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# Dissolution and solubility of the calcium-nickel carbonate solid solutions [(Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub>] at 25 °C

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# Abstract

A series of the calcium-nickel carbonate solid solutions  $[(Ca_{1-x}Ni_x)CO_3]$  were synthesized and their dissolution in N<sub>2</sub>-degassed water (NDW) and CO<sub>2</sub>-saturated water (CSW) at 25 °C was experimentally investigated. During dissolution of the synthetic solids (Ni-bearing calcite, amorphous Ca-bearing NiCO<sub>3</sub> and their mixtures), the Ni-calcite and the Ca-NiCO<sub>2</sub> dissolved first followed by the formation of the Ni-bearing aragonite-structure phases. After 240–300 days of dissolution in NDW, the water solutions achieved the stable Ca and Ni concentrations of 0.592–0.665 and 0.073–0.290 mmol/L for the solids with lower Ni/(Ca + Ni) mol ratios ( $X_{Ni}$ ), or 0.608–0.721 and 0.273–0.430 mmol/L for the solids with higher X<sub>Ni</sub>, respectively. After 240–300 days of dissolution in CSW, the water solutions achieved the stable Ca and Ni concentrations of 1.094–3.738 and 0.831–4.300 mmol/L, respectively. For dissolution in NDW and CSW, the mean values of log IAP (Ion activity products) in the final stable state ( $\approx \log K_{sn}$ , Solubility product constants) were determined to be  $-8.65 \pm 0.04$  and  $-8.16 \pm 0.11$  for calcite [CaCO<sub>3</sub>], respectively;  $-8.50 \pm 0.02$ and  $-7.69 \pm 0.03$  for the synthetical nickel carbonates [NiCO<sub>3</sub>], respectively. In respect to the bulk composition of the  $(Ca_{1-v}Ni_v)CO_3$  solid solutions, the final log IAP showed the highest value when  $X_{Ni} = 0.10-0.30$ . Mostly, the mean values of log IAP increased with the increasing X<sub>Ni</sub> in respect to the Ni-calcite, the Ni-aragonite and the amorphous Ca-Ni carbonate. The plotting of the experimental data on the Lippmann diagram for the (Ca<sub>1-v</sub>Ni<sub>v</sub>)CO<sub>3</sub> solid solution using the predicted Guggenheim parameters of  $a_0 = 2.14$  and  $a_1 = -0.128$  from a miscibility gap of  $X_{Ni} = 0.238$ to 0.690 indicated that the solids dissolved incongruently and the final Ca and Ni concentrations in the water solutions were simultaneously limited by the minimum stoichiometric saturation curves for the Ni-calcite, Ni-aragonite and the amorphous Ca-Ni carbonate. During dissolution in NDW, the Ni<sup>2+</sup> preferred to dissolve into the water solution and  $Ca^{2+}$  preferred to remain in the solid, while during dissolution in CSW for the solids with higher  $X_{Nir}$  the  $Ca^{2+}$ preferred to dissolve into the water solution and Ni<sup>2+</sup> preferred to remain in the solid. These findings provide valuable insights into understanding the mechanisms governing Ni geochemical cycle in natural environments.

Keywords Calcium carbonate, Nickel carbonate, Solid solution, Dissolution, Solubility

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## Introduction

Nickel (Ni) is widely distributed in the environment and an essential element for plants especially at low concentrations [1, 2], but excessive Ni can induce painful skin allergies, lung and nasopharyngeal cancers [3–7]. Therefore, environmental contamination by nickel is a serious problem [8], which has been reported recently in many countries [9, 10].

Nickel can be discharged into the environment by natural processes (volcano eruption, rock erosion and weathering) and human activities (mining, toilet fittings, electro-plating, radioactive waste disposal, land-fills, and battery manufacture) [6, 9, 11–14]. Transportation of Ni<sup>2+</sup> in the geological spheres played an important role in the mineral deposit formation and in the nickel distribution in natural environments. The interaction between Ni<sup>2+</sup> and calcite can significantly decrease the nickel mobility in mining areas [15, 16]. In a mining area in northeastern Iran, the Ni concentration was detected to be 321.7±113.27 mg/kg [17]. The Ni concentration increased to 26.4 g/kg in soils and 0.3 mg/L in polluted water [18]. Ni was considered as a key pollutant in southeastern China [19]. In a farmland soil from Quanzhou County, Guangxi, the Ni concentration was 6.99-249.00 mg/kg with the average of 28.51 mg/kg, exceeding the soil background value of China [20].

Carbonate minerals and rocks are of considerable environmental significance since they are reactive and broadly available in nature [21]. Precipitation of metal carbonate has been used for soil and wastewater remediation [8]. Coprecipitation of nickel with calcite was an efficient technique to remove Ni from drinking water [4, 22]. Microbial induced carbonate precipitation (MICP) could significantly reduce the Ni bioavailability in the nature environment [5, 8, 23, 24]. After the MICP handling of a highly contaminated soil (898 mg/kg Ni) from a battery factory in Shanghai, China, the bioavailable fraction was decreased to 38 mg/kg Ni [5]. At the initial  $Ni^{2+}$ concentration of 500 mg/L, the MICP treatment showed a high removal percentage of 89% [8]. Fly ash carbonation is also an efficient technique to stabilize heavy metals and reduce  $CO_2$  [25].

Better understanding of the geochemical and environmental properties of nickel could improve prediction of its transportation-distribution in natural environments and contribute to more efficient soil and water treatment techniques. Nickel is smaller than calcium, but it can also partly incorporate into calcite [26]. Due to the very limited substitution of  $Ca^{2+}$  in calcite by Ni<sup>2+</sup>, a complete series of the CaCO<sub>3</sub>–NiCO<sub>3</sub> solid solutions were not observed in nature [15]. The calculation of the density functional theory predicted that Ni<sup>2+</sup> replacement is favorable at the calcite-water interface to form a stable solid solution in comparison to the bulk substitution [27]. Reliable thermodynamic data describing the behavior and fate of Ni in natural systems are essential to validly assess risk and design efficient remediation strategies, surprisingly few experiments were previously carried out to investigate its interaction with sediment and soil minerals and only some articles studied its interaction with calcite [11, 26]. The research on nickel uptake by calcite suggested that Ni<sup>2+</sup> formed surface complexes, which remained hydrated until Ni<sup>2+</sup> entered into the bulk structure through re-crystallization [15, 28]. In the Ni<sup>2+</sup> interaction with calcite, nickel was eliminated not merely through physical trapping, but as a true solid solution [26]. Calcite could incorporate several percent Ni<sup>2+</sup> in its structure [15].

