

Chemistry of niobium(V) in alkaline aquatic carbonated systems containing Ca: Solubility phenomena and formation of ternary Ca-Nb(V)-O/OH solid phases

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ABSTRACT

Comprehensive solubility experiments with niobium(V) were conducted from oversaturation conditions in weakly alkaline, carbonated solutions equilibrated with calcite and carbonated cement. These conditions are expected in advanced degradation stages of cement, and are representative of cementitious environments as those foreseen in underground and near-surface repositories for short-lived low- and intermediate-level radioactive wastes (L/ILW-SL). Moderate niobium concentrations ($[\text{Nb}]_{\text{aq}} \approx 10^{-6} \text{ M}$) were quantified at short contact times ($t < 3$ days), matching thermodynamic calculations with $\text{Nb}_2\text{O}_5(\text{am})$ as solubility-controlling solid phase. At longer equilibration times ($t > 10$ days), a further decrease in solubility ($[\text{Nb}]_{\text{aq}} \leq 10^{-8} \text{ M}$) is observed, which evidences the formation of a sparingly soluble secondary phase transformation. Comparison of solubility data determined in this work with previous studies in carbonate-free systems support that Nb(V)-carbonate complexes can be neglected in the investigated range of carbonate concentrations ($\approx 10^{-3}$ – 10^{-4} M). Systematic characterization of the resulting solid phases by means of Raman spectroscopy and powder X-ray diffraction unequivocally point towards the predominance of hydrated Ca-Nb(V) solid phase/s of rather amorphous character and small (sub-nm) particle size. A conclusive assignment of the stoichiometry of this/these solid phase/s is not feasible at this stage, although available evidence points towards a Ca: Nb ratio clearly below 1.

1. Introduction

Niobium is present in steel and alloys used in structural components of nuclear reactor vessels (Ochs et al., 2016). The neutron activation of the naturally occurring ^{93}Nb isotope leads to the production of the long-lived β -emitter isotope ^{94}Nb ($t_{1/2} = 2.04 \cdot 10^4 \text{ a}$). This radionuclide is thus expected in materials resulting from the dismantling of nuclear power plants, as well as in waste streams produced from the treatment of the primary cooling circuit (Ochs et al., 2016). Some of these components will be disposed of as short-lived low- and intermediate-level radioactive wastes (L/ILW-SL), where cementitious materials are commonly used for construction purposes and for the stabilization of the waste (Wieland, 2014; Ochs et al., 2016). The degradation of cement

through the interaction with groundwater has been extensively described in the literature (Berner, 1992; Wieland, 2014; Ochs et al., 2016). In the final degradation stage of cement (usually referred to as stage IV for Ordinary Portland Cement, OPC), portlandite, calcium silicate hydrate (C-S-H) phases and other hydrated cement components are completely dissolved and the pH decreases to lower than 10. In this stage, the pore water composition is primarily controlled by the remaining aggregate minerals, mostly calcite, defining weakly alkaline pH conditions and moderate calcium and carbonate concentrations. In near-surface repositories for L/ILW-SL, a much faster degradation of cement involving carbonation is triggered by the contact with infiltrating water (Ochs et al., 2016).

Dissolution and precipitation phenomena are important processes

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controlling the chemical behaviour of several radionuclides and other elements of relevance in the context of repositories for radioactive waste disposal. An accurate knowledge of the solubility provides upper limits for dissolved concentrations of these elements in the near field. Niobium has an electronic configuration $[\text{Kr}] 4d^4 5s^1$ and occurs predominantly in the pentavalent oxidation state in aqueous solutions (Baes and Mesmer, 1976; Bard et al., 1985; Brown and Ekberg, 2016; Nikishina et al., 2012). It is characterized by a strong and amphoteric hydrolysis behaviour and the formation of the sparingly soluble oxide $\text{Nb}_2\text{O}_5(\text{s})$. Although a spectroscopic validation is so far missing, the formation and predominance of anionic hydrolysis species (e.g., $\text{Nb}(\text{OH})_6^-$, $\text{Nb}(\text{OH})_5^{2-}$) in weakly alkaline to hyperalkaline pH conditions is widely accepted (Peiffert et al., 2010; Hummel and Thoenen, 2023; Madé et al., 2025). This results in a significant increase in solubility, which reaches Nb concentrations above the millimolar range at pH higher than 10 (Peiffert et al., 2010; Deblonde et al., 2015; Jo et al., 2022). At high Nb concentrations and alkaline conditions, the formation of polyoxoniobates must also be considered. Hexaniobates, with the general formula $[\text{H}_x\text{Nb}_6\text{O}_{19}]^{(8-x)-}$, are expected to be particularly relevant, and the most plausible species at $\text{pH} \sim 8$ is the Lindqvist form $[\text{H}_3\text{Nb}_6\text{O}_{19}]^{5-}$ (Deblonde et al., 2015; Filella and May, 2020). Hexaniobates have been also reported to form several alkali- and alkali-earth hexaniobate solid phases (Deblonde et al., 2016). Crystalline ternary calcium pyrochlore-like structures such as $\text{Ca}_2\text{Nb}_2\text{O}_7(\text{s})$ or $\text{CaNb}_2\text{O}_6(\text{s})$ have also been reported in the literature, although neither unequivocal identification of the solubility-controlling solid phases nor a sound description of their solubility products are available so far (Lothenbach et al., 1999; Talerico et al., 2004; Jo et al., 2022; Ohira et al., 2023). Leitner and co-workers investigated the heat capacity, enthalpy and entropy of $\text{Ca}_2\text{Nb}_2\text{O}_7(\text{cr})$ and $\text{CaNb}_2\text{O}_6(\text{cr})$ by means of relaxation time method, differential scanning calorimetry and drop calorimetry (Leitner et al., 2008, 2009). The authors synthesized both solid phases by calcination of a stoichiometric mixtures of CaCO_3 and Nb_2O_5 at 1073 K (48 h), followed by a final heat treatment at 1173 K (142 h) or 1223 K (162 h). Although the authors reported accurate thermodynamic functions for both solid phases, the highly crystalline materials synthesized by Leitner et al. at high temperatures are not expected to form in aqueous system at room temperature. Instead, a solubility-control by amorphous or nano-crystalline solid phases is expected under these conditions.

In analogy to other transition metals in the +IV and +V oxidation states (e.g., Zr (Altmaier et al., 2008), Tc (Yalçıntaş et al., 2016)), the formation of ternary complexes Ca-Nb(V)-OH(aq) is also expected in the aqueous phase, although so far only indirect evidences of their existences have been discussed in the literature (Jo et al., 2022; Ohira et al., 2023). There are virtually no studies available in the literature dealing with the solubility and complexation of Nb(V) in aqueous solutions containing carbonate. A moderate to strong complexation with carbonate could be envisaged on the basis of the strong Lewis acid character of Nb(V) and considering the analogy with transition metals with similar charge-to-size ratios (e.g., Zr(IV) (Kobayashi and Sasaki, 2017) or Tc(IV) (Baumann et al., 2018)), but evidences reported from solubility studies at elevated temperatures ($T = 500^\circ\text{C}$) suggest instead a rather weak interaction, possibly due to the strong competition with hydrolysis (Aleksandrov, 1967; Kotova, 2011, 2012).

