (electromotive force) measurements and solubility experiments in the range $2.0 \leq -\log [H^+] \leq 8.5$ in the absence and presence of $CO_2(g)$. Besides the determination of the stoichiometry and stability of several ternary Be(II)–OH–CO_3 aqueous species, Bruno and co-workers quantified the solubility product of the crystalline phase β-$Be(OH)_2(cr)$ and the stability constants for the hydrolysis species $Be_n(OH)_m^{2n-m}$, with (n,m) (1,1), (1,2), (2,1), (3,3), (5, 6) and (6,8). The authors re-interpreted also the solubility data previously reported by Gilbert and Garrett (1956), and provided an updated value for $\log K^{\circ}_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\}$. The hydrolysis scheme proposed by Bruno and co-workers was later confirmed by the combined potentiometric and NMR study by Chinea et al. (1997). The recent review work by Brown and Ekberg (2016) supports also the hydrolysis scheme proposed by Bruno and co-workers, although acknowledging the existing controversy on the stability of the $Be(OH)_2(aq)$ species.

Besides the well-known formation of BeO(cr) and α-/β-$Be(OH)_2(cr)$ solid phases, a number of experimental studies have reported on the formation of ternary M–Be(II)–OH solid phases (with M Na, Ca, Sr and Ba) under hyperalkaline pH conditions (Fricke and Humme, 1929; Everest et al., 1962; Scholder and Schwarz, 1968; Schmidbaur et al., 1998; Schmidt et al., 1998). The structural definition of these solid phases was originally based on the predominant role of the anion $Be(OH)_4^{2-}$ (*i.e.* $Na_2[Be(OH)_4](cr)$, $Ca[Be(OH)_4](cr)$, etc.), although no proof of concept other than quantitative chemical analysis was provided in these publications. More recent studies have demonstrated that the structure of these solid phases is more complex than originally proposed and contains polyatomic moieties of Be(II) as those forming under acidic pH conditions. Hence, the compound $Na_2[Be_4(OH)_{10}] \cdot 5H_2O(cr)$ was reported to form in concentrated NaOH solutions (Schmidbaur et al., 1998), whereas the solid phase $Ca_2[Be_2(OH)_7][H_3O_2] \cdot 2H_2O(cr)$ was observed in alkaline $CaCl_2$ solutions (Schmidt et al., 1998). Note that the latter structure contains the hydrated OH^- ion, $H_3O_2^-$, which was previously reported in the literature (Ruf et al., 1996; Tuckerman et al., 1997). The role of these polyatomic Be(II) moieties in the aqueous phase and the corresponding equilibria with the monomeric $Be(OH)_4^{2-}$ species and solid phases remain so far unknown.

High level nuclear waste resulting from plutonium production is stored in more than 170 tanks in the Hanford Site, WA (USA). Most of these wastes are characterized by high pH (12–13.5) and the presence of concentrated salts ($NaNO_3$, $NaNO_2$, etc.). As a result of its use in specific Zircaloy fuel cladding processed in the PUREX plant and as a feed constituent in the plutonium finishing plant (PFP), beryllium is found in both solid and liquid phases of the Hanford waste (Johnson and Steeves, 1957; Reynolds, 2013). Although with a very heterogeneous distribution, Be(II) concentrations of up to 180 ppm and 3 ppm ($\approx 3.3 \cdot 10^{-4}$ M) are found in solid and liquid wastes, respectively. Provided the high concentration of carbonate and fluoride in the alkaline wastes, Reynolds speculated on the possible predominance of the species $Be(OH)_2CO_3^{2-}$ and $BeF_y(OH)_m^{2-y-m}$ in the aqueous phase of the Hanford tanks.

In spite of the numerous experimental studies focussing on Be(II) solution chemistry in a variety of boundary conditions, there is no systematic dataset available allowing the reliable prediction of the solubility and hydrolysis of Be(II) from acidic to hyperalkaline pH conditions and covering dilute to concentrated salt systems. In the context of the EU collaborative project "*Cement-based materials, properties, evolution, barrier functions*" (Cebama), the present study aims at a comprehensive investigation of Be(II) solubility and hydrolysis in dilute to concentrated NaCl and KCl solutions. The focus of this work is on the alkaline to hyperalkaline systems of relevance in cementitious systems, but extends to acidic conditions with the aim of systematically characterizing the thermodynamic properties of the solid phase/s controlling the solubility of Be(II) in the investigated systems. Solubility experiments are complemented with ^{9}Be NMR of the aqueous phase, and the characterization and identification of the stable, solubility-limiting Be(II) oxides/hydroxides in NaCl and KCl solutions. The hydrolysis scheme of Be(II) dominating in these salt systems is comprehensively evaluated by using new data derived in the present study and findings previously reported in literature. The final aim consists in developing complete chemical, thermodynamic and SIT activity models for the system Be^{2+}–Na^+–K^+–H^+–Cl^-–OH^-–$H_2O(l)$, thus providing scientifically sound solubility limits for source term estimations and a realistic Be(II) speciation scheme under boundary conditions relevant for nuclear waste disposal.

2. Experimental

2.1. Chemicals

Beryllium sulfate tetrahydrate ($BeSO_4{\cdot}4H_2O$, 99.99% purity), sodium chloride EMSURE® (NaCl), potassium chloride EMSURE® (KCl), NaOH Titrisol©, KOH Titrisol© and HCl Titrisol© were purchased from Merck. Ethanol (99%) was obtained from VWR Chemicals. All solutions were prepared with purified water (Milli–Q academic, Millipore, 18.2 MΩ cm) and purged with Ar for at least 1 h before use to remove $CO_2(g)$ dissolved in solution. All sample preparation and handling were carried out in an Ar–glove box ($O_2 < 1$ ppm) at T (22 ± 2) °C.

2.2. pH measurements

The proton concentration ($[H^+]$ in molal units, mol/kg$_w$, with pH_m $-\log [H^+]$) was measured using combination pH electrodes (ROSS Orion, with 3.0 M KCl as filling solution). Calibration of the electrode was performed with pH buffers (pH 1–12, Merck). The values of pH_m were calculated from the experimentally measured values (pH_{exp}) and considering the empiric expression pH_m $pH_{exp} + A_m$, where A_m values are correction factors entailing both the activity coefficient of H^+ and the liquid junction potential of the electrode for a given background electrolyte concentration. Such corrections are required in solutions of ionic strength $I \geq 0.1$ mol kg^{-1}, where pH_{exp} is an operational value significantly deviating from pH. A_m values in NaCl and KCl systems were taken as reported in Altmaier et al. (2003) and Baumann et al. (2017), respectively. In hyperalkaline systems with $[OH^-] > 0.03$ m and due to the alkaline error of the glass electrode, $[H^+]$ was calculated from the known hydroxide concentration and the conditional ion product (K'_w) of water. The values of K'_w in the investigated NaCl and KCl systems were calculated using the Specific ion Interaction Theory (SIT) and the corresponding values of water activity (a_w) as reported in Guillaumont et al. (2003).

2.3. Solid phase preparation and characterization. Solubility measurements

The $Be(OH)_2(s)$ solid phase used in the solubility experiments was prepared by slow titration under continuous agitation of a 0.35 M $BeSO_4$ solution with 2.0 M carbonate-free NaOH solution up to $pH_{exp} \approx 10.5$. The resulting solid phase was aged for 21 days and then characterized by X-ray diffraction (XRD). For this purpose, an aliquot of the solid phase (≈1–2 mg) was washed 7–8 times with approximately 1 mL ethanol under Ar-atmosphere to remove the matrix solution (containing NaCl, Na_2SO_4 and NaOH) after centrifugation. After the last cleaning step, the solid phase was re-suspended in ethanol, deposited on the XRD sample holder and dried under Ar atmosphere for a few minutes. The XRD diffractogram was collected outside the glovebox using a Bruker D8 Advance X-Ray powder diffractometer (Cu anode) at 2θ 5–80° with incremental steps of 0.02° and a measurement time of 0.4 s per step.

The solubility of Be(II) was investigated from undersaturation conditions using the $Be(OH)_2(s)$ solid phase synthesized in this work. A total of 96 independent batch samples were prepared by contacting 0.5–5 mg of solid phase (per sample) with the following systems:

(i). 0.1, 0.5, 1.0, 3.0 and 5.0 M NaCl–NaOH (with $5.5 \leq pH_m \leq 14.5$);
(ii). 0.1, 0.5, 1.0, 3.0 and 4.0 M KCl–KOH (with $7 \leq pH_m \leq 14.3$);
(iii). 0.01–4.0 M NaOH;
(iv). 0.01–3.0 M KOH (iii and iv in the absence of MCl salts).

Concentration of beryllium and pH_m values of each sample were monitored at regular time intervals from 7 to 600 days. An aliquot of the supernatant (100–500 µL) of each sample was centrifuged for 2–5 min with 10 kD filters (2–3 nm cut-off Nanosep® centrifuge tubes, Pall Life Sciences) to separate colloids or suspended particles. After centrifugation, a certain volume of the filtrate was diluted (1:100 to 1:5000, depending upon Be and salt concentration) in 2% ultrapure HNO_3, and [Be] was quantified by ICP–MS (inductively coupled plasma mass spectrometry, PerkinElmer ELAN 6100). The accuracy of ICP–MS measurements was ± 2–5%. Detection limits ranged between $\approx 10^{-6.5}$ and $\approx 10^{-8}$ M depending on the dilution factors applied for more saline samples. All concentration values obtained in molar units (M) were converted to molal units (m) using the conversion factors reported in the NEA–TDB (Guillaumont et al., 2003).

Equilibrium conditions were assumed after repeated measurements with constant [Be] and pH_m values. After attaining thermodynamic equilibrium, solid phases of selected samples were characterized by XRD as described above. The collected XRD patterns were compared to reference diffractograms available in the Joint Committee on Powder Diffraction Standards data base (JCPDS, 2001) and from literature.

A fraction of the washed solid phase (≈1 mg) was dissolved in 2% HNO_3 and characterized by quantitative chemical analysis to evaluate the ratio Be: Na or Be: K in the solid. The concentration of Be was quantified by ICP–MS, whereas ICP–OES (inductively coupled plasma–optical emission spectroscopy, Perkin–Elmer 4300 DV) was used for the quantification of Na and K.

A second fraction of the washed solid was characterized by SEM (scanning electron microscopy) and XPS (X-ray photoelectron spectroscopy). A FEI Quanta 650 FEG environmental scanning electron microscope (now Thermo Fisher Scientific Inc.) was used to image the carbon coated sample surfaces. The primary electron beam energy was set to 5 keV. XPS measurements were performed by an XPS system PHI 5000 VersaProbe II (ULVAC-PHI Inc.) equipped with a scanning microprobe X-ray source (monochromatic Al Kα (1486.7 eV) X-rays). Charge compensation at isolating samples is achieved by application of low energy electrons (1.1 eV) and low energy argon ions (8 eV). Survey scans were recorded with an X-ray source power of 31 W and pass energy of 187.85 eV of the analyzer. Narrow scans of elemental lines were recorded at 23.5 eV pass energy that yields an energy resolution of 0.69 eV FWHM at the Ag $3d_{for}$ elemental line of pure silver. Calibration of the binding energy scale of the spectrometer was performed using well-established binding energies of elemental lines of pure metals (monochromatic Al K_α: Cu $2p_{3/2}$ at 932.62 eV, Au $4f_{7/2}$ at 83.96 eV) (Seah et al., 1998). Error of binding energies of elemental lines is estimated to ±0.2 eV. C 1s of adventitious hydrocarbon at 284.8 eV is used as charge reference at isolating samples.