In brief, reliable thermodynamic data about Ca-Ni carbonates are still absent for modeling the transportation and distribution of nickel in environment. Therefore, in the present research, the Ca-Ni carbonate solid solutions  $[(Ca_{1-x}Ni_x)CO_3]$  of different Ni/(Ca + Ni) mol ratios (X<sub>Ni</sub>) between 0.00 and 1.00 were synthesized and characterized. The dissolution of the synthetic solids in N2-degassed water (NDW) and CO2-saturated water (CSW) was then investigated to examine the influence of initial pH and carbonate concentration on the release of the solid component, the dissolution and solubility of the solid phases. Lastly, the Lippmann diagrams for the (Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub> solid solutions were illustrated to explore the solid solution-aqueous solution (SSAS) interaction to assess the solubilities of Ca-Ni carbonates and the Ni redistribution in water environment.

# **Experimental methods**

# Solid synthesis

Solid samples (CN-00 ~ CN-10) of the  $(Ca_{1-x}Ni_x)$ CO<sub>3</sub> solid solutions were obtained by adding 1000 mL of 0.5 mol/L NH<sub>4</sub>HCO<sub>3</sub> solution at 1 mL/s into 5 mL of 2 mol/L mixed solution of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and  $Ni(NO_3)_2 \cdot 6H_2O$  with various Ni/(Ca + Ni) mol ratios in 1 L polyethylene bottles at 33 °C, which were vigorously stirred at 500 rpm (Table 1). The bottles were then agitated for 15 min and were put in the water baths at 85 °C for another 30 min. Finally, the precipitates were separated from the suspension through suction filtration, cleaned carefully using ethyl alcohol as quickly as possible and dried for 1 day at 90 °C. Calcium nitrate  $(Ca(NO_3)_2 \cdot 4H_2O)$ , nickel nitrate  $(Ni(NO_3)_2 \cdot 6H_2O)$ , ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) of analytical grade (Xilong Science Co., LTD., China) and ultrapure water were used in the preparation of the starting solutions.

Sample No	Starting solution (ml	_)	Ni/(Ca + Ni) mol ratio (X <sub>Ni</sub> )		
	2 mol/L Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	2 mol/L Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.5 mol/L NH <sub>4</sub> HCO <sub>3</sub>	Starting solution	Synthetic solid
CN-00	50	0	1000	0.000	0.000
CN-01	45	5	1000	0.100	0.057
CN-02	40	10	1000	0.200	0.099
CN-03	35	15	1000	0.300	0.180
CN-04	30	20	1000	0.400	0.289
CN-05	25	25	1000	0.500	0.381
CN-06	20	30	1000	0.600	0.511
CN-07	15	35	1000	0.700	0.622
CN-08	10	40	1000	0.800	0.773
CN-09	5	45	1000	0.900	0.894
CN-10	0	50	1000	1.000	1.000

**Table 1** Summary of synthesis and the Ni/(Ca + Ni) mol ratio of the  $(Ca_{1-x}Ni_x)CO_3$  solid solutions

## Characterization

The bulk component of the synthetical solid was determined using wet chemical analysis, i.e., ten milligrams of the sample were dissolved in 20 mL 1 mol/L HNO<sub>3</sub> solution, which was diluted to 100 mL using ultrapure water. The Ca and Ni concentrations were then analyzed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin-Elmer Optima 7000DV). All solid samples were recognized crystallographically by comparing their X-ray diffraction spectra, which were obtained by the X-ray diffractometer (XRD, X'Pert PRO, PANalytical B.V.), with the ICDD (the International Center for Diffraction Data) reference codes 01-081-2027 for calcite and 01-078-0210 for gaspeite (NiCO<sub>3</sub>) or the XRD spectrum of the nickel carbonate (NiCO<sub>3</sub>, the Rhawn's reagent). The morphology and surface component of the solids were examined by using a field-emission scanning electron microscope (FE-SEM, Jeol JEM-7800F) with an energy-dispersive spectrometer (EDS, Oxford X-MaxN50), which has the resolution of 0.7 nm at 15 kV.

## **Dissolution experiments**

Dissolution experiments were performed in two different solutions, i.e., N<sub>2</sub>-degassed water (NDW, initial pH 6.16) and CO<sub>2</sub>-saturated water (CSW, initial pH 4.96 and the total carbonate concentration of 0.011 mmol/L), to examine influence of initial pH and carbonate concentration on the dissolution and solubility of solid phases. Instrumental-grade N<sub>2</sub> and CO<sub>2</sub> were used to saturate the initial solutions. Ten grams of the synthetic solids and the purchased nickel carbonate (NiCO<sub>3</sub>, the Rhawn's reagent from Shanghai Yi En Chemical Technology Co., LTD) were added into a series of the labelled 5 L plastic bottles, into which 5 L of NDW or CSW were then put. The bottles were capped with sealed caps to avoid the gas exchange between air and solution as much as possible and placed in the rooms of air condition at 25 °C. Under the protection of  $N_2$ , one hundred milliliters of the water solution were collected from the bottle at definite time (1 h, 3 h, 6 h, 12 h, 1 d, 2 d, 3 d, 5 d, 10 d, 15 d, 20 d, 30 d, 40 d, 50 d, 60 d, 70 d, 80 d, 90 d, 120 d, 150 d, 180 d, 210 d, 240 d, 270 d and 300 d), the pHs were also analyzed at sampling by using the pH meter with a pH composite electrode (PHS-3E, INESA Scientific Instrument Co., Ltd). Twenty milliliters of the water solution were filtered using 0.22 µm membranes and acidized instantly by 0.2% HNO<sub>3</sub> for the determination of the total Ca and Ni concentrations by ICP-OES. The total carbonate (HCO<sub>3</sub><sup>-</sup> plus CO<sub>3</sub><sup>2-</sup>) concentrations were measured using an automatic potentiometric titrator (Metrohm 888 Titrando). At the end of the dissolution experiments, the residual solids in the bottles were sampled, cleaned carefully using ethyl alcohol, dried at 90 °C for 1 day and examined by the XRD and FE-SEM instruments as formerly described.