In this context, this work aims at a quantitative evaluation of Nb(V) solubility and at a thorough characterization of the solubility-controlling solid phases under conditions relevant to calcite and carbonated cement systems. For this purpose, a series of oversaturation solubility experiments are conducted in calcite- and carbonated cement

paste-equilibrated solutions, followed by a complementary characterization of the forming solid phases.

2. Methods

2.1. Chemicals and pH measurements

All samples were prepared and stored under air with Milli-Q water (Millipore Milli-Q Advantage A10; $18.2 \text{ M}\Omega \text{ cm}$ at 25°C , 4 ppb TOC with Millipore Millipak® 40 $0.22 \mu\text{m}$). NaOH Titrisol, calcite (CaCO_3 , 99.0%) and nitric acid (60% HNO_3 ultrapure) were purchased from Merck. Niobium(V) chloride (99%) was obtained from Sigma-Aldrich.

The pH values were measured using a ROSS Orion combination pH electrode with 3.0 M KCl as filling solution. Electrode calibration was performed with standard buffer solutions (7–12, Merck).

2.2. Preparation and characterization of calcite- and carbonated cement paste-equilibrated waters

Calcite-equilibrated water was prepared by contacting commercial CaCO_3 with Milli-Q water under air for at least 1 week at a solid to liquid ratio (S/L) of $1 \text{ g} \cdot \text{L}^{-1}$. Water composition was characterized by the determination of Ca concentration (inductive coupled plasma optical emission spectroscopy, ICP-OES), total inorganic carbon concentration (TIC) and pH measurements. This calcite-equilibrated water composition (Table 1) is in agreement with the target values calculated assuming equilibrium with atmospheric $\text{CO}_2(\text{g})$ and using the thermodynamic data selection in the ThermoChimie database (Madé et al., 2025), i.e., $\text{pH} = 8.3$, $[\text{Ca}] = 5.8 \cdot 10^{-4} \text{ M}$ and $C_{\text{tot}} = 1.21 \cdot 10^{-3} \text{ M}$. Before use, the calcite-equilibrated water was separated from the solid phase by centrifugation (5 min, 6000 rpm).

Carbonated cement paste-equilibrated water corresponds to the water equilibrated with carbonated hardened cement (OPC) paste (synthesis of the cement described in Huber et al. (2025)). This water composition was prepared on the basis of the analysis and recipe reported in Huber et al. (2025) (Huber et al., 2025) and reproduced in the Supporting Information. Huber and co-workers reported that the main components of this carbonated cement are calcite, amorphous SiO_2 and minor fractions of C-S-H phases. Calcium concentration in the carbonated cement-equilibrated water was slightly decreased with respect to the concentrations measured in leaching experiments in order to avoid oversaturation conditions and the possible precipitation of calcite (Huber et al., 2025).

The compositions of the calcite- and carbonated cement paste-equilibrated waters used in this work are summarized in Table 1.

2.3. Solubility of Nb(V) in calcite- and carbonated cement paste-equilibrated waters

The solubility of Nb(V) was investigated from oversaturation conditions in calcite- and carbonated cement paste-equilibrated waters. All experiments were conducted in air at $T = (22 \pm 2)^\circ\text{C}$. Individual batch samples were prepared with 50 mL of equilibrated waters, to which niobium was added as solid NbCl_5 to attain concentrations ranging between $\sim 10^{-4}$ and 10^{-3} M . A total of 12 independent solubility samples were prepared (8 samples for calcite- and 4 samples for carbonated cement paste-equilibrated waters), involving different initial niobium concentrations. In the pH conditions of this study (ca. 8.3–8.5), thermodynamic calculations conducted using the ThermoChime database

Table 1

Composition of calcite- and carbonated cement-equilibrated waters used for solubility experiments described in this work.

Solid phase	pH	$[\text{Ca}] [\text{mol} \cdot \text{L}^{-1}]$	$C_{\text{tot}} [\text{mol} \cdot \text{L}^{-1}]$	$[\text{Si}] [\text{mol} \cdot \text{L}^{-1}]$
Calcite	8.2–8.4	$(5.8 \pm 0.1) \cdot 10^{-4}$	$(1.2 \pm 0.1) \cdot 10^{-3}$	n.m.
Carbonated cement paste (OPC)	8.3–8.5	$(3.0 \pm 0.1) \cdot 10^{-3}$	$(2.1 \pm 0.2) \cdot 10^{-4}$	$(5.5 \pm 0.3) \cdot 10^{-5}$

predict a solubility limit of $\sim 10^{-6}$ M, with $\text{Nb}_2\text{O}_5(\text{s})$ as solubility-controlling solid phase. To maintain the original pH range of ≈ 8 –8.7, the solubility samples were adjusted with NaOH (stored under Ar atmosphere) to counteract the shift to more acidic conditions resulting from the strong hydrolysis of Nb(V).

The pH and concentration of niobium were regularly monitored after extended equilibration times ($t = 3$ –121 days). In each sampling, an aliquot (0.1 – 0.4 mL) of the aqueous phase was separated by ultrafiltration with 10 kDa filters (2–3 nm cut-off, Nanostep®, Pall Life Sciences), diluted in 2% HNO_3 and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) to quantify the concentration of niobium. Selected solid phases were separated by centrifugation (8000 rpm, 5–10 min), washed with ethanol and dried under air. Afterwards the solid phases were characterized by Raman spectroscopy and XRD after attaining equilibrium conditions, which were assumed after repeated measurements with constant pH and Nb concentrations.

2.4. Solid phase characterization: Raman spectroscopy and powder X-ray diffraction

Confocal Raman spectroscopic single spot measurements were performed on a WITec alpha300 R instrument equipped with UHTS300 spectrometer (300 mm focal length) and Zeiss microscope. Raman is a powerful technique for the characterization of solid phases, providing insights on molecular vibrations, crystal structure and chemical composition, both for crystalline and amorphous materials.

488 nm and 532 nm lasers operated by adjustable TruePower modules in the range between 10 and 40 mW (measured on the sample) were used as an excitation source. Single spot measurements were performed with a 100× objective (NA = 0.9) using 600 and 1800 lines/mm gratings. The corresponding spectral resolution was better than 3 cm^{-1} and 1 cm^{-1} , respectively. The detection of the Raman scattering was carried out with a back illuminated CCD Camera. Typical acquisition times were between 5 and 10 s with 5–10 scans. Data processing was performed with the Project 6.1 + software and included cosmic ray removal and background subtraction with a shape algorithm. WITec TrueMatch program with integrated RRUFF mineral database and own database was used for the purposes of phase identification. Between 20 and 45 spectra per sample were taken at different places of the samples. Averaged spectra were used for band assignment and to emphasize the differences between them.