2.4. ^{9}Be NMR

The aqueous speciation of beryllium in selected samples was characterized by means of ^{9}Be NMR. An aliquot of supernatant solution (540 μL) of the selected solubility samples was taken after ultrafiltration with 10 kD filters, 60 μL of D_2O (99,99%, Eurisotope GmbH) as an internal lock substance were added, transferred into NMR tubes (borosilicate glass, Wilmad LabGlass) and flame-sealed outside the glovebox. A negligible change in pH with respect to light water is expected in the presence of 10% D_2O (Rubinson, 2017). All ^{9}Be NMR spectra were recorded at T 300 K on a Bruker Avance III 400 spectrometer operating at 400.13 MHz for ^{1}H and 56.23 MHz for ^{9}Be. Chemical shifts are referenced to the signal of a 0.043 M $BeSO_4$ solution with pH 3.0 (set to δ 0 ppm) (Harris et al., 2001) by the lock signal, in which the aqueous speciation is dominated by Be^{2+} (>95% in mol fraction, as calculated with thermodynamic data summarized in Section 4.3). For all direct excitation spectra, the standard Bruker pulse sequences zg was were used. All 1D spectra were recorded with 32k data points and 2048 scans at a spectral width of 40 ppm. The spectra were zero filled to 64k points and the line broadening processed with 0.05 Hz.

3. Results and discussion

3.1. Solid phase characterization

X-ray diffraction patterns of Be(II) solid phases collected from selected solubility samples are shown in Fig. 1a (NaCl systems) and 1b (KCl systems). Both figures also include reference patterns reported for α-$Be(OH)_2$(cr) by Bear and Turnbull (1965). All patterns shown in Fig. 1a and b correspond to solubility samples after attaining equilibrium conditions (t 400–600 days), except for the red pattern shown in both figures that was collected from the starting material after an ageing time of 21 days. No relevant features are observed for the fresh precipitate, thus supporting its amorphous character *i.e.* $Be(OH)_2$(am). On the contrary, very similar and sharp features are observed for all other systems, in excellent agreement with reference data reported for α-$Be(OH)_2$(cr). This observation supports the transformation of an initially amorphous material into a crystalline phase ($Be(OH)_2$(am) → α-$Be(OH)_2$(cr)), following the so-called *Ostwald ripening* process. Such behaviour of $Be(OH)_2$(s) in alkaline systems was qualitatively described (without the support of XRD evidence) more than 100 years ago by Haber and Van Oordt (1904).

The additional features observed in the XRD of the solid phase equilibrated in 5.0 M NaCl at pH_m 12.8 are clearly assigned to NaCl, thus indicating that the washing steps were insufficient in this case featuring exceptionally high salinity. For all samples (except the solid equilibrated in 5.0 M NaCl at pH_m 12.8), quantitative chemical analysis disregarded the presence of Na or K in the investigated solid phases.

XPS data collected for the Be(II) solid phase equilibrated in 0.1 M NaCl at pH_m 12.9 for ≈ 700 days are shown in Fig. 1S in the Supplementary Material. The figure shows the binding energies for Be 1s and O 1s. The binding energy observed for the O 1s line (531.5 eV) is in

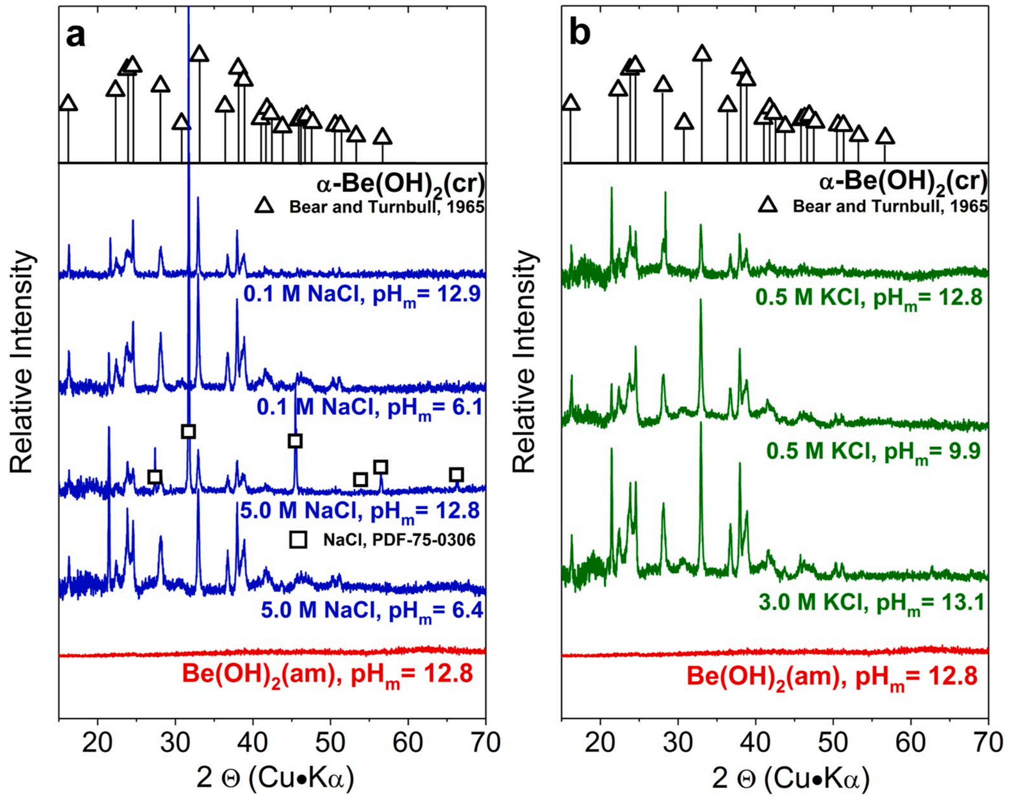

Fig. 1. XRD patterns of solid phases recovered from selected representative solubility experiments in dilute to concentrated (a) NaCl and (b) KCl solutions. All XRD collected for solid phases after an equilibration time of 400–600 days, except for the red diffractogram corresponding to the amorphous starting material after an ageing time of only 21 days. Reference patterns reported for α-$Be(OH)_2$(cr)(Bear and Turnbull, 1965) and NaCl (JCPDS file Nr. 75–0306) are included for comparison.

good agreement with the energies reported for other alkaline earth hydroxides (*i.e.* 530.8 eV for $Ca(OH)_2$ or 530.5 eV for $Sr(OH)_2$, Dupin et al., 2000), in contrast to the lower energies reported for the corresponding oxides (*i.e.* 528.5 eV for CaO or 527.5 eV for SrO). There is no previous XPS data on the Be(II) hydroxide system, but we note that the binding energy obtained in the present work for the Be 1s line (113.0 eV) is slightly lower than the values reported in the literature for BeO (113.4–113.7 eV) (Moulder et al., 1995; NIST, 2000; Mallinson et al., 2014, 2015). XPS data disregards the presence of Na or K in the investigated sample.

SEM images of solid phases recovered from selected solubility experiments in dilute to concentrated NaCl and KCl systems are shown in Fig. 2. In all cases, SEM images show a flower-like morphology formed by the assemblage of individual sheets of 1–3 μm width and 20–100 nm thickness. These observations provide additional evidence that the solubility is controlled by the same crystalline phase in all investigated systems.

Experimental evidences collected by XRD, quantitative chemical analysis, XPS and SEM unequivocally confirm that α-$Be(OH)_2$(cr) is the solid phase controlling the solubility in all investigated NaCl and KCl systems. None of the methods considered for solid phase characterization provides evidence on the formation of ternary Na/K–Be(II)–OH solid phases within the timeframe of this study ($t \leq 600$ days). Previous studies reporting the formation of such ternary phases were conducted in highly concentrated alkali solutions (*e.g.* > 30% NaOH: Fricke and Humme, 1929; Scholder et al., 1968), at very high temperatures (*e.g.* 700–800 °C; Kastner and Hoppe, 1975), or otherwise promoted the formation of the ternary solid phase in the presence of acetone (Schmidbaur et al., 1998) or alcohol (Krüss and Moraht, 1891). It appears evident that the formation of ternary Na/K–Be(II)–OH solid phases is not favoured within the boundary conditions considered in this work, *e.g.* aqueous systems, T (22 ± 2) °C and $[MOH] \leq 3.0$ M, even at equilibration times of 600 days.

3.2. Aqueous phase characterization: ^{9}Be NMR

Fig. 3a summarizes the ^{9}Be NMR spectra collected for aqueous reference samples with a concentration of $4.3\cdot10^{-2}$, $4.3\cdot10^{-3}$ and $4.3\cdot10^{-4}$ M $BeSO_4$, and pH 3.0, 3.7 and 4.7, respectively. Fig. 3b shows the ^{9}Be NMR spectra of the supernatant of selected solubility samples in 3.0 M NaCl solutions with pH$_m$ 5.8 and 14.1. All spectra are referenced internally to the resonance obtained for $4.3\cdot10^{-2}$ M $BeSO_4$ at pH 3.0 (δ 0 ppm) by the lock signal, for which thermodynamic calculations using data summarized in Section 4.3 predict the predominance of Be^{2+} (>0.95 mol fraction, see Fig. 2S in the Supplementary Material). Similar resonances with a slight low-field shifts are obtained for the references $4.3\cdot10^{-3}$ M $BeSO_4$ at pH 3.7 (δ 0.07 ppm) and $4.3\cdot10^{-4}$ M $BeSO_4$ at pH 4.7 (δ 0.27 ppm), although we note that the resonance collected for $4.3\cdot10^{-4}$ M $BeSO_4$ is very close to the detection limit. These observations are consistent with thermodynamic calculations shown in Fig. 2S (Supplementary Material), which predict the predominance of Be^{2+} in both references although with a larger contribution of hydrolysis species ($BeOH^+$ and $Be_3(OH)_3^{3+}$) at pH 4.7 (≈0.1 mol fraction).

The ^{9}Be NMR of the sample equilibrated in 3.0 M NaCl at pH$_m$ 5.8 shown in Fig. 3b has a main resonance at δ ≈ 0.88 ppm and a smaller peak at δ ≈ 0.49 ppm. This observation indicates the existence of (at least) two hydrolysis species at this pH$_m$ and salt concentration. For these boundary conditions, calculations using the thermodynamic and SIT activity models summarized in Section 4.3 foresee the predominance of $Be_3(OH)_3^{3+}$ and (to less extent) $Be_6(OH)_8^{4+}$. Our results are in moderate agreement with previous ^{9}Be NMR studies, which reported the resonance of $Be_3(OH)_3^{3+}$ at δ 0.76 ppm (Chinea et al., 1997) and δ 0.54 ppm (Cecconi et al., 1998). In all cases, significantly broader peaks are observed for $Be_3(OH)_3^{3+}$ compared to $Be(H_2O)_4^{2+}$, reflecting a less symmetric environment of Be in the trimeric moiety. The line-broadening effect of low-symmetry coordination spheres is very pronounced for ^{9}Be, as this nucleus has a nuclear spin of I 3/2, which leads to a considerable quadrupole moment.