## Thermodynamic calculations

The solubility product constant  $(K_{sp})$  can be estimated from the long-standing stable state or the extrapolated ion activity product (IAP) of the water solution at the mineral dissolution equilibrium [29], i.e., at dissolution equilibrium, the equilibrium constant  $(K_{sp})$  for the  $(Ca_{1-x}Ni_x)CO_3$  solid solutions can be defined by Eq. (1):

$$K_{\rm sp} = {\rm IAP} = \left\{ {{\rm Ca}^{2+}} \right\}^{1-x} \left\{ {{\rm Ni}^{2+}} \right\}^x \left\{ {{\rm CO}_3}^{2-} \right\}$$
 (1)

where {} is the free ion activity. The free ion activities of Ni<sup>2+</sup>, Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> were first computed with the geochemical program PHREEQC [30], and then the ion activity product (IAP) was computed according to its definition that is equal to the solubility product constant ( $K_{sp}$ ) for the (Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub> solid solution at dissolution equilibrium. The built-in database of PHREEQC "minteq. v4.dat" comprised the thermodynamical parameters of all minerals and aqueous species in the computing (Table S1—Supplementary material). The ionic strength values lay in the applicable range for the extended Debye-Hückel equation.

## Construction of the Lippmann diagram

The solid solution–aqueous solution (SSAS) interaction is fundamentally important to realize the geochemical and environmental processes. In spite of numerous studies, thermodynamical data for the SSAS system are still lacking. Lippmann diagram has been constructed in many works to describe some SSAS systems [31–41]. It is a diagram depicting the relationship between the "solidus" phase and the "solutus" phase in the SSAS system, which defines all possible thermodynamic saturations as a function of the solid and water compositions. The "solidus" and "solutus" curves are the plot of the "total activity product" ( $\Sigma\Pi_{SS}$ ), i.e., the sum of the partial activity products of the endmembers at equilibrium, versus the solid and water compositions, respectively.

For the  $(Ca_{1-x}Ni_x)CO_3$  solid solutions, the "*solidus*" curve is expressed with:

$$\Sigma \Pi_{SS} = \left( \left\{ Ca^{2+} \right\} + \left\{ Ni^{2+} \right\} \right) \left\{ CO_3^{2-} \right\}$$
  
= K<sub>Ca</sub>X<sub>Ca</sub> γ<sub>Ca</sub> + K<sub>Ni</sub>X<sub>Ni</sub> γ<sub>Ni</sub> (2)

where {} is the aqueous activity.  $K_{Ca}$  and  $K_{Ni}$ ,  $X_{Ca}$  and  $X_{Ni}$ ,  $\gamma_{Ca}$  and  $\gamma_{Ni}$  are the solubility product constants, the mol ratios (x, 1–x) and the activity coefficients of CaCO<sub>3</sub> and NiCO<sub>3</sub> in the solids, respectively.

The "solutus" curve is described with:

$$\Sigma \Pi_{SS} = \frac{1}{\frac{X_{Ca^{2+},aq}}{K_{Ca}\gamma_{Ca}} + \frac{X_{Ni^{2+},aq}}{K_{Ni}\gamma_{Ni}}}$$
(3)

where  $X_{Ca^{2+},aq}$  and  $X_{Ni^{2+},aq}$  are the aqueous  $Ca^{2+}$  and  $Ni^{2+}$  activity ratios, respectively.

For the members of fixed  $X_{Ca}=1-X_{Ni}$ , a series of the minimum stoichiometric saturation curves in terms of  $X_{Ca^{2+},aq}$  can be calculated with:

$$\Sigma \Pi_{SS} = \frac{IAP}{\left(X_{Ca^{2+},aq}\right)^{X_{Ca}} \left(X_{Ni^{2+},aq}\right)^{X_{Ni}}}$$
(4)

For  $CaCO_3$  and  $NiCO_3$ , the two endmembers of the solid solution, their saturation curves can be calculated with:

$$\Sigma \Pi_{CaCO_3} = \frac{\{Ca^{2+}\}\{CO_3^{2-}\}}{\left(X_{Ca^{2+},aq}\right)^{X_{Ca}}} = \frac{K_{Ca}}{\left(X_{Ca^{2+},aq}\right)^{X_{Ca}}}$$
(5)

$$\Sigma \Pi_{\text{NiCO}_3} = \frac{\{\text{Ni}^{2+}\}\{\text{CO}_3^{2-}\}}{\left(X_{\text{Ni}^{2+},\text{aq}}\right)^{X_{\text{Ni}}}} = \frac{K_{\text{Ni}}}{\left(X_{\text{Ni}^{2+},\text{aq}}\right)^{X_{\text{Ni}}}}$$
(6)

## **Results and discussion** Solid characterization *Chemical composition*

The Ni/(Ca + Ni) mol ratios (X<sub>Ni</sub>) of the synthetic solids were lower than the Ni/(Ca + Ni) mol ratios of the starting solutions (CN-01–CN-09) (Table 1). After dissolution of the synthetic solids in N<sub>2</sub>-degassed water (NDW) for 300 days, the X<sub>Ni</sub> values of the solid residuals increased slightly, showing a prior releasing of Ca into the water solution and a preferential retaining of Ni in the solid. After the dissolution in CO<sub>2</sub>-saturated water (CSW) for 300 days, the X<sub>Ni</sub> values of the solid residuals decreased slightly for the (Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub> solid solutions with lower X<sub>Ni</sub> (CN-01–CN-05), while increased slightly for the solid is with higher X<sub>Ni</sub> (CN-06–CN-09) (Tables 1 and 2).