Powder X-ray diffraction was performed with Empyrean

diffractometer (Malvern-Panalytical) operated with a Cu tube and power of 1.6 kW. Measurements were conducted at $2\theta = 10$ – 100° with 0.013° incremental steps and a measurement time of 2 s per step. Because of the low quantity of the samples, they were prepared by drop-casting (diluted in ethanol) on the surface of low-background Si sample holders. Prior to measurement, the empty Si sample holders were measured at exactly the same conditions in terms of optical arrangement (slits, soller slits etc.) and measurement time.

After measurements, the patterns of the empty holders were subtracted from these of the sample patterns. The data were evaluated with HighScore-plus v.5 software. Whole powder pattern decomposition (WPPD) with the Le-Bail method and Rietveld refinements (WPPR) were performed on raw measurements implemented in TOPAS 7 (Bruker-AXS). The size of the coherent scattering domains was evaluated by the double Voigt approach. Structure drawings and XRD simulations were performed with CrystalMaker 11 and CrystalDiffract 7, respectively.

3. Results and discussion

3.1. Solubility of Nb(V) in calcite- and carbonated cement paste-equilibrated waters

Fig. 1 shows the results of the oversaturation solubility experiments conducted in calcite- and carbonated cement paste-equilibrated waters, together with solubility data reported in the literature for alkaline Ca-Nb (V)- $\text{H}_2\text{O}(\text{l})$ systems. The figure includes also the solubility of $\text{Nb}_2\text{O}_5(\text{am})$ calculated using the thermodynamic data selection in the ThermoChimie database (version 13a) (Madé et al., 2025). Independently of the initial Nb(V) concentration ($1.0 \cdot 10^{-4} \text{ M} \leq [\text{Nb}(\text{V})]_0 \leq 1.4 \cdot 10^{-3} \text{ M}$), a fast and remarkable decrease in the concentration of niobium is observed, with $[\text{Nb}(\text{V})] \approx 10^{-6} \text{ M}$ at $t = 3$ days, which attains equilibrium conditions at $t \geq 28$ days with $[\text{Nb}(\text{V})] \leq 10^{-8} \text{ M}$. These concentrations are well below the solubility calculated for $\text{Nb}_2\text{O}_5(\text{am})$ at the same pH conditions, thus pointing towards the formation of a secondary Nb(V) phase with lower solubility, possibly involving the stoichiometric contribution of Ca. Note that the niobium concentrations determined in carbonated cement paste-equilibrated water at long equilibration times are ca. 1 order of magnitude lower than those determined for the calcite system (Fig. 1). Although the pH in both equilibrated waters is virtually the same, significantly higher concentrations of Ca are present in the carbonated cement paste-equilibrated water, as compared to calcite-equilibrated water (see Table 1). Considering a possible

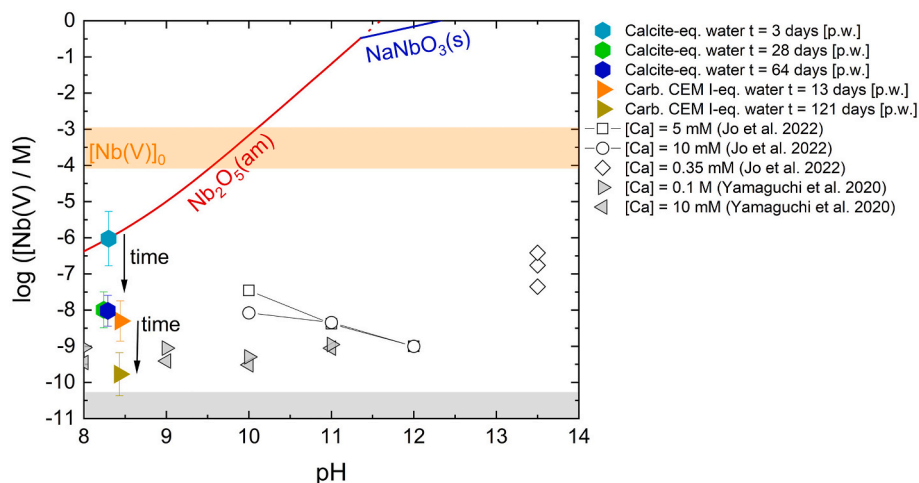


Fig. 1. Niobium solubility determined in this work in calcite- and carbonated cement paste-equilibrated waters (colored symbols), and comparison with data reported in Jo et al. (Jo et al., 2022) (systems with $\text{pH} \geq 10$ and $7 \cdot 10^{-4} \text{ M} \leq [\text{Ca}] \leq 3 \cdot 10^{-2} \text{ M}$) and Yamaguchi et al. (Yamaguchi et al., 2020) (systems with $8 \leq \text{pH} \leq 11$ and $10^{-3} \text{ M} \leq [\text{Ca}] \leq 0.1 \text{ M}$). All systems approached from oversaturation conditions. Thermodynamic calculations for $\text{Nb}_2\text{O}_5(\text{am})$ and $\text{NaNbO}_3(\text{s})$ conducted at $I = 0.01 \text{ M}$ using data selected in the ThermoChimie database version v13a (Madé et al., 2025). Uncertainties in experimental data are calculated as two times the standard deviation of independent measurements.

solubility-control defined by a ternary solid phase Ca-Nb(V)-OH(s) , the enhanced Ca concentrations in the carbonated cement system are consistent with the lower concentrations of Nb(V) determined in the aqueous phase. This trend is consistent with previous results reported by Talerico and co-workers for Nb(V) oversaturation solubility experiments at $9.5 \leq \text{pH} \leq 13$ and $10^{-5} \text{ M} \leq [\text{Ca}] \leq 10^{-2} \text{ M}$ (Talerico et al., 2004).

The solubility of Nb(V) in Ca-containing solutions has been investigated in a number of previous studies. Jo and co-workers conducted systematic oversaturation solubility experiments with Nb(V) in alkaline solutions with $\text{pH} \geq 10$ and $7 \cdot 10^{-4} \text{ M} \leq [\text{Ca}] \leq 3 \cdot 10^{-2} \text{ M}$ (Jo et al., 2022). Although in a higher pH-regime compared to the present work, the authors observed a similar decrease of the initial niobium concentration, resulting in $[\text{Nb(V)}] \leq 10^{-7} \text{ M}$ at $\text{pH} \approx 10$. Solid phase characterization conducted after attaining equilibrium conditions unequivocally pointed towards a solubility-control by Ca-Nb(V)-OH(s) secondary phases, but no thermodynamic data (i.e., solubility product) were derived by the authors. Ohira and co-workers investigated the effect of calcium on niobium solubility in alkaline solutions with $7.5 \leq \text{pH} \leq 12$ and $1 \cdot 10^{-3} \text{ M} \leq [\text{Ca}] \leq 0.1 \text{ M}$ (Ohira et al., 2023). Solubility was approached from oversaturation conditions, with $[\text{Nb(V)}]_0 = 2.5 \cdot 10^{-4} \text{ M}$. The authors reported solubility limits ranging from $\sim 10^{-6}$ to $\sim 10^{-8} \text{ M}$, with a clear tendency of the solubility to decrease with increasing pH. The wide diffractions patterns supported the amorphous character of the newly formed solid phases. Based on the analysis of the SEM-EDS data, the authors proposed a solubility-control by the solid phase $\text{Ca}_4\text{Nb}_6\text{O}_{19}(\text{am})$. Note however that only the solid phase equilibrated at $\text{pH} = 11.5$ and $[\text{Ca}] = 0.01 \text{ M}$ was characterized, which expectedly may not be the solid phase controlling the solubility at lower pH values and/or Ca concentrations (e.g., see discussion in Jo et al., 2022). Yamaguchi and co-workers investigated the solubility of $\text{Nb}_2\text{O}_5(\text{s})$ in alkaline solutions with $7 \leq \text{pH} \leq 11$ and $1 \cdot 10^{-3} \text{ M} \leq [\text{Ca}] \leq 0.1 \text{ M}$ (see Fig. 1) (Yamaguchi et al., 2020). Due to the low Nb concentrations determined in the aqueous phase ($[\text{Nb(V)}] \approx 10^{-10} - 10^{-9} \text{ M}$), the authors speculated with a solubility-control by the solid phase $\text{CaNb}_2\text{O}_6(\text{s})$, even though no solid phase characterization was conducted in the frame of this study. Yamaguchi et al. proposed also the formation of the ternary complex $\text{CaNb}(\text{OH})_6^+$ in the aqueous phase. Further experimental evidences are required to confirm this hypothesis.