A larger chemical shift (δ ≈ 1.8 ppm) is observed in the ^{9}Be NMR of the sample equilibrated in 3.0 M NaCl at pH$_m$ 14.1, for which the sharpest peak of all investigated samples is observed. This shift is in good agreement with the value reported by Schmidbaur et al. (1998) for samples at pH ≈ 12–14 (δ ≈ 2 ppm). The characterization by single crystal XRD of the solid phases precipitating in such alkaline solutions (with the addition of acetone) confirmed the presence of the moiety $Be_4(OH)_{10}^{2-}$, which may be indicative of the presence of such species in solution. In contrast to this interpretation, Alderighi et al. (2000) attributed this peak to the ion $Be(OH)_4^{2-}$. These authors suggested that the near tetrahedral symmetry of this ion would be subject to little quadrupolar broadening, thus resulting in the very sharp peak observed. Based on the peak widths observed for monomeric and polynuclear Be(II) hydrolysis species forming in acidic conditions, the very sharp peak observed in this work at pH$_m$ 14.1 rather points to a highly symmetric monomeric moiety ($Be(OH)_4^{2-}$) with clear analogies with the Be^{2+} ion prevailing in very acidic conditions ($Be(H_2O)_4^{2+}$).

3.3. Solubility measurements

The experimental solubility data collected for α-$Be(OH)_2$(cr) in 0.1–5.0 M NaCl–NaOH, 0.1–4.0 M KCl–KOH and 0.01–3.0 M NaOH/KOH (in the absence of MCl) are shown in Figs. 4–6, respectively. The solubility data shows a minimum in Be(II) concentration at pH$_m$ ≈ 9.5 (with [Be] ≈ $10^{-6.8}$ M), whereas concentration increases above and below this pH$_m$ thus confirming the amphoteric character of Be(II). Solubility data in Fig. 4 shows a slope of ≈ 3 in the pH$_m$ region ≈5.5–7 (depending upon NaCl concentration), which indicates the predominance of hydrolysis species with charge +3 (either Be_2OH^{3+} or $Be_3(OH)_3^{3+}$) in equilibrium with α-$Be(OH)_2$(cr). Above pH$_m$ ≈ 8.5, the solubility of α-$Be(OH)_2$(cr) in NaCl and KCl systems (Figs. 4 and 5) follow sequentially a slope of 0, +1 and + 2, which can be assigned to the predominance in the aqueous phase of the hydrolysis species $Be(OH)_2$(aq), $Be(OH)_3^-$ and $Be(OH)_4^{2-}$, respectively.

The solubility determined in pure NaOH systems are compared in Fig. 6a with previous data reported by Gilbert and Garrett (1956) in 0.02–0.71 M NaOH solutions. The agreement between both datasets is good for the more alkaline samples, but significant deviations (≈0.5 log-units) arise in the less alkaline systems. Such deviations lead to differences in the slopes of both solubility datasets, and accordingly affect the distribution of the hydrolysis species prevailing in this pH region ($Be(OH)_3^-$ and $Be(OH)_4^{2-}$). Gilbert and Garrett used the crystalline phase α-$Be(OH)_2$(cr)[1] for their solubility experiments in acidic conditions, whereas a mixture of α-$Be(OH)_2$(cr) and $Be(OH)_2$(am) was used for the solubility experiments in alkaline systems. The authors argued that "*transformation from the amorphous to crystalline state takes place rapidly in alkaline solutions*", and thus considered unproblematic the use of an amorphous material in their solubility experiments in alkaline systems. In view of the long contact times required in this work to attain equilibrium conditions (up to 400 days in some cases), the timeframe considered in the solubility experiments by Gilbert and Garrett (7–14 days) appears clearly insufficient to reach equilibrium and full solid phase transformation, especially in those samples with lower solubility.

In line with results obtained from solid phase characterization, solubility data collected in hyperalkaline NaCl/NaOH and KCl/KOH systems do not provide evidence on the formation of ternary solid phases Na/K–Be(II)–OH(s), even up to 3.0 M NaOH/KOH and considering very long equilibration times. Higher alkali concentrations, elevated temperatures, or the use of organic solvents appear necessary for the formation of such ternary phases.

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[1] The authors claimed the characterization of this solid phase by XRD, although no diffraction data are provided in the publication.

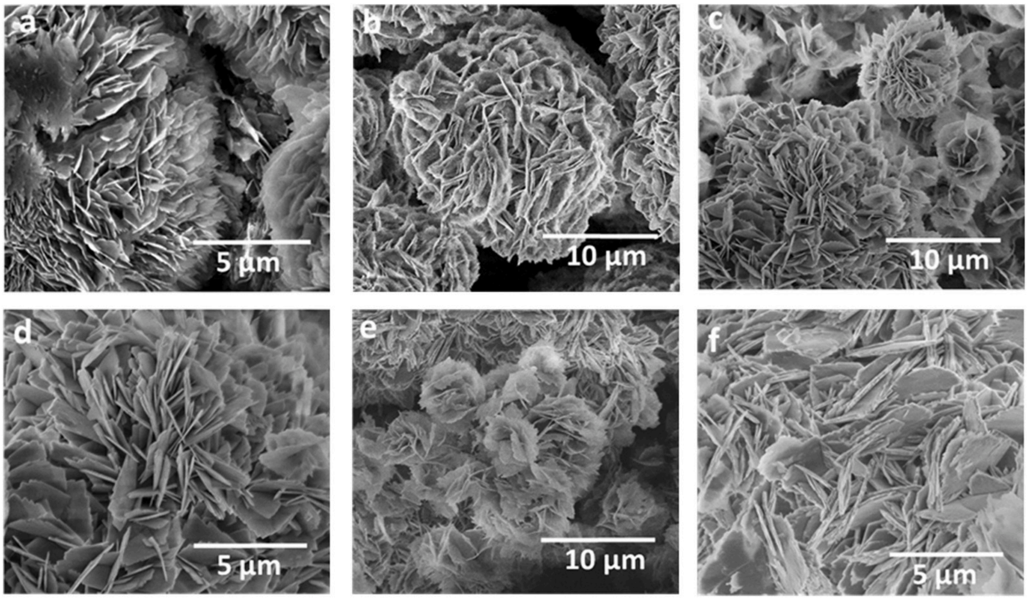

Fig. 2. SEM images of α-$Be(OH)_2(cr)$ solid phase equilibrated in (a) 0.1 M NaCl at $pH_m = 12.9$; (b) 5 M NaCl at $pH_m = 6.4$; (c) and (d) 0.5 M KCl at $pH_m = 9.9$ and (e) and (f) 3.0 M KCl at $pH_m = 13.1$.

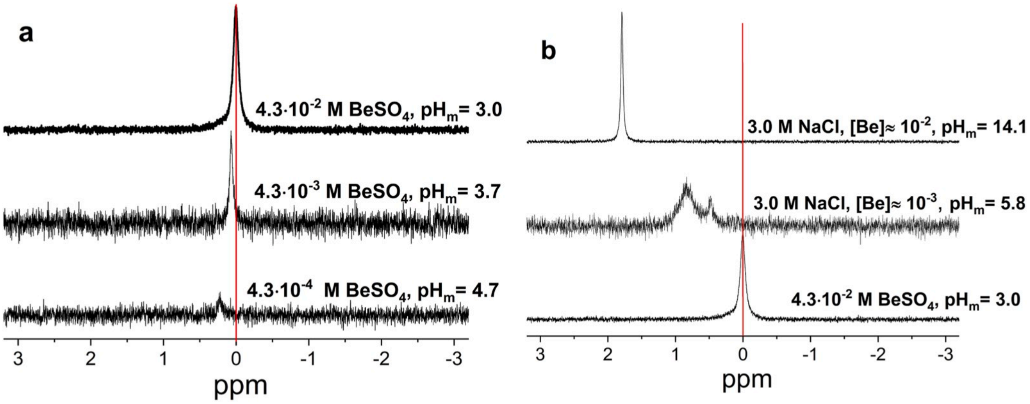

Fig. 3. ^{9}Be NMR spectra collected for (a) reference samples with $4.3\cdot 10\ ^{2}$, $4.3\cdot 10\ ^{3}$ and $4.3\cdot 10\ ^{4}$ M $BeSO_4$, and pH = 3.0, 3.7 and 4.7, respectively; (b) supernatant of solubility samples equilibrated in 3.0 NaCl at $pH_m = 5.8$ and 14.1. All spectra referred to the resonance observed for the reference solution with $4.3\cdot 10\ ^{2}$ M $BeSO_4$ and pH = 3.0, for which thermodynamic calculations predict the predominance of Be^{2+}.

4. Chemical, thermodynamic and SIT activity models

Chemical, thermodynamic and activity models are derived on the basis of the solubility data collected in NaCl and KCl systems, and considering α-$Be(OH)_2(cr)$ as only solid phase controlling the solubility in all investigated systems. Previous studies (Mattock, 1954; Gilbert and Garrett, 1956; Kakihana and Sillen, 1956; Schindler and Garett, 1960; Carell and Olin, 1961, 1962; Schwarzenbach, 1962; Hietanen and Sillen, 1964; Bertin et al., 1967; Mesmer and Baes, 1967; Ohtaki, 1967; Ohtaki and Kato, 1967; Lanza and Carpéni, 1968; Pâris and Gregoire, 1968; Schwarzenbach and Wenger, 1969; Kakihana and Maeda, 1970; Tsukuda et al., 1975; Vanni et al., 1975; Baes and Mesmer, 1976; Brown et al., 1983; Bruno, 1987; Bruno et al., 1987a, 1987b; Chinea et al., 1997) have shown the very complex speciation scheme of Be(II) in acidic to near-neutral pH conditions, including the formation of several monomeric and polynuclear species. Slope analysis in solubility studies provides direct insight on the charge of the species prevailing in the aqueous phase, but cannot distinguish between monomeric and polynuclear species of the same charge. For this reason and because of the good agreement in the equilibrium constants available in the literature for positively charged hydrolysis species of Be(II), thermodynamic data previously reported for these species have been used for the description of our solubility data in acidic to near-neutral pH conditions. It was also used for the corresponding determination of the solubility constant of α-$Be(OH)_2(cr)$, log $^{*}K^{\circ}_{s,0}$ (see Section 4.1). The predominance of monomeric hydrolysis species in alkaline to hyperalkaline conditions (*i.e.* $Be(OH)_2(aq)$, $Be(OH)_3^-$ and $Be(OH)_4^{2-}$) is supported by ^{9}Be NMR data obtained in this work and is in line with related discussions available in the literature (Alderighi et al., 2000; Brown and Ekberg, 2016). A negligible contribution of Be(II)-chloride complexes is expected within the boundary conditions of this study, and accordingly such species are disregarded in the thermodynamic description of the experimental solubility data. Based on a solvent extraction study with 0.5 M $\leq$ [HCl] $\leq$ 9.4 M, Hardy et al. (1961) reported the formation of the very weak complex $BeCl^+$, with log $\beta^{\circ}{}_{(1,1)}$ 0.7. The potentiometric study of Mesmer and Baes (1967) also supported the very weak complexation between Be(II) and chloride. These authors argued that, if forming, Be(II)-chloride complexes should be of outer-sphere nature. The substitution of a water molecule in $Be(H_2O)_4^{2+}$ by the larger chloride ion would result in the significant lengthening of all Be^{2+}–H_2O distances or