## XRD

The strong peaks for the synthesized solid of  $X_{Ni} = 0.00$ (CN-00) agreed well with calcite (ICSD reference code 01-081-2027) (Fig. 1). The strong peaks for the synthesized solid of  $X_{Ni} = 1.00$  (CN-10) were not obviously observed, but its XRD spectrum was consistent with that of the nickel carbonate (NiCO<sub>3</sub>, the Rhawn's reagent) (Fig. 1). The synthesized solid phases of  $X_{Ni} = 0.00 - 0.70$ (CN-00-CN-07) were pure Ni-bearing calcite solid solutions (Fig. 1). The reflection peaks, predominantly (104), moved from lower angle slightly to higher angle with the increasing Ni substitution, due to the smaller inter-planar distances of the Ni-bearing calcite compared to the calcite without Ni-incorporation (Fig.S1-Supplementary material). The synthesized solid phases of  $X_{Ni} = 0.80 - 0.90$ (CN-08-CN-09) showed the similar XRD spectra to the synthesized solid of  $X_{Ni}$  = 1.00 (CN-10) and the nickel carbonate (NiCO<sub>3</sub>, the Rhawn's reagent).

After 300 days of dissolution in NDW and CSW, no obvious variations were found for pure calcite (CN-00) and nickel carbonates (CN-10 and Rhawn's reagent) (Fig. 1). The synthesized solids of  $X_{\rm Ni}$ =0.10–0.90

Sample No	Synthetic solid before dissolution			After dissolution in water							
				N <sub>2</sub> -degassed				CO <sub>2</sub> -saturated			
	Cal	Ara	Am	Bulk	Cal	Ara	Am	Bulk	Cal	Ara	Am
CN-00	0.000			0.000	0.000			0.000	0.000		
CN-01	0.078			0.053	0.108	0.022		0.027	0.084	0.007	
CN-02	0.130		0.813	0.101	0.142	0.068	0.690	0.037	0.103	0.019	
CN-03	0.160		0.747	0.200	0.144	0.096	0.701	0.072	0.188	0.116	0.697
CN-04	0.199		0.739	0.327	0.176	0.128	0.787	0.219	0.238	0.166	0.769
CN-05	0.205		0.840	0.426	0.199	0.131	0.821	0.341	0.219	0.224	0.789
				0.421	0.197	0.134	0.821	0.336	0.228	0.221	0.792
CN-06	0.228		0.802	0.564	0.195	0.127	0.859	0.569	0.212	0.215	0.814
CN-07	0.212		0.776	0.684	0.178	0.166	0.894	0.686	0.184	0.124	0.886
CN-08	0.208		0.816	0.838		0.223	0.968	0.863		0.080	0.940
CN-09			0.918	0.964		0.197	0.975	0.983			0.980
CN-10			1.000	1.000			1.000	1.000			1.000

**Table 2** Ni/(Ca + Ni) mol ratio ( $X_{Ni}$ ) of calcite-structure, aragonite-structure and amorphous solid phases in the (Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub> solid solutions

Cal Calcite-structure phase, Ara Aragonite-structure phase, Am Amorphous phase

X<sub>Ni</sub> of the bulk component was calculated after the chemical analysis; X<sub>Ni</sub> of the Cal, Ara and Am solid phase was calculated after the EDS analysis



**Fig. 1** XRD spectra of the  $(Ca_{1-x}Ni_x)CO_3$  solid solutions before dissolution (**a**), after dissolution for 300 days in N<sub>2</sub>-degassed water (**b**) and in  $CO_2$ -saturated water (**c**)

(CN-01–CN-09) were the mixture of the solid phases with the calcite-structure and the solid phases with the aragonite-structure (ICSD reference code 00-001-0628) (Fig. 1), indicating a transformation of the calcite-structure to the aragonite-structure during dissolution of the solids.

## SEM-EDS

The solid morphologies were strongly depended on the Ni concentration of the precursor solution. Different crystal habits were observed, indicating that Ni<sup>2+</sup> even at very low concentration could significantly affect the calcite crystal growth [31]. The synthesized calcite (CN-00) exhibited a typical rhombohedral morphology with a

grain size of  $\sim 10 \ \mu m$  (Fig. 2). As the increasing Ni incorporation into calcite, the solids changed from blocky crystals to spheroids for the synthesized solids (CN-00–CN-04), which was similar to the morphologic variation

of the (Mn,Ca)CO<sub>3</sub> crystals following the change of Mn content in the aqueous solution, i.e., the individual is a crystal, the surface of which is formed by the aggregation of numerous minuscule blocks of {104} facets that appear



**CN-03** 

CN-04

CN-05



**CN-06** 

CN-07





 $\frac{CN\text{--}09}{\text{Fig. 2}} \frac{CN\text{--}10}{\text{SEM images of the (Ca}_{1-x}\text{Ni}_x)\text{CO}_3 \text{ solid solutions before dissolution}}$ 

NiCO3(Rhawn's reagent)

slightly disoriented, as they are tracing the external shape of a solid that can be considered as spherical [31]. The synthesized solids (CN-09-CN-10) and the purchased nickel carbonate (NiCO<sub>3</sub>, the Rhawn's reagent) were aggregates of amorphous calcium-bearing nickel carbonate (ACNC) with fine particle size. In the synthesized solids (CN-05–CN-08), both the calcite-structure (Ca<sub>1–</sub> "Ni")CO3 solids and the fine particles of amorphous calcium-bearing nickel carbonate (ACNC) were observed (Figs. 2 and 3). Amorphous phases are metastable with respect to their crystalline equivalents [42]. Although there have been studies showing that amorphous calcium carbonate (ACC) can transform into vaterite within 15 min of reacting in solution, which will further transform to calcite via dissolution-reprecipitation [43, 44], it was not observed that amorphous nickel carbonate (ANC) can transform to vaterite-structure or calcitestructure crystals (Figs. 1 and 2), which may be related to the significantly lower solubility of ANC than ACC.

After 300 days of dissolution in NDW and CSW, no obvious morphological variations were found for pure calcite (CN-00) and nickel carbonates (CN-10 and Rhawn's reagent) (Fig.S2 and Fig.S3-Supplementary material). In according with the XRD results (Fig. 1), the synthesized solids of  $X_{Ni} = 0.10 - 0.90$  (CN-01-CN-09) after dissolution were the mixture of calcite-structure solid phases, aragonite-structure solid phases and amorphous solids of nickel carbonates (Figs. S2 and S3-Supplementary material), indicating a transformation of the calcite-structure to the aragonite-structure during dissolution, which would affect the surface area of the original material and consequently the amount of time required for aqueous Ca and Ni concentrations to stabilize. The aragonite-structure solid phases were flattened prismatic or tabular (Fig. 4).