We note that the solubility of Nb determined in this work in carbonate-containing solutions ($C_{\text{tot}} = (1.2 \pm 0.1) \cdot 10^{-3}$ and $(2.1 \pm 0.2) \cdot 10^{-4} \text{ M}$, for calcite and carbonated cement paste, respectively) is in line with solubility data reported under similar pH and Ca concentrations, but in the absence of carbonate (Talerico et al., 2004; Yamaguchi et al., 2020; Ohira et al., 2023). This observation strongly suggests that under the investigated boundary conditions, carbonate cannot outcompete hydrolysis and thus does not impact Nb(V) solubility. No thermodynamic data for Nb(V)-carbonate complexes are selected in the main thermodynamic databases available in the field of nuclear waste disposal, e.g., ThermoChimie (Madé et al., 2025), PSI-Nagra TDB (Hummel and Thoenen, 2023), JAEA-TDB (Kitamura, 2020), or key references dealing with niobium, e.g., Lothenbach and Ochs (Lothenbach et al., 1999) or Filella and May (2020). The solubility of Nb in Na_2CO_3 systems under hydrothermal conditions was investigated by Aleksandrov (1967) and Kotova (Kotova, 2011, 2012). At $T = 550^\circ \text{C}$ and $P = 500 \text{ bar}$, Kotova reported no impact of carbonate on Nb(V) solubility up to a Na_2CO_3 concentration of $2 \text{ mol} \cdot \text{kg}_w^{-1}$. The extrapolation of these results to standard conditions ($T = 25^\circ \text{C}$, $P = 1 \text{ bar}$) is not straight forward. Sn(IV) and Zr(IV) have been often considered as qualitative analogs of Nb(V) for the assessment of the complexation and sorption properties of the latter (Ochs et al., 2016; Çevirim-Papaioannou et al., 2022). Kobayashi and co-workers investigated the complexation of Zr(IV) with carbonate in near-neutral to hyperalkaline pH conditions. The authors observed a remarkable impact of carbonate, and defined the predominance of the complexes $\text{Zr}(\text{CO}_3)_4^{4-}$, $\text{Zr}(\text{CO}_3)_5^{5-}$ and $\text{Zr}(\text{OH})_2(\text{CO}_3)_2^{2-}$ (Kobayashi and Sasaki, 2017). Calculations using the thermodynamic data reported by Kobayashi et al. and the boundary

conditions considered in this study suggest the predominance of the complex $\text{Zr}(\text{OH})_2(\text{CO}_3)_2^{2-}$ (see Fig. SI-1 in the Supporting Information). In the absence of carbonate, the aqueous speciation of Zr(IV) and Nb(V) at $\text{pH} \approx 8.3$ is dominated by $\text{Zr}(\text{OH})_4(\text{aq})$ and $\text{Nb}(\text{OH})_6^-/\text{Nb}(\text{OH})_5^{2-}$. Such differences in the speciation may also explain the observed differences in the affinity of Zr(IV) and Nb(V) for carbonate.

3.2. Solid phase characterization of Nb(V) in calcite- and carbonated cement paste-equilibrated waters

3.2.1. Raman spectroscopy

Fig. 2 shows the Raman spectra collected for selected solid phases precipitated in calcite- (C1 to C3, with $[\text{Nb(V)}]_0 = 4.0 \cdot 10^{-4} \text{ M}$, $1.1 \cdot 10^{-3} \text{ M}$ and $1.4 \cdot 10^{-3} \text{ M}$, respectively; $t_{\text{eq}} \leq 64$ days) and carbonated cement paste- (CC1 and CC2, with $[\text{Nb(V)}]_0 = 1.1 \cdot 10^{-3} \text{ M}$ and $1.4 \cdot 10^{-3} \text{ M}$, respectively; $t_{\text{eq}} \leq 121$ days) equilibrated solutions. The spectra show in general a clear similarity to those typical for cubic pyrochlore structures. The observed Raman bands are fairly broad suggesting low crystallinity and/or high degree of structural disorder. For comparison purposes, Fig. 2 includes also some Raman spectra of related compounds taken from the RRUFF database (Lafuente et al., 2015).

Comparing the Raman spectra of this study with spectra obtained for Nb_2O_5 , (Jehng and Wachs, 1991; Deblonde et al., 2015; Riemke et al., 2026), which is the only solid phase considered in thermodynamic databases (e.g. ThermoChimie) (Madé et al., 2025), we can exclude