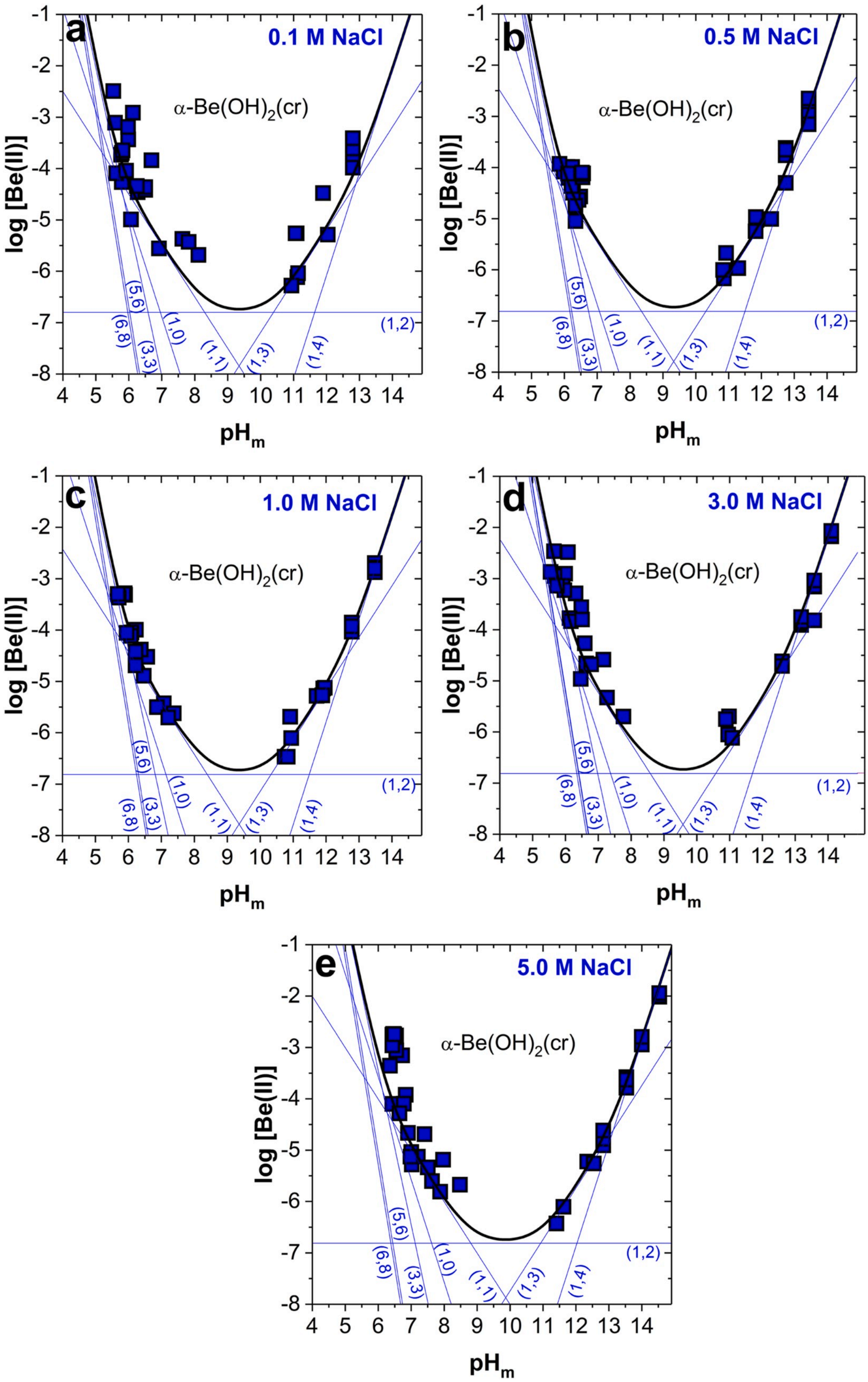

Fig. 4. Solubility of α-Be$(OH)_2$(cr) in acidic to hyperalkaline systems: (a) 0.1 M; (b) 0.5 M, (c) 1.0 M, (d) 3.0 M and (e) 5.0 M NaCl. Thick solid (black) lines correspond to the solubility of α-Be$(OH)_2$(cr) calculated with thermodynamic and SIT activity models summarized in Section 4.3. Thin solid (blue) lines show the Be(II) aqueous speciation underlying α-Be$(OH)_2$(cr) solubility. The hydrolysis species (2,1) is present in small fractions ($\leq$10%) and is not shown in the figure, although it is considered in the calculation of $[Be]_{tot}$.

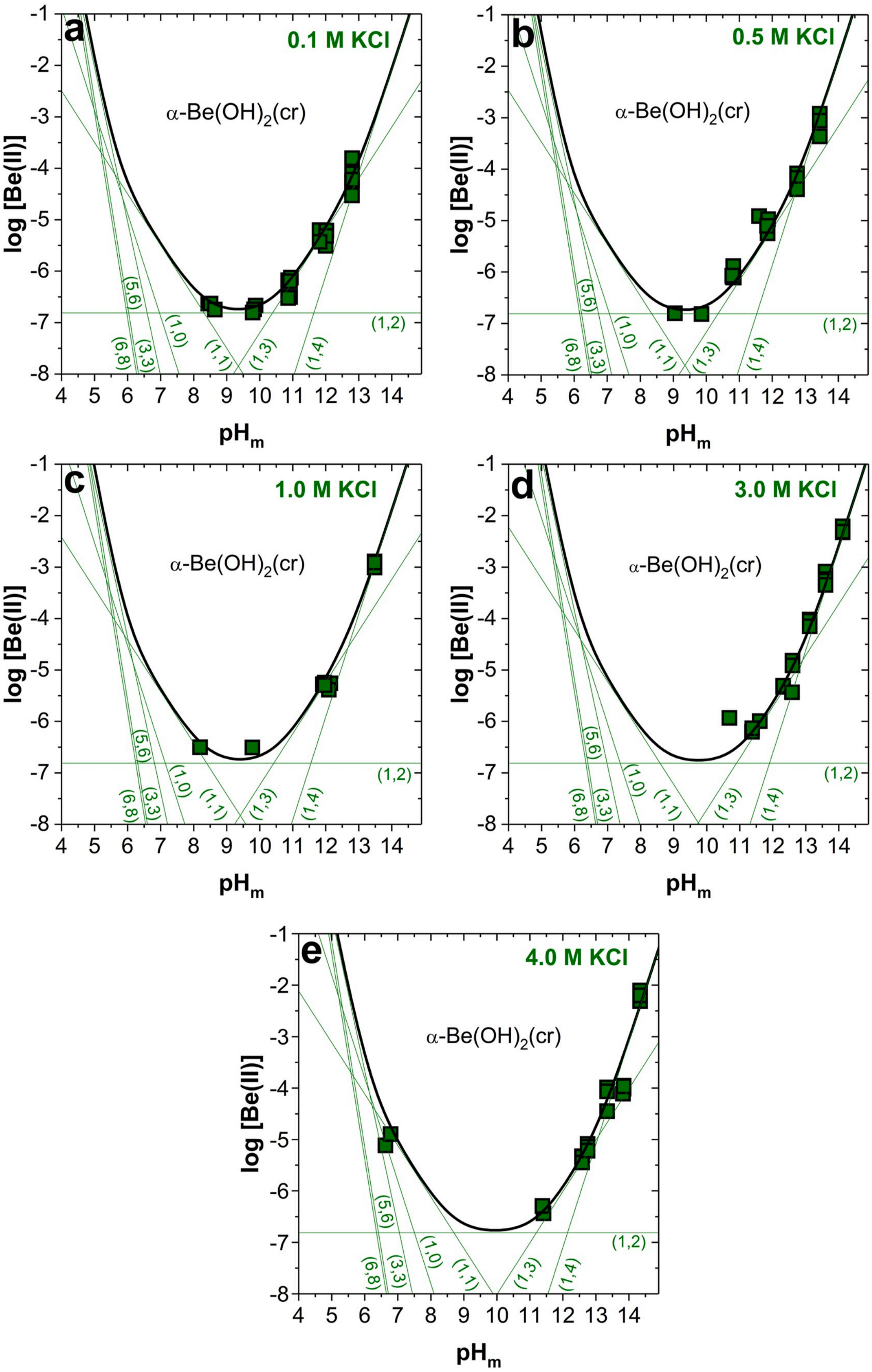

Fig. 5. Solubility of α-Be$(OH)_2$(cr) in acidic to hyperalkaline systems: (a) 0.1 M; (b) 0.5 M, (c) 1.0 M, (d) 3.0 M and (e) 4.0 M KCl. Thick solid (black) lines correspond to the solubility of α-Be$(OH)_2$(cr) calculated with thermodynamic and SIT activity models summarized in Section 4.3. Thin solid (green) lines show the Be(II) aqueous speciation underlying α-Be$(OH)_2$(cr) solubility. The hydrolysis species (2,1) is present in small fractions (≤10%) and is not shown in the figure, although it is considered in the calculation of $[Be]_{tot}$.

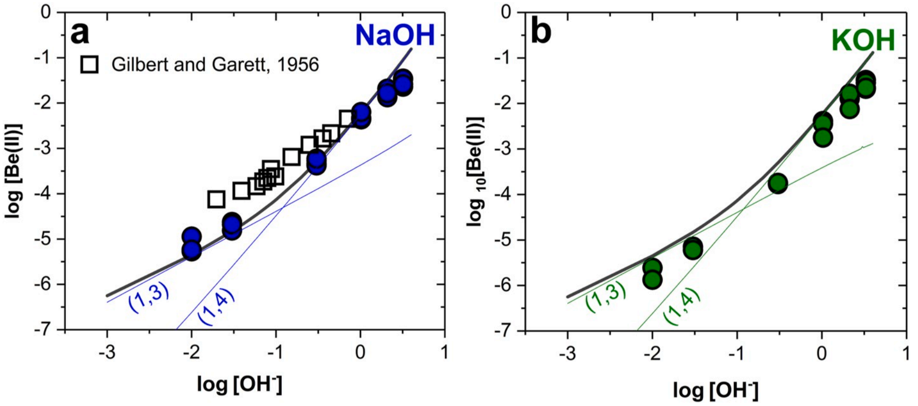

Fig. 6. Solubility of α-$Be(OH)_2(cr)$ in 0.01, 0.03, 0.3, 1.0, 2.0 and 3.0 M (a) NaOH and (b) KOH systems. Thick solid (black) lines correspond to the solubility of α-$Be(OH)_2(cr)$ calculated with thermodynamic and SIT activity models summarized in Section 4.3. Thin solid (blue, green) lines show the Be(II) aqueous speciation underlying α-$Be(OH)_2(cr)$ solubility. Empty squares correspond to the solubility of Be(II) in 0.02–0.71 M NaOH as reported in Gilbert and Garrett (1956).

otherwise in the reduction of the coordination number of Be^{2+}, with both processes being energetically highly unfavourable. Such type of weak interactions between Be(II) cationic species and chloride are included in the activity model as described below.