EDS analyses indicated that the calcite-structure solid phases had a very low  $X_{Ni}$  (0.000–0.228) depending on the  $X_{Ni}$  of the starting solutions and the amorphous solids had a higher  $X_{Ni}$  (0.739–1.000) (Table 2 and Fig. 3). After 300 days of dissolution in NDW and CSW, the aragonite-structure solid phases formed had a relatively lower  $X_{Ni}$  values than the calcite-structure solid phases. The  $X_{Ni}$  values of the amorphous Ca-bearing nickel carbonates in the solid residuals increased from 0.776–0.918 to 0.859–0.975 and 0.814–0.980 after 300 days of dissolution of the synthesized solids (CN-06–CN-09) in NDW and CSW, respectively, showing a prior retaining of Ni in the amorphous solids, i.e., the main component of the solid phases with high  $X_{Ni}$  (Table 2 and Fig. 4).

## Change of the water solution

Upon dissolution of the solids of  $X_{Ni}$  = 0.10–0.90 (CN-01–CN-09) in NDW, the pHs of water solutions increased



Fig. 3 SEM–EDS analysis of the  $({\rm Ca}_{1-x}{\rm Ni}_x){\rm CO}_3$  solid solutions before dissolution

quickly from 6.16 to 8.95–9.72 within 1 h and then decreased gradually to a stable state of 8.12–8.32 after 240–300 days (Fig. 5). Commonly, the Ca concentrations of water solutions increased rapidly to 0.581–0.643 mmol/L within 60 days and then increased slowly to a stable state of 0.592–0.665 mmol/L after 240–300 days for the solids with lower  $X_{Ni}$  (CN-01–CN-03), while they increased rapidly to



Fig. 4 SEM–EDS analysis of the (Ca $_{1-x}$ Ni<sub>x</sub>)CO<sub>3</sub> solid solutions (CN-05) before dissolution (**a**), after dissolution in N<sub>2</sub>-degassed water (b) and in CO<sub>2</sub>-saturated water (**c**)

0.750–0.999 mmol/L within 30–50 days and then declined progressively to a stable state of 0.608–0.721 mmol/L after 240–300 days for the solids with higher  $X_{\rm Ni}$  (CN-04–CN-09). The Ni concentrations of water solutions varied increasingly to a stable state of 0.073–0.290 mmol/L after 240–300 days for the solids with lower  $X_{\rm Ni}$  (CN-01–CN-05), while they increased rapidly to 0.349–0.498 mmol/L in 50 days and then declined gradually to

a stable state of 0.273–0.430 mmol/L after 240–300 days for the solids with higher  $X_{\rm Ni}$  (CN-06–CN-09) (Fig. 5). The HCO<sub>3</sub>+CO<sub>3</sub> concentrations of water solutions varied increasingly to a stable state of 1.208–2.093 mmol/L after 240–300 days for the solids with lower  $X_{\rm Ni}$  (CN-01–CN-05), while they increased rapidly to 2.814–3.692 mmol/L in 20–30 days and then declined slowly to a stable state of 2.428–3.021 mmol/L after 240–300 days for the solids with higher  $X_{\rm Ni}$  (CN-06–CN-09) (Fig. 5).

Upon dissolution of the solids with  $X_{Ni}=0.10-0.90$  (CN-01–CN-09) in CSW, the pHs of water solutions increased gradually from 4.96 to a stable state of 7.72–8.01 after 240–300 days (Fig. 6). Commonly, the Ca concentrations of water solutions increased rapidly to 1.705–9.053 mmol/L within 5–50 days and then varied increasingly to a stable state of 1.094–3.738 mmol/L after 240–300 days. The Ni concentrations of water solutions varied increasingly to 1.048–8.015 mmol/L within 40–90 days and then declined gradually to a stable state of 0.831–4.300 mmol/L after 240–300 days (Fig. 6). The HCO<sub>3</sub>+CO<sub>3</sub> concentrations of water solutions varied increasingly to 16.328–19.882 mmol/L within 5–50 days s and then declined gradually to a stable state of 4.443–12.866 mmol/L after 240–300 days (Fig. 6).

The largest pHs of water solutions were observed in dissolution of the solid samples CN-03 and CN-04 (Fig.S4-Supplementary material). The  $HCO_3 + CO_3$  concentration of water solution was positively related with the Ca concentration of water solutions. The Ca, Ni and  $HCO_3 + CO_3$ concentrations of water solutions increased with the increase in X<sub>Ni</sub> of the solids (Fig.S4-Supplementary material). During dissolution in NDW, the aqueous Ni/(Ca+Ni) mol ratios (X<sub>Ni2+,aq</sub>) were noticeably lesser than the Ni/ (Ca + Ni) atomic ratios of the solid solutions  $(X_{Ni})$ , except for dissolution of the solids of lower X<sub>Ni</sub> (CN-01–CN-03) after 80 days. On the contrary, during dissolution in CSW, the aqueous Ni/(Ca + Ni) mol ratios  $(X_{Ni2+,aq})$  were noticeably larger than the solid X<sub>Ni</sub>, except for dissolution of the solids of higher  $\rm X_{Ni}$  (CN-07–CN-09) after 2–210 days (Fig. S5—Supplementary material).

The stoichiometric dissolution of the calcium-nickel carbonate solid solutions  $[(Ca_{1-x}Ni_x)CO_3]$  can be given as:

$$(Ca_{1-x}Ni_x)CO_3 = (1-x)Ca^{2+}{}_{(aq)} + xNi^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$$
(7)

$$Ca^{2+} + OH^{-} = Ca(OH)^{+}$$
 (8)

$$Ni^{2+} + nOH^{-} = Ni(OH)_n^{(2-n)}$$
 (n = 1 ~ 3)  
(9)

$$Ca^{2+} + H^+ + CO_3^{2-} = CaHCO_3^+$$
 (10)



Fig. 5 Change of the aqueous pH and components during the dissolution of the  $(Ca_{1-x}Ni_x)CO_3$  solid solutions in  $N_2$ -degassed water

$$Ni^{2+} + H^{+} + CO_3^{2-} = NiHCO_3^{+}$$
(11)

$$\text{CO}_3^{2-} + n\text{H}^+ = \text{H}_n\text{CO}_3^{(2-n)-}$$
 (n = 1, 2) (12)

$$Ca^{2+} + CO_3^{2-} = CaCO_3^0$$
 (13)

$$Ni^{2+} + CO_3^{2-} = NiCO_3^0$$
 (14)