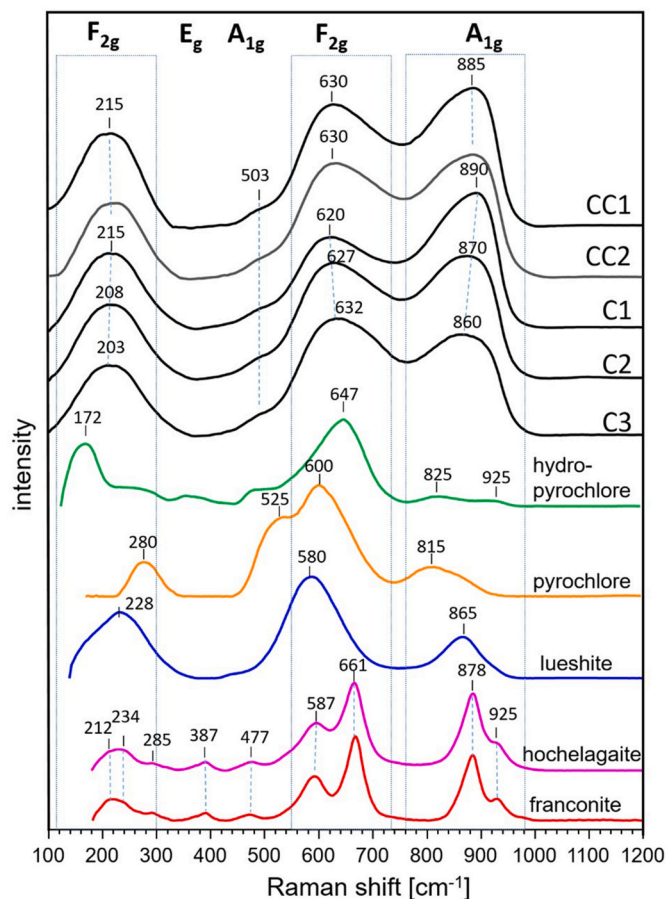


Fig. 2. Averaged Raman spectra of selected solubility samples in calcite- (C1–C3) and carbonated cement paste- (CC1–CC2) equilibrated waters. Raman spectra of franconite ($\text{NaNb}_2\text{O}_5(\text{OH}) \cdot 3\text{H}_2\text{O}$, R110185), hochelagaite ($\text{CaNb}_4\text{O}_{11} \cdot 8\text{H}_2\text{O}$, R110182), lueshite (NaNbO_3 , R090025), pyrochlore ($\text{Ca}_2\text{Nb}_2\text{O}_7$, R060151) and hydro-pyrochlore ($(\text{H}_2\text{O}, \square)_2\text{Nb}_2(\text{O}, \text{OH})_6(\text{H}_2\text{O})$, R060980) are provided for comparison.

presence of niobium oxide.

In the studies cited above, low temperature Nb₂O₅ shows its strongest bands in the range 650–690 cm^{−1} (depending on presence of H₂O and corresponding H-bridges) assigned to stretching of Nb–O. Further, bands at around 850–900 cm^{−1} (assigned to stretching of terminal Nb=O), are either not present or are very broad and with low intensity which is in striking discrepancy with the spectra of our samples.

The pyrochlore structure with ideal formula $\text{A}_2^{\text{VIII}}\text{B}_2^{\text{VI}}\text{X}_6^{\text{IV}}\text{Y}$ crystallizes in space group *Fd-3m* and is regarded as an anion-deficient derivative of the fluorite structure (AX₂). The pyrochlore structure allows great variety in its ability to incorporate a large number of different cations (Chakoumakos, 1984; Glerup et al., 2001; Ewing et al., 2004; Atencio et al., 2010). The factor group analysis of the cubic pyrochlore (space group *Fd-3m*) predicts six Raman-active modes R, seven IR modes, and one F_{1u} acoustic mode (McCauley, 1973; Ewing et al., 2004; Zietlow et al., 2017):

$$\Gamma = \text{A}_{1g}\text{R} + \text{E}_{g}\text{R} + 4\text{F}_{2g}\text{R} + 7\text{F}_{1u}\text{IR} + \text{F}_{1u} + 4\text{F}_{2u} + 2\text{F}_{1g} + 3\text{A}_{2u} + 3\text{E}_u$$

The intensity of the stretching bands in the range 860–890 cm^{−1} is lower in the spectrum of sample C3 than that of samples C1, C2, CC1 and CC2. It could be postulated that probably increasing of the defects in the pyrochlore structure after Ca→2H substitution should lead to increasing of the intensity of the “defect” band in the range 860–890 cm^{−1} and increasing the H₂O content. This behavior is also observed along the series C3–C2–C1. Correspondingly, the band at 630 cm^{−1} is the strongest one observed in the Raman spectrum of sample C3, which suggests best crystallinity of this sample according to the findings of Zietlow et al. (2017). This is further supported by the observed ordering of natural pyrochlore samples after annealing. With increase ordering upon annealing, the corresponding Raman spectra show increasing ratio of the F_{2g} “defect” band (Reissner et al., 2020). Opposite behavior is observed for pyrochlores subjected to irradiation damage (Sattonnay et al., 2010). In addition, the increased intensity of the band at 890 cm^{−1} observed in the spectrum of sample C1 may be an indication for formation of Nb–Ot (t denotes terminal oxygen) environments in orthorhombic, columbite-like structures as in fersmite, CaNb₂O₆ (Cummings and Simonsen, 1970).

The presence of more bands in the Raman spectra of franconite and hochelagaite is due to the fact that these possess monoclinic symmetry, in contrast to “pure” cubic pyrochlore. Whereas bands in the range 350–490 cm^{−1} assigned to E_g modes are missing in the spectra of the present samples, the bands with highest intensity in the monoclinic symmetry spectra (≈660 and ≈880 cm^{−1}) correlate well with those observed in this study. The broadness of the latter implies structural disorder and low crystallinity. Therefore, a symmetry lower than cubic cannot be excluded.

The presence of a clear band in the range 924–931 cm^{−1} in the spectra of franconite, hochelagaite and hydroxyrochlore in Fig. 2, could be assigned to symmetrical stretching of Nb=O double bond (Haring

and McDonald, 2017). The great resemblance of the Raman spectra of all samples with that of lueshite (perovskite structure) in the “finger print” region 100–1200 cm^{−1} could be due to structural similarities and exchangeability between Na and Ca.

The spectrum of pyrochlore shows similar number of broad bands, but also a clear shift of the F_{2g} and A_{1g} bands to lower frequencies of 600 and 815 cm^{−1}, respectively. The low frequency F_{2g} band is positioned at 280 cm^{−1}. These features may be due to the presence of H₂O as next environment of Ca and Nb.

Among the minerals with a hydro-pyrochlore structure, the Raman spectrum of hydroxynatropyrochlore (Na,Ca,Ce)₂Nb₂O₆(OH) shows a striking similarity with the spectra observed in this study (Ivanyuk et al., 2019) (see Table 2). The strongest band at 624 cm^{−1} (compared to 632 cm^{−1}, sample C3) could be assigned to Nb–O stretching. Charleshatchettite, CaNb₄O₁₀(OH)₂·8H₂O (Haring and McDonald, 2017), is another hydrated pyrochlore mineral listed in Table 2, which shows a great resemblance to hochelagaite in its Raman spectrum. Besides pyrochlore itself, Ca₂Nb₂O₇, Raman spectra of such hydrated pyrochlore-like minerals as, hochelagaite: CaNb₄O₁₁·8H₂O (Jambor, 1986), franconite NaNb₂O₅(OH)·3H₂O (Haring and McDonald, 2014), hydroxyrochlore, (H₂O,□)₂Nb₂(O,OH)₆(H₂O) (Ercit et al., 1994; Lafuente et al., 2015) (reference R060980 in RRUFF database) and lueshite (NaNbO₃) (Safiannikoff, 1959) were considered. Additionally, the frequencies observed in the spectra of the three minerals showing greatest resemblance with samples C and CC and namely, franconite, hochelagaite and hydroxyrochlore are presented in Table 2. Data for hydroxynatropyrochlore and charleshatchettite (not available in the RRUFF database) are also shown in the Table, as reported in (Haring and McDonald, 2014, 2017), respectively.