In this study, the specific ion interaction theory (SIT) (Ciavatta, 1980) derived from the Brønsted-Guggenheim-Scatchard specific ion interaction method is used to account for ion interaction processes in systems at $I > 0$. In SIT, the activity coefficient of a given ion j (γ_j) is calculated according to:

$$\log\gamma_j \qquad z_j^2 D + \sum_k \varepsilon(j,k,I_m)m_k \tag{1}$$

where z_j is the charge of the ion j, D is the Debye-Hückel term $\left(D \quad \frac{0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}}\right)$, m_k is the molality of the oppositely charged ion k, and $\varepsilon(j, k, I_m)$ is the specific ion interaction parameter. The ionic strength is calculated as $I_m \quad 1/2\sum m_i z_i^2$.

The Debye Hückel term in equation (10) accounts for the electrostatic, non-specific long range interactions (prevailing in dilute systems), whereas the term $\sum_k \varepsilon(j,k,I_m)m_k$ accounts for short range, non-electrostatic interactions that consider also differences between ions of the same charge but different size. The SIT is usually considered for the correction of ionic strength effects up to $I \quad 3.5\ m$ (Grenthe et al., 2013), although this limit can be safely extended to higher ionic strengths, especially in the case of 1:1 electrolytes (Neck et al., 2009; Gaona et al., 2013; Altmaier et al., 2017; Cevirim-Papaioannou et al., 2018).

4.1. Thermodynamic data derived from Be(II) solubility experiments in acidic to near neutral NaCl systems

The chemical model of Be(II) in acidic to near-neutral pH conditions (up to $pH_m \approx 8$) in the absence complexing ligands except water includes the well-defined solid phase α-$Be(OH)_2(cr)$ and a number of positively charged monomeric and polynuclear hydrolysis species, $Be_n(OH)_m^{2n-m}$. The extensive literature reporting on the aqueous speciation of Be(II) in these conditions shows consensus in the predominance of the species $BeOH^+$, Be_2OH^{3+}, $Be_3(OH)_3^{3+}$, $Be_5(OH)_6^{4+}$ and $Be_6(OH)_8^{4+}$ (see Section 1 and Table 1S in the Supplementary Material), which have been accordingly considered in this work without further evaluation.

The solubility datasets determined in 0.1–5.0 M NaCl systems are considered to evaluate thermodynamic and activity models of Be(II) in acidic conditions. These data are fitted at each ionic strength by minimizing the function $\sum((\log [Be]_{exp} - \log [Be]_{calc})^2)^{1/2}$, where $[Be]_{calc}$ is the sum of $[BeOH^+]$, $[Be_2OH^{3+}]$, $[Be_3(OH)_3^{3+}]$, $[Be_5(OH)_6]^{4+}]$ and $[Be_6(OH)_8^{4+}]$ calculated based on equation (2) – (6):

$$\alpha\text{-}Be(OH)_2(cr) + 2H^+ \Leftrightarrow Be^{2+} + 2H_2O(l) \tag{2}$$

$$^*K^\circ_{s,0} \qquad a_{Be^{2+}} a_w^2 \Big/ a_{H^+}^2 \tag{3}$$

and

$$nBe^{2+} + mH_2O(l) \Leftrightarrow Be_n(OH)_m^{2n-m} + mH^+ \tag{4}$$

$$^*\beta^\circ_{(n,m)} \qquad a_{Be_n(OH)_m^{2n\ m}}\ a_{H^+}^{\ m} \Big/ a_{Be^{2+}}^n a_w^m \tag{5}$$

with

$$[Be]_{calc} \qquad K^\circ_{s,0}\ {}^*\gamma_{H^+} m_{H^+}^2\ a_w^{\ 2}\left(1+\sum \beta^\circ_{(n,m)}\,{}^*\gamma_{Be^{2+}} m_{Be^{2+}}^{n\ 1} \gamma_{H^+} m_{H^+}^{\ m}\ m a_w^n\right) \tag{6}$$

where $a_i \quad \gamma_i \cdot m_i$, γ_i is the activity coefficient calculated by SIT, m_i is the concentration in molal units and a_w is the activity of water for the given background electrolyte concentration (Guillaumont et al., 2003). In the minimization of the function $\sum((\log [Be]_{exp} - \log [Be]_{calc})^2)^{1/2}$, the hydrolysis constants $\log \beta^\circ_{(1,1)}$, $\log \beta^\circ_{(2,1)}$, $\log \beta^\circ_{(3,3)}$, $\log \beta^\circ_{(5,6)}$ and $\log \beta^\circ_{(6,8)}$ are kept constant as reported in Brown and Ekberg (2016). These equilibrium constants are essentially the same as reported in Bruno (1987) with slight changes that account for new literature (see Table 1S, Supplementary Material). SIT coefficients are also set constant as reported in Bruno (1987) or estimated using the approach described in Hummel (2009) (see values summarized in Section 4.3). The only variable remaining is the conditional solubility constant, $\log {}^*K'_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\}$, which is accordingly fitted for each NaCl concentration. The values of $\log {}^*K'_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\}$ (see Table 2S, Supplementary Material) are extrapolated to $I \quad 0$ following the SIT approach:

$$\log {}^*K'_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\} \qquad \log [Be^{2+}] - 2 \log [H^+] \tag{7}$$

$$\log {}^*K^\circ_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\} \qquad \log {}^*K'_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\} + \log\gamma_{Be^{2+}} \\ 2 \log\gamma_{H^+} \quad 2 \log a_w \tag{8}$$

with

$$\log {}^*K^\circ_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\} \qquad \log {}^*K'_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\}\Big\} \quad 2D \\ +2 \log a_w + \Delta\varepsilon[NaCl] \tag{9}$$

The linear regression $\log {}^*K'_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\} - 2\ D + 2 \log a_w$ *vs.* [NaCl] (SIT-plot) shown in Fig. 7 results in $\log {}^*K^\circ_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\}$ (6.9 ± 0.4) as the intercept of the SIT-plot. This value is in good agreement with the one reported by Gilbert and Garrett (1956) for the same solid phase, *i.e.* $\log {}^*K^\circ_{s,0}\{\alpha\text{-}Be(OH)_2(cr)\} \quad (6.85 \pm 0.05)$. The

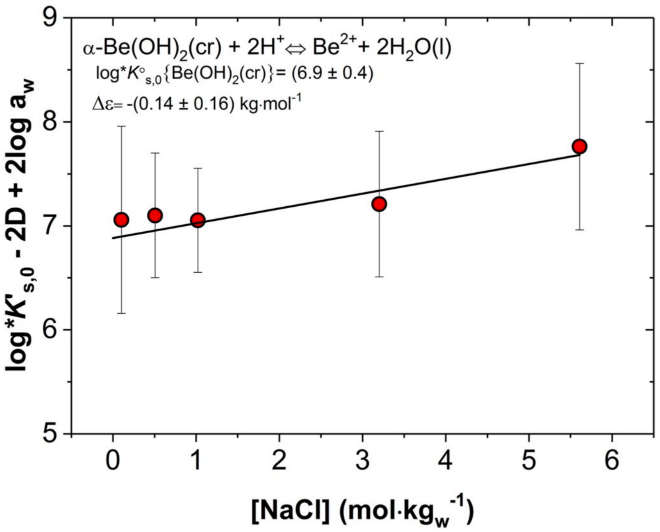

Fig. 7. SIT-plot for the solubility reaction α-$Be(OH)_2$(cr) + $2H^+$ ⇔ Be^{2+} + $2H_2O$(l) using conditional solubility constants, log $^*K'_{s,0}$\{α-$Be(OH)_2$(cr)\}, determined in this work in 0.1–5.0 M NaCl solutions.

transformation of α-$Be(OH)_2$(cr) into β-$Be(OH)_2$(cr) was not observed within the timeframe of this solubility study ($t \leq 600$ days), although β-$Be(OH)_2$(cr) is expectedly the stable solid phase at room temperature. This observation can be argued considering two main aspects: (i) the stability of both solid phases is very similar at room temperature, *i.e.* α-$Be(OH)_2$(cr) ⇔ β-$Be(OH)_2$(cr) with log $K^\circ \leq 0.5$ (this work; Brown and Ekberg, 2016); (ii) all previous studies investigating β-$Be(OH)_2$(cr) synthesized this solid phase under hydrothermal conditions; (Fricke and Humme, 1929; Seitz et al., 1950; Bear and Turnbull, 1965; Soboleva et al., 1977; Bruno et al., 1987a; Stahl et al., 1998), *i.e.* elevated temperature is required to promote the transformation of one phase into the other, which otherwise does not occur at $T = 25$ °C.

The SIT coefficient $\varepsilon(Be^{2+}, Cl^-) = (0.10 \pm 0.16)$ kg·mol^{-1} is calculated from the slope of the SIT-plot ($-\Delta\varepsilon = -\varepsilon(Be^{2+}, Cl^-) + 2\varepsilon(H^+, Cl^-) = (0.14 \pm 0.16)$ kg·mol^{-1}) in combination with $\varepsilon(H^+, Cl^-) = (0.12 \pm 0.01)$ kg·mol^{-1} reported in Guillaumont et al. (2003). The value $\varepsilon(Be^{2+}, Cl^-)$ determined in this work is consistent with $\varepsilon(Be^{2+}, Cl^-) = (0.17 \pm 0.05)$ kg·mol^{-1} estimated in Bruno (1987) from other divalent cations (Mg^{2+}, Ni^{2+} and Ca^{2+}).

4.2. *Thermodynamic data derived from Be(II) solubility experiments in alkaline to hyperalkaline NaCl–NaOH and KCl–KOH systems*

Be(II) solubility in alkaline to hyperalkaline NaCl–NaOH and KCl–KOH systems is described by the equilibrium reactions (10)–(18):

$$\alpha\text{-}Be(OH)_2(cr) \Leftrightarrow Be(OH)_2(aq) \quad (10)$$

$$\alpha\text{-}Be(OH)_2(cr) + H_2O(l) \Leftrightarrow Be(OH)_3^- + H^+ \quad (11)$$

$$\alpha\text{-}Be(OH)_2(cr) + 2H_2O(l) \Leftrightarrow Be(OH)_4^{2-} + 2H^+ \quad (12)$$

with

$$\log {}^*K'_{s,(1,2)} = \log [Be(OH)_2(aq)] \quad (13)$$

$$\log {}^*K^\circ_{s,(1,2)} = \log {}^*K'_{s,(1,2)} + \log \gamma_{Be(OH)_2} \quad (14)$$

$$\log {}^*K'_{s,(1,3)} = \log [Be(OH)_3^-] + \log [H^+] \quad (15)$$

$$\log {}^*K^\circ_{s,(1,3)} = \log {}^*K'_{s,(1,3)} + \log \gamma_{Be(OH)_3} + \log \gamma_{H^+} - \log a_w \quad (16)$$

$$\log {}^*K'_{s,(1,4)} = \log [Be(OH)_4^{2-}] + 2\log [H^+] \quad (17)$$

$$\log {}^*K^\circ_{s,(1,4)} = \log {}^*K'_{s,(1,4)} + \log \gamma_{Be(OH)_4^2} + 2\log \gamma_{H^+} - 2\log a_w \quad (18)$$

The solubility constant for the neutral species $Be(OH)_2$(aq), log $^*K^\circ_{s,2}$ is determined from experimental data in 0.1, 0.5 and 1.0 M KCl systems. Following equations (13) and (14) and considering $\varepsilon(Be(OH)_2(aq), K^+/Cl^-) = 0$ (per definition in SIT), we calculate log $^*K^\circ_{s,2} = -(6.8 \pm 0.3)$ as the average log $[Be]_{tot}$ for these systems in the pH_m-independent region of the solubility ($\approx 8 \leq pH_m \leq \approx 10$).