Initially, the solids dissolved congruently (Eq. (7)). For dissolution in NDW, the formation of Ca(OH)<sup>+</sup> and Ni(OH)<sub>n</sub><sup>(2-n)</sup> [Eqs. (8) and (9)] resulted in OH<sup>-</sup> consumption and so a decrease in pHs of water solutions. For dissolution in CSW, the formation of CaHCO<sub>3</sub><sup>+</sup>, NiHCO<sub>3</sub><sup>+</sup> and H<sub>n</sub>CO<sub>3</sub><sup>(2-n)-</sup> [Eqs. (10)–(12)] resulted in H<sup>+</sup> consumption and so an increase in pHs of water solutions. The obvious change of pHs indicated that the dissolution was initially controlled by pH of water solution [45, 46]. More calcium was released into water solution than nickel, except for dissolution of the solids of higher X<sub>Ni</sub> in CSW, indicating an incongruent dissolution of the solids

[46] and a dissolution–recrystallization at the solid-water interface, and nickel preferred to nucleate on the solid surface to form a new solid phase [46, 47].

## Determination of the stoichiometric solubility

The dissolution experiments were executed until the difference in IAPs (Ion activity products) computed from the last three water solutions (i.e., 240 d, 270 d and 300 d) were generally  $<\pm 0.25$  log units, and by now a stable state was presumably approached [32]. The analysis result and the computed log IAPs at the last stable state ( $\approx \log K_{sp}$ ) for the calcium-nickel carbonate solid solutions [(Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub>] are listed in Tables 3 and 4, which indicates that the (Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub> solid solutions were less soluble in NDW than in CSW.

For dissolution in NDW and CSW at 25 °C, the mean log IAPs at the last stable state ( $\approx \log K_{sp}$ ) were estimated for calcite [CaCO<sub>3</sub>] to be  $-8.65\pm0.04$  and  $-8.16\pm0.11$ , respectively (Tables 3 and 4). The result is in accord with the  $K_{sp}$  data for calcite reported in literature. For example, the log  $K_{sp}$  of -8.48 is chosen in both the minteq.



Fig. 6 Chang of the aqueous pH and components during the dissolution of the (Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub> solid solutions in CO<sub>2</sub>-saturated water

Table 3 Solubility for the (Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub> solid solutions after 240–300 d dissolution in N<sub>2</sub>-degassed water at 25 °C

Sample	Calcite-stru	ucture phase	Aragonite-	structure phase	Amorphous phase	
	*X <sub>Ni</sub>	Mean log IAP	*X <sub>Ni</sub>	Mean log IAP	*X <sub>Ni</sub>	Mean log IAP
<sup>a</sup> CN-00	0.000	$-8.65 \pm 0.04$				
<sup>b</sup> CN-00	0.000	$-8.70 \pm 0.06$				
CN-01	0.108	$-8.48 \pm 0.09$	0.022	$-8.39 \pm 0.10$		
CN-02	0.142	$-8.39 \pm 0.00$	0.068	$-8.33 \pm 0.01$	0.690	$-8.85 \pm 0.02$
CN-03	0.144	$-8.36 \pm 0.01$	0.096	$-8.32 \pm 0.01$	0.701	$-8.77 \pm 0.02$
CN-04	0.176	$-8.26 \pm 0.01$	0.128	$-8.23 \pm 0.01$	0.787	$-8.68 \pm 0.02$
<sup>a</sup> CN-05	0.199	$-8.27 \pm 0.01$	0.131	$-8.23 \pm 0.01$	0.821	$-8.65 \pm 0.03$
<sup>b</sup> CN-05	0.197	$-8.25 \pm 0.02$	0.134	$-8.22\pm0.01$	0.821	$-8.62 \pm 0.03$
CN-06	0.195	$-8.21 \pm 0.03$	0.127	$-8.17 \pm 0.03$	0.859	$-8.61 \pm 0.03$
CN-07	0.178	$-8.19 \pm 0.01$	0.166	$-8.18 \pm 0.01$	0.894	$-8.58 \pm 0.02$
CN-08			0.223	$-8.23 \pm 0.01$	0.968	$-8.59 \pm 0.02$
CN-09			0.197	$-8.22 \pm 0.02$	0.975	$-8.52\pm0.01$
<sup>a</sup> CN-10					1.000	$-8.50\pm0.02$
<sup>b</sup> CN-10					1.000	$-8.51 \pm 0.02$
Rhawn's NiCO <sub>3</sub>					1.000	$-8.39 \pm 0.01$

 $^{\rm a,\,b}$  Duplication; \*EDS surface composition after dissolution

Sample	Calcite-stru	ucture phase	Aragonite	-structure phase	Amorphous phase	
	*X <sub>Ni</sub>	Mean log IAP	*X <sub>Ni</sub>	Mean log IAP	*X <sub>Ni</sub>	Mean log IAP
<sup>a</sup> CN-00	0.000	-8.16±0.11				
<sup>b</sup> CN-00	0.000	$-8.10 \pm 0.08$				
CN-01	0.084	$-7.93 \pm 0.04$	0.007	$-7.89 \pm 0.05$		
CN-02	0.103	$-7.87 \pm 0.02$	0.019	$-7.86 \pm 0.02$		
CN-03	0.188	$-7.67 \pm 0.03$	0.116	$-7.67 \pm 0.04$	0.697	$-7.72 \pm 0.03$
CN-04	0.238	$-7.36 \pm 0.03$	0.166	$-7.33 \pm 0.03$	0.769	$-7.58 \pm 0.02$
<sup>a</sup> CN-05	0.219	$-7.47 \pm 0.01$	0.224	$-7.47 \pm 0.01$	0.789	$-7.68 \pm 0.04$
<sup>b</sup> CN-05	0.228	$-7.49 \pm 0.01$	0.221	$-7.49 \pm 0.01$	0.792	$-7.68 \pm 0.03$
CN-06	0.212	$-7.40 \pm 0.02$	0.215	$-7.40 \pm 0.02$	0.814	$-7.61 \pm 0.01$
CN-07	0.184	$-7.48 \pm 0.02$	0.124	$-7.47 \pm 0.02$	0.886	$-7.61 \pm 0.02$
CN-08			0.080	$-7.58 \pm 0.03$	0.940	$-7.63 \pm 0.01$
CN-09					0.980	$-7.63 \pm 0.03$
<sup>a</sup> CN-10					1.000	$-7.69 \pm 0.03$
<sup>b</sup> CN-10					1.000	$-7.62 \pm 0.01$
Rhawn's NiCO <sub>3</sub>					1.000	$-7.66 \pm 0.03$

Table 4 Solubility for the (Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub> solid solutions after 240-300d dissolution in CO<sub>2</sub>-saturated water at 25 °C

<sup>a, b</sup> Duplication; \*EDS surface composition after dissolution

v4.dat database [48] and the phreeqc.dat database [30, 49]. Calcite shows a very well-defined solubility product constant (log  $K_{sp}$ ) that lies between -8.30 [50] and -8.58 [51].