Divalent pyrochlores as Ca_{0.4}H_{1.2}Nb₂O₆·H₂O or Ca_{0.4}Nb₂O₅(OH)_{1.2}·H₂O crystallize in cubic *Fd-3m* structure (Groult et al., 1975). A closer look reveals that compounds like hochelagaite and charleshatchettite (both similar to franconite and most probably polymorphs with same composition) differ only in the degree of Ca ↔ 2H substitution and the H₂O content. The formula of charleshatchettite (and hochelagaite) could be easily rewritten as Ca_{0.5}Nb₂O₅(OH)·4H₂O. Comparison with Ca_{0.4}Nb₂O₅(OH)_{1.2}·H₂O of Groult et al. makes this clear (Groult et al., 1975). Deblonde and co-workers investigated the transition of niobic acid to sodium hexaniobate phases in alkaline solutions (7 ≤ pH ≤ 12) and absence of Ca (Deblonde et al., 2015). The authors described a condensation of Nb(V)-oxo units and the formation of short-range structures related to polyoxoniobates. Raman spectra were characterized by very broad bands (specially in less alkaline conditions), indicating the formation of a poorly crystalline or amorphous solid phase containing. Although some of the Raman bands show some similarities to those observed in this work, the absence of Ca in the system investigated by Deblonde et al. prevents a direct comparison of both Raman datasets.

Fig. 3 shows the Raman spectra in the range 1400–3800 cm^{−1}. All five solubility samples under investigation show presence of H₂O bands

Table 2

Observed frequencies and mode assignment of the bands in the Raman spectra of solubility samples C1, C2, C3 and related compounds. Data for franconite (R110185), hochelagaite (R110182) and hydroxyrochlore (R060980) taken from RRUFF (Lafuente et al., 2015). Charleshatchettite (Haring and McDonald, 2017) and hydroxynatropyrochlore (Ivanyuk et al., 2019), respectively.

Assignment	Sample C1	Sample C2	Sample C3	Hydroxynatropyrochlore (Na,Ca,Ce) ₂ Nb ₂ O ₆ (OH)	Franconite NaNb ₂ O ₅ (OH)·3H ₂ O	Hochelagaite CaNb ₄ O ₁₁ ·8H ₂ O	Charleshatchettite CaNb ₄ O ₁₀ (OH) ₂ ·8H ₂ O	Hy Pyrochlore (H ₂ O,□) ₂ Nb ₂ (O,OH) ₆ (H ₂ O)
F _{2g}	215	208	203	75, 94, 128, 170, 265	212, 297,	234,	234,	170, 273
E _g					391, 461	387, 477	378, 489	365, 387, 482
A _{1g}	503	503	503	545	583	587	599	
F _{2g}	620	627	632	624	661	663	658	647
“Defect” mode or ν _{1,3} Nb=O(A _{1g})	890	870	860	810	879, 924	878, 925	878, 930	810, 931
δ(H ₂ O)	1632	1630	1605			1665	1459	1638
ν(H ₂ O)	3422	3422	3433	3250, 3460, 3540	3416*, 3430	3426	3046, 3314	3458, 3580

in their structures manifested by bending bands at $1630\text{--}1635\text{ cm}^{-1}$ (samples C1, C2, CC1, CC2) and 1605 cm^{-1} (sample C3) and stretching bands at 3422 cm^{-1} (samples C1, C2) $3430\text{--}3433\text{ cm}^{-1}$ (sample C3, CC1, CC2). The stretching bands (ν_1, ν_3 OH) are very broad possessing broad shoulders at lower frequency (around 3250 cm^{-1}) and most probably are due to H_2O rather than OH groups. The spectra of the C and CC samples in the OH range show best similarity with those of hochelagaite, franconite and hydropyrochlore.

Comparison with the Raman spectra in the range of H_2O bending and stretching modes with spectra of the same minerals as in Fig. 2 shows that franconite and particularly hochelagaite possess similar H_2O environments as the spectra of both C and CC samples. Assuming a possible exchange of Na by Ca in franconite according to $\text{Na}^+ + \text{OH}^- \leftrightarrow \text{Ca}^{2+} + \text{O}^{2-}$, there should not be OH group present which is consistent with the observed spectra. Next closest spectrum is shown by hydropyrochlore. The latter shows in addition to the H_2O band at 3458 cm^{-1} an OH-band at 3580 cm^{-1} , which reflects fairly well its composition. Pyrochlore shows no H_2O bands which is expected as water-free mineral, but a well-defined OH band at 3613 cm^{-1} implies either defect structure or impurity. The spectrum of lueshite does not show any resemblance with these of samples C and CC in the range $1400\text{--}3800\text{ cm}^{-1}$ lacking H_2O and OH species. The spectrum of hydroxynatropyrochlore (Table 2) show presence of OH groups (3540 cm^{-1}) consistent with its formula. Charleschettite shows rather low frequencies of H_2O bending and stretching bands which implies presence of H-bonding system in accordance with the chemical composition.

3.2.2. XRD and Rietveld analysis

The powder patterns of solubility samples C1, C2, C3 as well as of CC1 and CC2 are shown in Fig. 4. All diffractograms reflect the poor

crystallinity of the investigated samples. The best diffraction pattern is delivered from samples C3 and CC1, CC2 which might be due to 1) higher sample quantity or/and 2) lower H_2O content as seen by Raman. Nevertheless, the patterns of all samples are strikingly similar apart from the intensity discrepancies. They show a broad scattering in the range

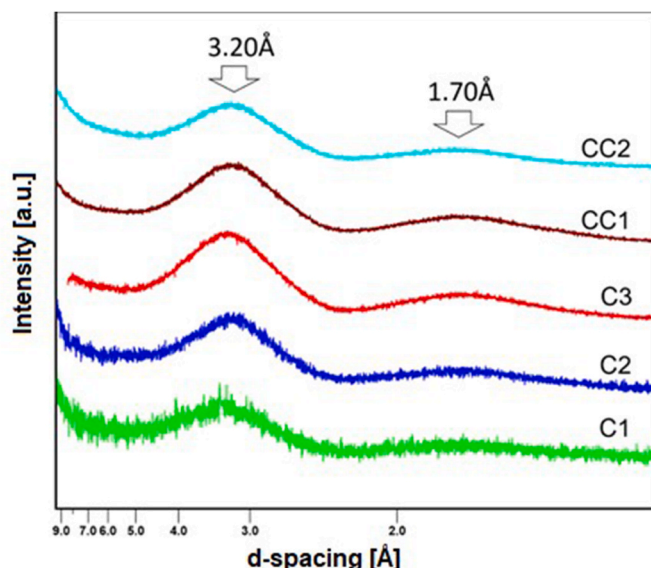


Fig. 4. XRD patterns of solubility samples C1, C2, C3 and CC1, CC2. The diffractograms are corrected for the contribution of the sample holders.