Conditional solubility constants log $^*K'_{s,(1,3)}$ and log $^*K'_{s,(1,4)}$ are determined (see Table S2, Supplementary Material) from solubility data in (0.1, 0.5, 1.0, 3.0 and 5.0 M) NaCl and (0.1, 0.5, 1.0, 3.0 and 4.0 M) KCl systems at $pH_m \geq 11$. These solubility constants are simultaneously determined for each background electrolyte concentration by minimizing the function $\sum((\log [Be]_{exp} - \log [Be]_{calc})^2)^{1/2}$ and using equation (5) to calculate $[Be]_{calc}$. A weighted multi-linear least–squares regression procedure as described in Hummel et al. (2005) is used to extrapolate log $^*K'_{s,(1,3)}$ and log $^*K'_{s,(1,4)}$ to $I = 0$ (see Fig. 8). This approach is based on the simultaneous fit of NaCl and KCl systems for the determination of log $^*K^\circ_{s,(1,x)}$ (with $x = 3$–4). A unique intercept (*i.e.* log $^*K^\circ_{s,(1,x)}$) is imposed for both background electrolyte systems, whereas slopes (*i.e.* providing $\varepsilon(Be(OH)_x^{2-x}, Na^+)$ and $\varepsilon(Be(OH)_x^{2-x}, K^+)$ are allowed to vary. The fit of log $^*K^\circ_{s,(1,x)}$ is weighted with the uncertainties of each independent log $^*K'_{s,(1,x)}$.

The multi-linear least-squares SIT regression in Fig. 8 results in log $^*K^\circ_{s,(1,3)} = -(17.4 \pm 0.6)$ and log $^*K^\circ_{s,(1,4)} = -(30.7 \pm 0.5)$, as well as in the SIT coefficients $\varepsilon(Be(OH)_3^-, Na^+) = (0.02 \pm 0.16)$ kg·mol^{-1}, $\varepsilon(Be(OH)_3^-, K^+) = (0.11 \pm 0.05)$ kg·mol^{-1}, $\varepsilon(Be(OH)_4^{2-}, Na^+) = (0.03 \pm 0.16)$ kg·mol^{-1} and $\varepsilon(Be(OH)_4^{2-}, K^+) = (0.16 \pm 0.05)$ kg·mol^{-1}.

The combination of log $^*K^\circ_{s,(1,2)}$, log $^*K^\circ_{s,(1,3)}$ and log $^*K^\circ_{s,(1,4)}$ with log $^*K^\circ_{s,0}$\{α-$Be(OH)_2$(cr)\} obtained in Section 4.1 allows the determination of the corresponding hydrolysis constants for reactions (19)–(21):

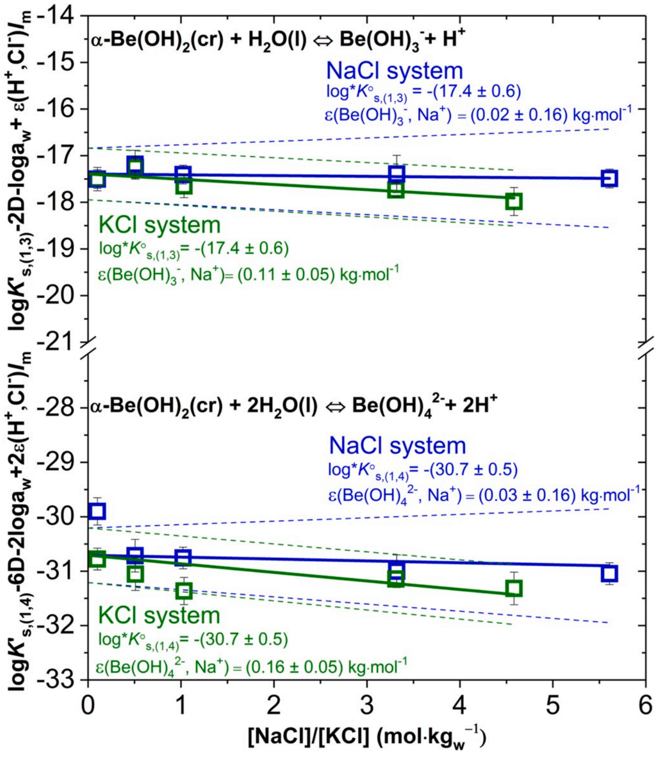

Fig. 8. Multi-linear least-squares SIT regression for the solubility reactions α-$Be(OH)_2$(cr) + H_2O(l) ⇔ $Be(OH)_3^-$ + H^+ and α-$Be(OH)_2$(cr) + $2H_2O$(l) ⇔ $Be(OH)_4^{2-}$ + $2H^+$ considering log $^*K'_{s,(1,3)}$ and log $^*K'_{s,(1,4)}$ experimentally determined in dilute to concentrated NaCl (blue symbols) and KCl (green symbols) solutions. Dashed lines indicate the uncertainty of each linear fit.

Table 1

Selected solubility and hydrolysis constants of Be(II) at I = 0 as determined in this work or reported in selected references.

Solid phase	log $^*K^\circ_{s,0}$	Reference
α-$Be(OH)_2(cr) + 2\ H^+ \Leftrightarrow Be^{2+} + 2\ H_2O(l)$	(6.9 ± 0.4)	p.w
Hydrolysis reactions	log $^*\beta^\circ_{(n,m)}$	
$Be^{2+} + H_2O(l) \Leftrightarrow BeOH^+ + H^+$	– (5.39 ± 0.14)	Brown and Ekberg (2016)
$Be^{2+} + 2\ H_2O(l) \Leftrightarrow Be(OH)_2(aq) + 2\ H^+$	– (13.7 ± 0.5)	p.w.
$Be^{2+} + 3\ H_2O(l) \Leftrightarrow Be(OH)_3^- + 3\ H^+$	– (24.3 ± 0.6)	p.w.
$Be^{2+} + 4\ H_2O(l) \Leftrightarrow Be(OH)_4^2\ + 4\ H^+$	– (37.6 ± 0.7)	p.w.
$2\ Be^{2+} + H_2O(l) \Leftrightarrow Be_2OH^{3+} + H^+$	– (3.54 ± 0.05)	Brown and Ekberg (2016)
$3\ Be^{2+} + 3\ H_2O(l) \Leftrightarrow Be_3(OH)_3^{3+} + 3\ H^+$	– (8.83 ± 0.05)	Brown and Ekberg (2016)
$5\ Be^{2+} + 6\ H_2O(l) \Leftrightarrow Be_5(OH)_6^{4+} + 6\ H^+$	– (19.1 ± 0.1)	Brown and Ekberg (2016)
$6\ Be^{2+} + 8\ H_2O(l) \Leftrightarrow Be_6(OH)_8^{4+} + 8\ H^+$	– (26.3 ± 0.1)	Brown and Ekberg (2016)

p.w. stands for present work.

$$Be^{2+} + 2\ H_2O(l) \Leftrightarrow Be(OH)_2(aq) + 2\ H^+ \tag{19}$$

$$Be^{2+} + 3\ H_2O(l) \Leftrightarrow Be(OH)_3^- + 3\ H^+ \tag{20}$$

$$Be^{2+} + 4\ H_2O(l) \Leftrightarrow Be(OH)_4^{2-} + 4\ H^+ \tag{21}$$

with

$$\log {}^*\beta^\circ_{(1,2)} \quad -(13.7 \pm 0.5)$$

$$\log {}^*\beta^\circ_{(1,3)} \quad -(24.3 \pm 0.6)$$

$$\log {}^*\beta^\circ_{(1,4)} \quad -(37.6 \pm 0.7)$$

The value of log $^*\beta^\circ_{(1,2)}$ obtained in this work is in excellent agreement with the hydrolysis constant determined by Green and Alexander (1965) by solvent extraction, log $^*\beta^\circ_{(1,2)}$ – (13.65 ± 0.05). However, our value shows very large discrepancies (>2.5 log-units) with log $^*\beta^\circ_{(1,2)}$ reported in several potentiometric studies (Kakihana and Sillen, 1956; Bertin et al., 1967; Schwarzenbach and Wenger, 1969; Kakihana and Maeda, 1970; Vanni et al., 1975; Brown et al., 1983; Bruno, 1987; Chinea et al., 1997). The reference book by Baes and Mesmer (1976) already supported that log $^*\beta^\circ_{(1,2)}$ determined in potentiometric studies might be largely overestimated, and favoured the selection of the hydrolysis constant determined in the solvent extraction study by Green and Alexander (1965). On the contrary, the recent review book by Brown and Ekberg (2016) considered the work by Green and Alexander (1965) inconclusive and selected a log $^*\beta^\circ_{(1,2)}$ value in line with potentiometric data. Our solubility data provides conclusive and independent evidence of the large overestimation of log $^*\beta^\circ_{(1,2)}$ determined in potentiometric studies and, in our view, closes this long-lasting discussion. Although potentiometry is a very robust and reliable method in undersaturated systems, artifacts potentially arise when approaching the solubility limit of a given metal oxide/hydroxide. This is clearly the case of beryllium and $Be(OH)_2(aq)$, whose concentration in equilibrium with α-$Be(OH)_2(cr)$ ($\approx 10^{-7}$ M) is well below the reach of potentiometric techniques. It is worthy to note the discussion on $Be(OH)_2(aq)$ provided in the potentiometric study by Schwarzenbach and Wenger (1969). These authors reported a log $^*\beta'_{(1,2)}$ – (10.9 ± 0.2) at I 3.0 M $NaClO_4$, in line with other potentiometric studies. However, the authors also elaborated on the equilibrium between “unstable” $Be(OH)_2{}^*(aq)$ and “stable” $Be(OH)_2(aq)$, with log K ’ 2 for the reaction $Be(OH)_2{}^*(aq) \Leftrightarrow Be(OH)_2(aq)$ at I 0.1 M $NaClO_4$. In a titration series at $[Be]_{tot}$ $3 \cdot 10^{-3}$ M and pH 4–7, the “unstable” $Be(OH)_2{}^*(aq)$ (with log $^*\beta'_{(1,2)} \approx$ 13) was observed after ≈ 5 ms, whereas “stable” $Be(OH)_2(aq)$ (with log $^*\beta'_{(1,2)} \approx$ 11) formed after a few minutes involving a clear drop in pH. On the basis of our solubility data in Figs. 4 and 5, it appears evident that a large fraction of the potentiometric titrations in Schwarzenbach and Wenger (1969) were oversaturated with respect to α-$Be(OH)_2(cr)$, and that their “stable” $Be(OH)_2(aq)$ most likely corresponded to a solid nanoporticle or colloidal “$Be(OH)_2$” moiety.

Table 2

Selected SIT ion interaction coefficients, ε(i,j), for Be(II) hydrolysis species as determined in this work or reported in selected references.