For dissolution in NDW and CSW at 25 °C, the mean log IAPs at the last stable state ( $\approx \log K_{sp}$ ) were determined for the synthesized nickel carbonate [NiCO<sub>3</sub>] to be  $-8.50\pm0.02$  and  $-7.69\pm0.03$ , respectively, which were slightly smaller than  $-8.39 \pm 0.01$  and  $-7.66 \pm 0.03$  for the nickel carbonate [NiCO<sub>3</sub>, the Rhawn's reagent] (Tables 3 and 4). Significant difference in the log  $K_{sp}$  values for gaspeite [anhydrous nickel carbonate, NiCO<sub>3</sub>] can be found in literature, e.g., -6.87 [52]; -11.2±0.3 [53, 54] and  $-\,11.03\pm0.18$  [55]. Consequently, different log  $K_{\rm sp}$  values for gaspeite [anhydrous nickel carbonate, NiCO<sub>3</sub>] were applied by different databases. For instance, whereas the database minteq.v4.dat [48] and the database phreeqc.dat [30, 49] compile a log  $K_{sp}$  of -6.84, the log  $K_{sp}$  of -11.2 is accepted in the Nagra/PSI database [53]. The discrepancy among the literature  $K_{sp}$  values was prominently due to the absence of the experimental data, the disparity of the aqueous speciation reactions [56] and the impurity in the solids used [57]. Generally, amorphous nickel carbonate (ANC) is significantly less soluble than amorphous calcium carbonate (ACC), which was reported to have the ion activity product (log IAP value) at 25 °C of -6.393 [58], -6.28 [59], -7.51 for "calcite-like" ACC and -7.42 for "vaterite-like" ACC [60].

In respect to the bulk composition of the  $(Ca_{1-x}Ni_x)$ CO<sub>3</sub> solid solutions, the log IAPs at the last stable state showed the highest value when  $X_{Ni} = 0.10 \sim 0.30$  (Tables 3 and 4; Fig.S6—Supplementary material). Generally, the log IAPs at the last stable state increased with the increase in  $X_{Ni}$  in respect to the Ni-bearing calcite solid phases, the aragonite-structure solid phases and the fine particles of amorphous calcium-bearing nickel carbonate (Tables 3 and 4; Fig.S6—Supplementary material).

#### Solid solution-aqueous solution interaction

A comprehensive understanding of the equilibrium performance in a SSAS system needs the data of solid-phase activity coefficients, which is challenging due to limited data on excess free energy functions for solid solutions at low-temperature. To address this issue, researchers have often relied on miscibility gaps observed in mineral compositions found in natural settings to estimate mixing parameters when experimental data are lacking [61].

In this work, the EDS analysis showed that the largest Ni content in the calcite phase from sample CN-04 was measured to be  $X_{Ni}=0.238$ , while the lowest Ni content in the fine particles of amorphous calcium-nickel carbonate from the sample CN-02 was found to be  $X_{Ni}=0.690$  (Table 2). By utilizing the MBSSAS program [61], the dimensionless Guggenheim parameters for the calcium-nickel carbonate solid solutions [(Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub>] at 25 °C were predicted to  $a_0=2.14$  and  $a_1=-0.128$  based on a miscibility gap ranging from  $X_{Ni}=0.238$  to 0.690. In computing the thermodynamic properties of a solid solution system, MBSSAS uses only the first two parameters  $a_0$  and  $a_1$  of Guggenheim's excess-free-energy equation [61].

Figures 7 and 8 depict the Lippmann diagram for the calcium-nickel carbonate solid solutions  $[(Ca_{1-x}Ni_x)]$ 

 $CO_3$ ] at 25 °C. The calculations were based on values of  $a_0$ =2.14 and  $a_1$ =-0.128, along with the  $K_{sp}$  data calculated from the dissolution in NDW and CSW for both calcite [CaCO<sub>3</sub>] and NiCO<sub>3</sub>. In addition to pure calcite (X<sub>Ni</sub>=0.000) and pure NiCO<sub>3</sub> (X<sub>Ni</sub>=1.000), the minimum stoichiometric saturation curves for the Ni-bearing calcite, Ni-bearing aragonite and the amorphous Ca-Ni carbonate of the sample CN-05 were also computed and plotted on the diagram alongside the *solutus* curve and the *solidus* curve.

The little disparity in the  $K_{sp}$  values of CaCO<sub>3</sub> and NiCO<sub>3</sub> resulted in a very small separation of the *solidus* curve from the *solutus* curve. The *solutus* curve is very close to the saturation curve for pure NiCO<sub>3</sub> owing to the restricted range of the solid constituents at equilibrium with the water composition defined by the *solutus* curve [34]. The saturation curve for CaCO<sub>3</sub> and NiCO<sub>3</sub>



**Fig. 7** Lippmann diagram for the non-ideal (Ca<sub>1-x</sub>Ni<sub>x</sub>)CO<sub>3</sub> solid solutions together with the plot of some stoichiometric saturation curves and the experimental data to show the aqueous evolution during the dissolution in N<sub>2</sub>-degassed water at 25 °C



**Fig. 8** Lippmann diagram for the non-ideal  $(Ca_{1-x}Ni_x)CO_3$  solid solutions together with the plot of some stoichiometric saturation curves and the experimental data to show the aqueous evolution during the dissolution in CO<sub>2</sub>-saturated water at 25 °C

consistently remained above the *solutus* curve; thus, any solution in thermodynamic equilibrium with respect to any  $(Ca_{1-x}Ni_x)CO_3$  solid is always undersaturated concerning CaCO<sub>3</sub> and NiCO<sub>3</sub>. In fact, there exists a certain threshold for CaCO<sub>3</sub> and CoCO<sub>3</sub> activity coefficients beyond which an unstable or metastable solid solution forms, preventing an water solution from reaching thermodynamic equilibrium. The upper limit depicted on the *solutus* curve by both CaCO<sub>3</sub> and NiCO<sub>3</sub> saturation curves can also be described by considering that the pure endmember will invariably possess larger free energy compared to the solid containing a non-zero proportion of substitutional impurity [34].