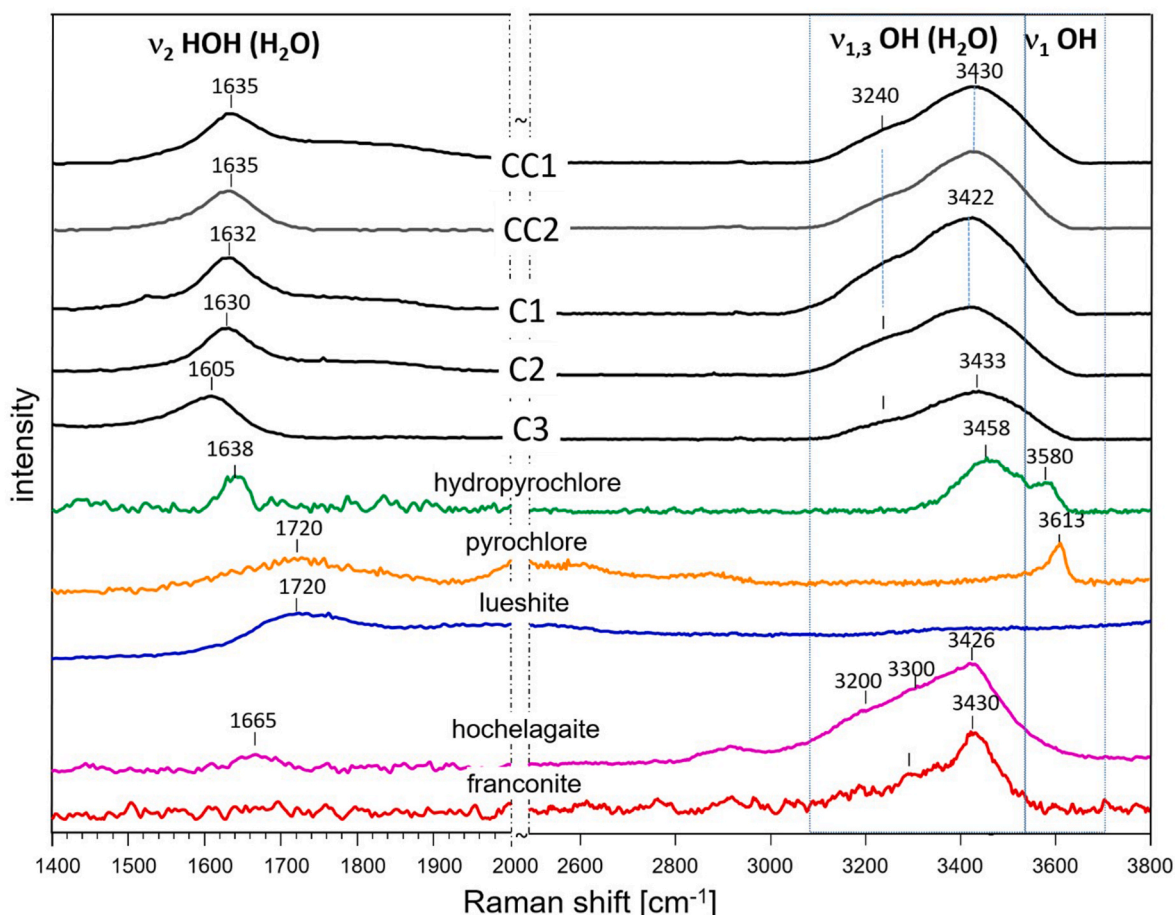


Fig. 3. Raman spectra in the region of HOH bending ($1400\text{--}2000\text{ cm}^{-1}$) and OH stretching ($3100\text{--}3800\text{ cm}^{-1}$) modes.

20–35° 2 θ , centered at 37.5° 2 θ corresponding to 3.2 Å. Further, another broad hump between 40 and 60° 2 θ is observed, centered at 1.7 Å.

Following the discussion about the similarities of the Ca (OH, H₂O) pyrochlore-like compounds, the XRD pattern of sample C3 was separately evaluated by both, WPPR (Fig. 5a) and WPPD (Fig. 5b). For the Rietveld method, the monoclinic structure of charleshatchettite, CaNb₄O₁₀(OH)₂·8H₂O (ICSD 244333) was used. Without refinement of the atomic positions or preferred orientation, the fit converged to reasonable R values. The unit cell parameters were refined to values differing in the *a* and *b* from the original structure the *a* being larger and *b* smaller, respectively. The size of the coherent scattering domains was as expected very low and resulted in 0.8 nm calculated by the double Voigt approach (Coelho, 2020). A fragment of the structure of charleshatchettite is shown along [101] with the net planes (20-4 and 004) contributing to the scattering around 3.2 Å. For the WPPD method, a HKL phase with space group *Fd-3m*, typical for pyrochlore structure with

a starting lattice parameter of 11 Å was refined with the Le-Bail method (Fig. 5b). The latter resulted in 11.2 Å after refinement. The insert in Fig. 5b shows the structure of cubic pyrochlore (Groult et al. (1975), ICSD 41857) along [01-1]. It becomes clear that the net planes (222) and (−222) and their conjugates are mostly responsible for the scattering at 3.2 Å. They are interconnecting rows of Nb and Ca atoms. The net planes (622) are contributing to the scattering around 1.7 Å (45–55° 2 θ) and their first order (311) net planes are responsible for the left flank of the biggest hump scattering at 3.4 Å. The calculated size of the coherent scattering domains is for both refinements well below 1 nm (0.8 and 0.6, Fig. 5). This explains why the reflections (111) in the cubic structure and (200, 110, and 002) of the monoclinic one are missing. Therefore, we are only able to observe a short-range order, but it seems that XRD is providing enough data for this. Although both alternatives considering monoclinic and cubic arrangement in the short-range ordering could explain the XRD results, the cubic approach seems to be more