Be(II) species	SIT coefficients		References
I	*J*	ε(*i,j*) [kg·mol 1]	
$BeOH^+$	Cl	(0.05 ± 0.10)	Hummel (2009)[a]
Be^{2+}	Cl	(0.10 ± 0.16)	p.w.
		(0.17 ± 0.05)	Bruno (1987)
Be_2OH^{3+}	Cl	(0.30 ± 0.05)	Bruno (1987)
$Be_3(OH)_3^{3+}$	Cl	(0.30 ± 0.05)	Bruno (1987)
$Be_5(OH)_6^{4+}$	Cl	(0.6 ± 0.2)[b]	Bruno (1987)
$Be_6(OH)_8^{4+}$	Cl	(0.6 ± 0.2)[b]	Bruno (1987)
$Be(OH)_3^-$	Na^+	(0.02 ± 0.16)	p.w.
	K^+	(0.11 ± 0.05)	p.w.
$Be(OH)_4^{2-}$	Na^+	(0.03 ± 0.16)	p.w.
	K^+	(0.16 ± 0.05)	p.w.
$Be(OH)_2(aq)$	Na^+, K^+, Cl	0	c

p.w. stands for present work.

c. By definition in SIT.

[a] Estimated based on charge correlations.

[b] These values estimated in Bruno are likely overestimated, but have been used in this work for the sake of consistency. Their impact on the thermodynamic calculations shown in Figs. 4 and 5 is negligible, as these species are very minor in the conditions of this study. A better estimate can be probably obtained by the charge correlations proposed in Hummel (2009), leading to ε($Be_5(OH)_6^{4+}$, Cl) = ε($Be_6(OH)_8^{4+}$, Cl) = (0.35 ± 0.10) kg·mol^{-1}.

The values of log $^*\beta^\circ_{(1,3)}$ and log $^*\beta^\circ_{(1,4)}$ determined in this work are slightly lower but in line with the corresponding values reported in Gilbert and Garrett (1956) and in Green and Alexander (1965) (see Table 1S, Supplementary Material). The equilibrium constant for the step-wise reaction $Be(OH)_3^- + H_2O(l) \Leftrightarrow Be(OH)_4^{2-} + H^+$, log $^*K^\circ_4$ 13.9, suggests that $Be(OH)_4^{2-}$ prevails only above pH ≈ 14. However, the stability of both anionic species is strongly dependent on the ionic strength, and thus $Be(OH)_4^{2-}$ becomes predominant in the pore water conditions befined by cement in degradation stage I (*i.e.* ≈ 0.1 M NaOH, ≈ 0.2 M KOH and pH 13.3).

4.3. *Summary of chemical, thermodynamic and activity models for the system Be^{2+}–H^+–K^+–Na^+–Cl^-–OH^-–$H_2O(l)$*

Tables 1 and 2 summarize the comprehensive and consistent chemical, thermodynamic and SIT activity models for the system Be^{2+}–Na^+–K^+–H^+–Cl^-–OH^-–$H_2O(l)$ as derived in this work (solubility, hydrolysis in alkaline conditions) or reported in the literature (hydrolysis in acidic conditions). Figs. 4 and 5 show that the model explains very well solubility data determined in this work in NaCl–NaOH and KCl–KOH systems. Experimental solubility data collected in pure NaOH and KOH solutions was not used in the calibration of the model, and thus can be considered for independent validation. Hence, Fig. 6 shows also an excellent agreement between experimental data in pure hydroxide systems and calculated solubility, and thus gives additional support to the validity of the thermodynamic and activity models derived.

5. Summary and conclusions

The solid phase α-$Be(OH)_2(cr)$ controls the solubility of Be(II) in acidic to hyperalkaline, dilute to concentrated NaCl and KCl systems. Within the boundary conditions of this study ([MOH] ≤ 4.0 M, T (22 ± 2) °C, $t \leq$ 600 days), no solid phase transformation into β-$Be(OH)_2(cr)$ or ternary M(I)–Be(II)–OH(cr) phases was observed.

Solubility data determined in weakly acidic to near-neutral pH_m-conditions, in combination with thermodynamic data critically reviewed by Brown and Ekberg (2016) for cationic hydrolysis species of Be(II) ($Be_n(OH)_m^{2n-m}$, with (n,m) (1,1), (2,1), (3,3), (5,6), (6,8)) allow the quantification of the solubility constant of α-$Be(OH)_2(cr)$, log $^*K^\circ_{s,0}$ (6.9 ± 0.4). This value is in good agreement with the only solubility study available in the literature for this solid phase (Gilbert and Garrett, 1956). In alkaline to hyperalkaline systems, slope analysis of the solubility data and ^{9}Be NMR support the predominance of the monomeric hydrolysis species $Be(OH)_2(aq)$, $Be(OH)_3^-$ and $Be(OH)_4^{2-}$. These species play a relevant role within the pH-region relevant in cementitious systems, *e.g.* 10 ≤ pH_m ≤ 13.3. The neutral species $Be(OH)_2(aq)$ prevails within pH_m ≈ 8.5 and ≈ 11, and the fit of the corresponding solubility results in log $^*K^\circ_{s,2}$ – (6.8 ± 0.3) and log $^*\beta^\circ_{(1,2)}$ – (13.7 ± 0.5). These results indicate that the value of log $^*\beta^\circ_{(1,2)}$ determined in previous potentiometric studies is largely overestimated. The hydrolysis constants determined in this work for $Be(OH)_3^-$ and $Be(OH)_4^{2-}$, log $^*\beta^\circ_{(1,3)}$ – (24.3 ± 0.6) and log $^*\beta^\circ_{(1,4)}$ – (37.6 ± 0.7), are in line with the sparse data available in the literature for these hydrolysis species (Gilbert and Garrett, 1956; Green and Alexander, 1965).

The comprehensive chemical, thermodynamic and (SIT) activity models derived in this work for the system Be^{2+}–Na^+–K^+–H^+–Cl^-–OH^-–$H_2O(l)$ represent an accurate and robust tool for the evaluation of Be(II) solubility and speciation in a diversity of geochemical conditions of relevance for nuclear waste disposal, including cementitious systems in different degradation stages (I–III). The established solubility limits also set boundary conditions for the proper investigation of Be sorption in cementitious environments, which will be presented by KIT-INE in separate future publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2020.104601.

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Supplementary Material

Thermodynamic description of Be(II) solubility and hydrolysis in acidic to hyperalkaline NaCl and KCl solutions

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Content

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Table 1S. *Summary of thermodynamic data reported in the literature for the solubility and hydrolysis of Be(II).*

Reference	**Method**	**Medium**	***T*** **(°C)**	**log *K***	**log *K*°**
α-$Be(OH)_2(cr) + 2\ H^+ \Leftrightarrow Be^{2+} + 2\ H_2O(l)$					
Gilbert and Garrett (1956)	solubility	HCl / $HClO_4$	25		(6.86 ± 0.05) (6.69 ± 0.02)[b] (6.87 ± 0.05)[c]
β-$Be(OH)_2(cr) + 2\ H^+ \Leftrightarrow Be^{2+} + 2\ H_2O(l)$					
Bruno et al. (1987)	solubility	3.0 M $NaClO_4$	25	(6.18 ± 0.03)	(5.9 ± 0.1)
$Be^{2+} + H_2O \Leftrightarrow Be(OH)^+$					
Mattock (1954)	e.m.f	1.0 M $NaClO_4$	25	– 6.52	
Schwarzenbach (1962)	e.m.f	0.1 M $NaClO_4$	20	– (5.70 ± 0.10)[a]	
Schwarzenbach and Wenger (1969)	e.m.f	0.1 M KCl	20	– (5.70 ± 0.10)	
Renders and Anderson (1987)	solubility	$I = 0$	25		– (5.40 ± 0.10)[a]
Bruno *et al.* (1987a)	e.m.f	3 M $NaClO_4$	25	– (6.02 ± 0.09)	
$2\ Be^{2+} + H_2O(l) \Leftrightarrow [Be_2OH]^{3+} + H^+$					
Kakihana and Sillen (1956)	e.m.f	3.0 M $NaClO_4$	25	– (3.24 ± 0.04)	
Carell and Olin (1961)	e.m.f	3.0 M $NaClO_4$	25	– (3.22 ± 0.05)	
Mesmer and Baes (1967)	e.m.f	1.0 m $NaCl$	25	– (3.42 ± 0.07)	
Bertin *et al.* (1967)	e.m.f	0.1 M $LiClO_4$	25	– (3.20 ± 0.10)[a]	
Pâris and Gregoire (1968)	e.m.f	3.0 M KCl	25	– (3.18 ± 0.10)[a]	
Lanza and Carpéni (1968)	e.m.f	2.0 M KNO_3	25	– (3.28 ± 0.10)[a]	
Kakihana and Maeda (1970)	e.m.f	3.0 M $NaClO_4$	25	– (3.16 ± 0.04)	
Tsukuda *et al.* (1975)	e.m.f	0.1 M $LiClO_4$	25	– (3.32 ± 0.14)	
Vanni *et al.* (1975)	e.m.f	1.0 M KNO_3	25	– (3.22 ± 0.14)	

Reference	**Method**	**Medium**	***T* (°C)**	**log *K***	**log *K*°**
2 $Be^{2+} + H_2O(l) \Leftrightarrow [Be_2OH]^{3+} + H^+$					
Brown *et al.* (1983)	e.m.f	0.1 M KNO_3	25	– (2.96 ± 0.007)	
Bruno (1987)	e.m.f	3.0 M $NaClO_4$	25	– (3.23 ± 0.05)	– (3.47 ± 0.05)
Maeda *et al.* (1987)	e.m.f	1.0 M $NaClO_4$	25	– (3.52 ± 0.07)	
Mederos *et al.* (1987)	e.m.f	0.5 M $NaClO_4$	25	– (3.20 ± 0.10)[a]	
Wood (1992)	literature	$I = 0$	25		– (3.47 ± 0.10)[a]
Chinea *et al.* (1997)	e.m.f	0.5 M $NaClO_4$	25	– (3.20 ± 0.01)	
3 Be^{2+} + 3 $H_2O(l) \Leftrightarrow [Be_3(OH)_3]^{3+}$ + 3 H^+					
Kakihana and Sillen (1956)	e.m.f	3.0 M $NaClO_4$	25	– (8.66 ± 0.03)	
Gilbert and Garrett (1956)	solubility	$I = 0$	25		– (8.90 ± 0.10)[a]
Carell and Olin (1961)	e.m.f	3.0 M $NaClO_4$	25	– (8.66 ± 0.03)	
Mesmer and Baes (1967)	e.m.f	1.0 m NaCl	25	– (8.907 ± 0.007)	
Bertin *et al.* (1967)	e.m.f	0.1 M $LiClO_4$	25	– (8.80 ± 0.10)[a]	
Pâris and Gregoire (1968)	e.m.f	3.0 M KCl	25	– (8.87 ± 0.10)[a]	
Lanza and Carpéni (1968)	e.m.f	2.0 M KNO_3	25	– (8.86 ± 0.10)[a]	
Kakihana and Maeda (1970)	e.m.f	3.0 M $NaClO_4$	25	– (8.662 ± 0.007)	
Tsukuda *et al.* (1975)	e.m.f	0.1 M $LiClO_4$	25	– (8.807 ± 0.005)	
Tsukuda *et al.* (1975)	e.m.f	3.0 M $LiClO_4$	25	– (8.671 ± 0.002)	
Vanni *et al.* (1975)	e.m.f	1.0 M KNO_3	25	– (8.87 ± 0.01)	
Brown *et al.* (1983)	e.m.f	0.1 M KNO_3	25	– (8.804 ± 0.002)	
Bruno (1987)	e.m.f	3.0 M $NaClO_4$	25	– (8.656 ± 0.002)	– (8.86 ± 0.05)
Maeda *et al.* (1987)	e.m.f	1.0 M $NaClO_4$	25	– (8.700 ± 0.002)	
Mederos *et al.* (1987)	e.m.f	0.5 M $NaClO_4$	25	– (8.91 ± 0.10)[a]	
Wood (1992)	solubility	$I = 0$	25		– (8.87 ± 0.10)
Chinea *et al.* (1997)	e.m.f	0.5 M $NaClO_4$	25	– (8.68 ± 0.03)	
5 Be^{2+} + 6 $H_2O(l) \Leftrightarrow [Be_5(OH)_6]^{4+}$ + 6 H^+					
Bruno (1987)	e.m.f	3.0 M $NaClO_4$	25	– (18.81 ± 0.03)	– (19.5 ± 0.1)
Chinea *et al.* (1997)	e.m.f	0.5 M NaClO4	25	– (18.31 ± 0.05)	
6 Be^{2+} + 8 $H_2O(l) \Leftrightarrow [Be_6(OH)_8]^{4+}$ + 8 H^+					
Mesmer and Baes (1967)	e.m.f	1.0 m NaCl	25	– (27.46 ± 0.03)	
Lanza and Carpéni (1968)	e.m.f	2.0 M KNO_3	25	– (27.38 ± 0.10)[a]	
Tsukuda *et al.* (1975)	e.m.f	3.0 $LiClO_4$	25	– (27.337 ± 0.05)	
Bruno(1987)	e.m.f	3.0 M $NaClO_4$	25	– (26.70 ± 0.05)	– (26.30 ± 0.1)
Maeda *et al.* (1987)	e.m.f	1.0 M $NaClO_4$	25	– (26.82 ± 0.02)	
Chinea *et al.* (1997)	e.m.f	0.5 M $NaClO_4$	25	– (25.77 ± 0.05)	