In addition, the experimental points were also illustrated as  $({Ca^{2+}} + {Ni^{2+}}){CO_3^{2-}}$  against  $X_{Ni^{2+},aq}$  upon dissolution in NDW (Fig. 7; Fig.S7—Supplementary material) and CSW (Fig. 8; Fig.S8—Supplementary material).

Upon dissolution of the  $(Ca_{1-x}Ni_x)CO_3$  solid solutions with  $X_{Ni} = 0.10 \sim 0.90$  (CN-01–CN-09) in NDW (Fig. 7; Fig.S7–Supplementary material), it was observed that the dissolution of the  $(Ca_{1-x}Ni_x)CO_3$  solids occurred non-stoichiometrically over time, the "total activity product" ( $\Sigma\Pi_{SS}$ ) decreased slightly with the interaction time, the data points of the water solutions moved from left to right and finally approached to the intersection points of the minimum stoichiometric saturation curves for the Ni-bearing calcite, Ni-bearing aragonite and the amorphous Ca-Ni carbonate for each solid sample. The Ni<sup>2+</sup> preferred to dissolve into the water solution, while Ca<sup>2+</sup> SS and AS consistently resulted in an increase in aqueous  $\mathrm{Ni}^{2+}$  concentration and maximum Ca content in the solid.

Upon dissolution of the solids with  $X_{Ni} = 0.10 - 0.90$ (CN-01-CN-09) in CSW (Fig. 8; Fig.S8-Supplementary material), the "total activity product" ( $\Sigma\Pi_{SS}$ ) increased obviously with the interaction time, the data points of the water solutions moved from left to right for the solids with a low X<sub>Ni</sub> (CN-01–CN-03), and finally approached to the intersection points of the minimum stoichiometric saturation curves for the Ni-bearing calcite, Ni-bearing aragonite and the amorphous Ca-Ni carbonate for each solid sample. This means that the Ni<sup>2+</sup> preferred to dissolve into the water solution, while Ca2+ preferred to remain in the solid. In contrary, for the solids with a high  $X_{Ni}$  (CN-04–CN-09), the "total activity product" ( $\Sigma\Pi_{SS}$ ) increased obviously with the interaction time, the data points of the water solutions moved from left to right and finally approached to the intersection points of the minimum stoichiometric saturation curves for the Ni-bearing calcite, Ni-bearing aragonite and the amorphous Ca-Ni carbonate for each solid sample. The Ca<sup>2+</sup> preferred to dissolve into the water solution, while Ni<sup>2+</sup> preferred to remain in the solid.

## Conclusions

This is the first comprehensive study to give the reliable thermodynamic data about Ca-Ni carbonates for modeling the transportation and distribution of nickel in environment. During dissolution of the synthesized  $(Ca_{1-x}Ni_x)CO_3$  solid solutions (Ni-calcite, amorphous Ca-bearing NiCO<sub>3</sub> and their mixtures) in water, the solid phases with the aragonite-type structure was detected, indicating a transformation of the calcite-type structure and the Ca-bearing nickel carbonates to the aragonite-type structure.

The  $(Ca_{1-x}Ni_x)CO_3$  solid solutions were less soluble in NDW than in CSW. For dissolution in NDW and CSW at 25 °C, the mean log IAPs at the last stable state ( $\approx \log K_{sp}$ ) were estimated to be  $-8.65\pm0.04$  and  $-8.16\pm0.11$  for calcite  $[CaCO_3]$ ,  $-8.50\pm0.02$  and  $-7.69\pm0.03$  for the synthesized nickel carbonates [NiCO<sub>3</sub>], respectively. In respect to the bulk composition of the solids, the log IAPs at the last stable state showed the highest value when  $X_{Ni}=0.10-0.30$ . Generally, the log IAPs at the last stable state increased with the increase in  $X_{Ni}$  in respect to Ni-bearing calcite, Ni-bearing aragonite and amorphous Ca-bearing nickel carbonate.

The plotting of the experimental data on the Lippmann diagrams for the calcium-nickel carbonate solid solutions [ $(Ca_{1-x}Ni_x)CO_3$ ] with the Guggenheim parameters of  $a_0=2.14$  and  $a_1=-0.128$  predicted from a miscibility gap ranging from X<sub>Ni</sub>=0.238 to 0.690 indicated that the

solids dissolved incongruently and the aqueous Ca and Ni concentrations at the lats stable state of dissolution were simultaneously limited by the minimum stoichiometric saturation curves for the Ni-bearing calcite, Ni-bearing aragonite and the amorphous Ca-Ni carbonate.

## Abbreviations

NDW	N <sub>2</sub> -degassed water
CSW	CO <sub>2</sub> -saturated water
ICP-OES	Inductively coupled plasma-Optical emission spectrometer
XRD	X-ray diffractometer
ICDD	International Center for Diffraction Data
FE-SEM	Field emission scanning electron microscope
EDS	Energy-dispersive spectrometer
IAP	lon activity product
K <sub>sp</sub>	Solubility product constant
SSAS	Solid solution-aqueous solution

## Supplementary Information

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Supplementary Material 1.

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## Author contributions

ZZ and YZ initiated the arrangement of the experiment and drafted the manuscript. CM, XN, FX, PN, FL and LZ carried out most of the experiment and the XRD, FT-IR and FE-SEM–EDS analyses. ST and ZK made their effort to interpretate the data. All authors read and approved the final manuscript.

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#### Availability of data and materials

No datasets were generated or analysed during the current study.

#### Declarations

**Ethics approval and consent to participate** Not applicable.

## **Competing interests**

The authors declare no competing interests.

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