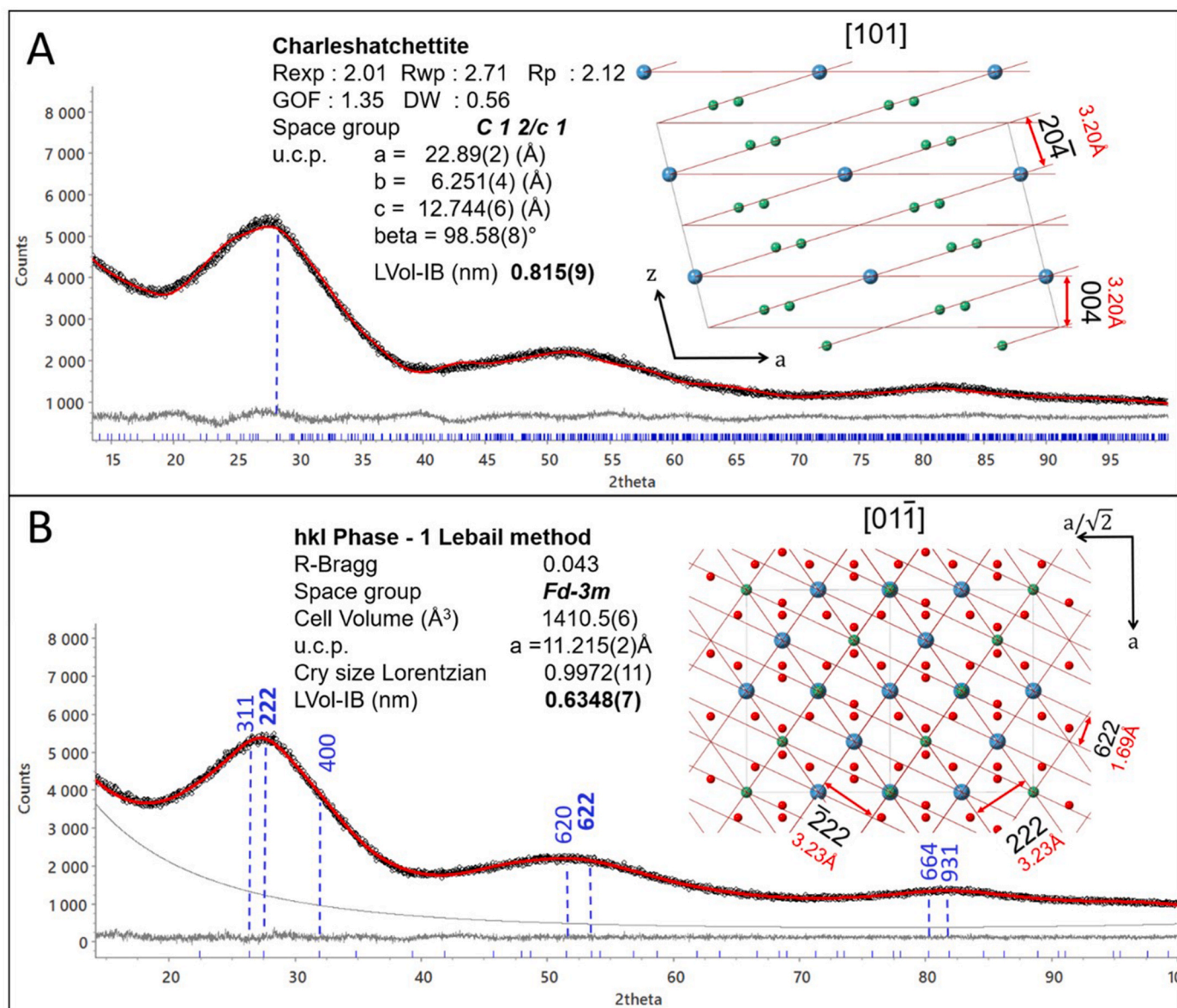


Fig. 5. Refinements of the XRD pattern of sample C3 with WPPR (Rietveld method) using the structure of charleshatchettite, CaNb₄O₁₀(OH)₂·8H₂O (A) The structure is shown along [101] with the net planes (20-4 and 004) contributing together with (220) and (020) (not shown) to the scattering around 3.2 Å. (B): WPPD (Le-Bail) of sample 4 using HKL phase with *Fd-3m* space group and lattice parameter of 11.2 Å. The insert shows the structure of cubic pyrochlore (ICSD 41857) along [01-1]. Atoms are colored as follows: Nb-green, Ca-blue, O-red. The net planes (222) and (−222) responsible for the scattering at 3.2 Å and these of (622) contributing to the scattering around 1.7 Å (45–55° 2 θ) are also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

straightforward.

All observations collected by Raman spectroscopy and XRD point towards the predominance of hydrated Ca-Nb(V) solid phase/s of rather amorphous and sub-nanoparticulate character. A definitive assignment of the stoichiometry of this/these solid phase/s is not feasible at this stage, although available evidence points towards a Ca: Nb ratio clearly below 1.

4. Summary and conclusions

This work aimed at a quantitative evaluation of Nb(V) solubility and at a as well as a thorough characterization of the solubility-controlling solid phases under conditions relevant to calcite and carbonated cement systems at pH values below 10.

The solubility of niobium(V) was investigated from oversaturation conditions in weakly alkaline solutions characterized by $\text{pH} \approx 8.3$, $[\text{Ca}] \approx 6 \cdot 10^{-4}$ – $3 \cdot 10^{-3}$ M and $C_{\text{tot}} \approx 10^{-4}$ – 10^{-3} M. These aqueous compositions are representative of calcite- and (OPC) carbonated cement paste-equilibrated waters, as those expected for degraded cement systems eventually forming in near-surface and underground repositories for L/ILW-SL.

Solubility measurements resulted in very low niobium concentrations (i.e., $[\text{Nb(V)}] \leq 10^{-8}$ M) at $t \geq 28$ days. These low concentrations cannot be explained with thermodynamic data currently selected in ThermoChimie (version 13a) (Madé et al., 2025) and other reference databases, which predict Nb concentrations above 10^{-6} M at $\text{pH} \approx 8.3$. These observations clearly indicate the formation of secondary niobium solid phase/s, likely involving the participation of calcium. Niobium concentrations determined in this work are in line with previous solubility studies conducted in analogous carbonate-free systems, thus evidencing that carbonate complexes do not outcompete the strong hydrolysis of niobium in the range of pH and carbonate concentrations investigated in this work.

Raman spectra collected for selected solid phases precipitated in calcite- and carbonated cement paste-equilibrated solutions show in general a clear similarity to those typical for cubic pyrochlore structures, $\text{Ca}_2\text{Nb}_2\text{O}_7$. All Raman bands are fairly broad suggesting a low crystallinity and small particle size. Raman spectra in the range of H_2O bending and stretching modes shows strong evident similarities with franconite ($\text{NaNb}_2\text{O}_5(\text{OH}) \cdot 3\text{H}_2\text{O}$) and particularly hochelagaite ($\text{CaNb}_4\text{O}_{11} \cdot 8\text{H}_2\text{O}$). XRD characterization and Rietveld analysis of the solid phases forming under these conditions point to very small crystallite size (0.6–0.8 nm) of pyrochlore-like compounds, e.g., hochelagaite or charlesthatchettite ($\text{CaNb}_4\text{O}_{10}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$), with typical average reflections characteristic for Nb-Nb, Ca-Nb- and Ca-Ca plane distances of ~ 3.2 and 1.7 Å.

This work provides the first quantitative determination of niobium solubility limits in weakly alkaline, carbonated systems representative of an advanced degradation stage of cement. Comprehensive characterization methods point towards a solubility-control by Ca-Nb(V)-O/OH(s) solid phase/s with a ratio Ca: Nb < 1, although so far no thermodynamic data are available for these compounds, which accordingly cannot be implemented in geochemical calculations.

CRedit authorship contribution statement

Nils Huber: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Krassimir Garbev:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Rosa Ester Guidone:** Writing – review & editing, Supervision, Methodology. **Xavier Gaona:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Florian Bocchese:** Writing – review & editing, Project administration, Conceptualization. **Stéphane Brassinnes:** Writing – review & editing, Project administration, Conceptualization. **Marcus Altmaier:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Horst Geckeis:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: KIT-INE reports financial support was provided by ONDRAF-NIRAS. If there are other authors, they 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.2026.107125>.

Data availability

Data will be made available on request.

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