Reference	**Method**	**Medium**	***T* (°C)**	**log *K***	**log *K*°**
$Be^{2+} + 2\ H_2O(l) \Leftrightarrow Be(OH)_2(aq)$					
Kakihana and Sillen (1956)	e.m.f	3.0 M $NaClO_4$	25	– (10.90 ± 0.2)	
Green and Alexander (1965)	sol. ext.	”self medium”	25	– (13.65 ± 0.04)	– (13.65 ± 0.05)[b]
Bertin *et al.* (1967)	e.m.f	0.1 M $LiClO_4$	25	– (10.98 ± 0.2)[a]	
Schwarzenbach and Wenger (1969)	e.m.f	0.1 M KCl	20	– (11.20 ± 0.1)[a]	
Kakihana and Maeda (1970)	e.m.f	3.0 M $NaClO_4$	25	– (11.16 ± 0.06)	
Vanni *et al.* (1975)	e.m.f	1.0 M KNO_3	25	– (11.26 ± 0.01)	
Brown *et al.* (1983)	e.m.f	0.1 M KNO_3	25	– (11.320± 0.008)	
Bruno (1987)	e.m.f	3.0 M $NaClO_4$	25	– (11.09 ± 0.04)	– (11.00 ± 0.05)
Renders and Anderson (1987)	solubility	$I = 0$	25		– 13.68
Chinea *et al.* (1997)	e.m.f	0.5 M $NaClO_4$	25	– (11.68 ± 0.06)	
$Be^{2+} + 3\ H_2O(l) \Leftrightarrow Be(OH)_3^{-} + 3\ H^{+}$					
Gilbert and Garrett (1956)	solubility	NaOH	25		– (23.35 ± 0.06)[a] – (23.26 ± 0.05)[b] – (23.46 ± 0.05)[c]
Green and Alexander (1965)	sol. ext.	NaOH	25	– (24.11 ± 0.03)	
Renders and Anderson (1987)	solubility	$I = 0$	25		– 13.68
$Be^{2+} + 4\ H_2O(l) \Leftrightarrow Be(OH)_4^{2-} + 4\ H^{+}$					
Gilbert and Garrett (1956)	solubility	NaOH	25		– (37.4 ± 0.2)[b] – (37.59 ± 0.05)[c]

a. accepted uncertainty estimated by Brown and Ekberg (2016) b. recalculated in Baes and Mesmer (1976); c. recalculated in Bruno (1987)

Table 2S. *Conditional solubility constant log* $^{*}K'_{s,(1,3)}$, *log* $^{*}K'_{s,(1,4)}$ *and log* $^{*}K'_{s,0}$ *for the reactions* α-$Be(OH)_2(cr) + H_2O(l) \Leftrightarrow Be(OH)_3^{-} + H^{+}$, α-$Be(OH)_2(cr) + 2H_2O(l) \Leftrightarrow Be(OH)_4^{2-} + 2H^{+}$ and α-$Be(OH)_2(cr) + 2H^{+} \Leftrightarrow Be^{2+} + 2H_2O(l)$, respectively. *The conditional constants determined for each background electrolyte and used for the extrapolations to I= 0 with the SIT approach.*

[NaCl] ($mol\cdot L^{-1}$)	log $^{*}K'_{s,(1,3)}$	log $^{*}K'_{s,(1,4)}$	log $^{*}K'_{s,0}$
0.1	– (17.3 ± 0.3)	– (29.3 ± 0.3)	(7.3 ± 0.9)
0.5	– (16.9 ± 0.3)	– (29.8 ± 0.3)	(7.4 ± 0.6)
1.0	– (17.1 ± 0.2)	– (29.8 ± 0.2)	(7.4 ± 0.5)
3.0	– (17.3 ± 0.4)	– (30.4 ± 0.3)	(7.8 ± 0.7)
5.0	– (17.7 ± 0.2)	– (31.0 ± 0.2)	(8.6 ± 0.8)

[KCl] ($mol\cdot L^{-1}$)	log $^{*}K'_{s,(1,3)}$	log $^{*}K'_{s,(1,4)}$
0.1	– (17.3 ± 0.2)	– (30.2 ± 0.2)
0.5	– (17.0 ± 0.3)	– (30.1 ± 0.3)
1.0	– (17.4 ± 0.3)	– (29.9 ± 0.3)
3.0	– (17.7 ± 0.2)	– (30.5 ± 0.2)
4.0	– (18.1 ± 0.3)	– (31.0 ± 0.3)

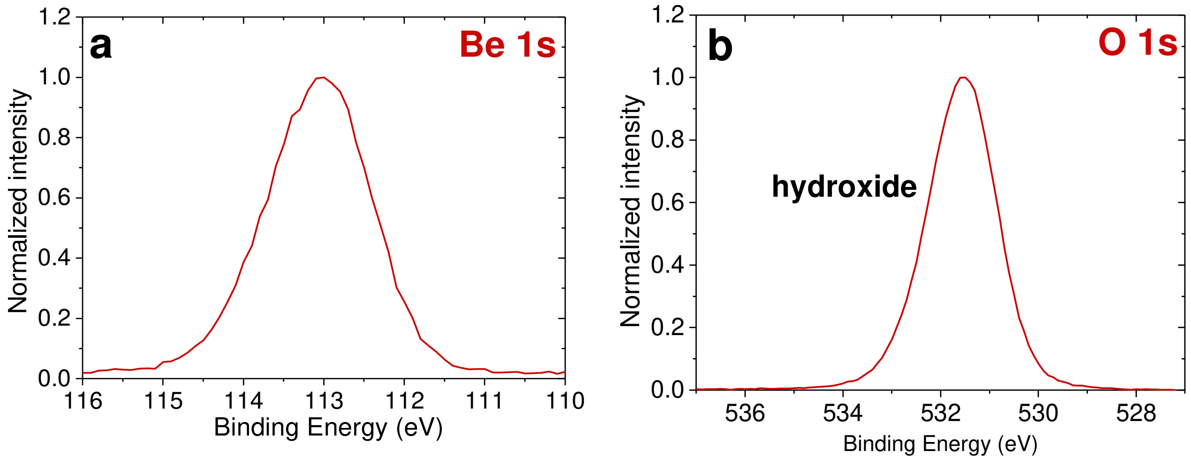

Figure 1S. *XPS data collected for the solid phase equilibrated in 0.1 M NaCl at* pH_m*= 12.9: a. Be 1s spectra, and b. O 1s spectra.*

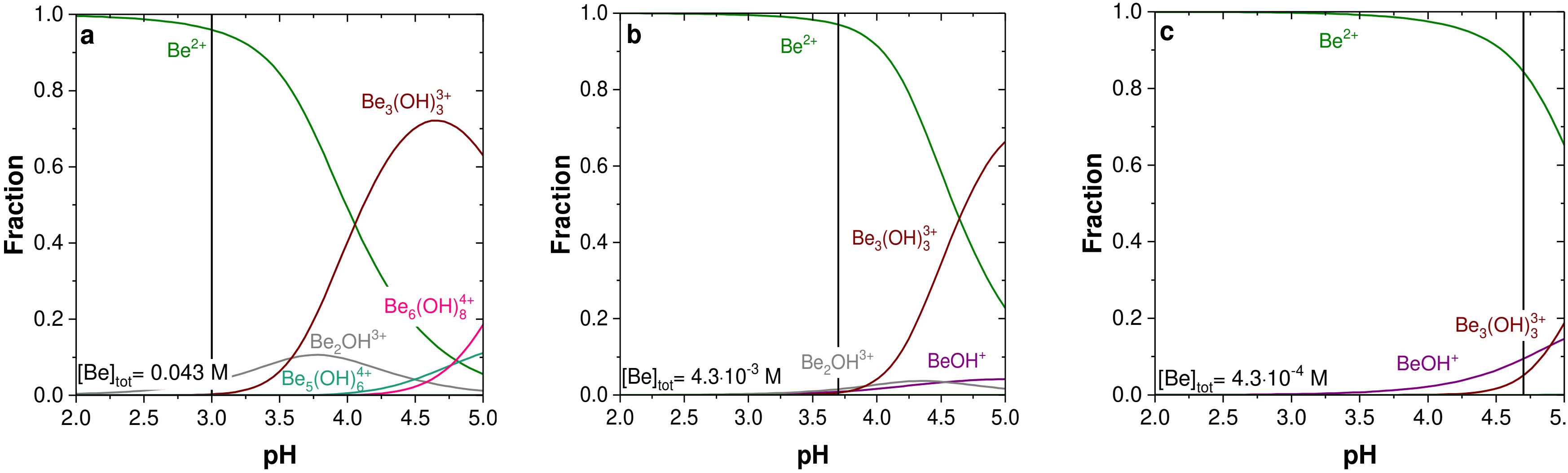

Figure 2S. *Fraction diagram of Be(II) hydrolysis species calculated using the values summarized in Table 1 for the systems containing: a.* $[Be]_{tot}$ *=* $4.3\cdot10^{-2}$ *M (pH= 3.0), b.* $[Be]_{tot}$ *=* $4.3\cdot10^{-3}$ *M, (pH=3.7) and c.* $[Be]_{tot}$ *=* $4.3\cdot10^{-4}$ *M (pH= 4.7). Black vertical lines are indicating the pH of the each system.*