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The long-term stability of calcium arsenates: Implications for phase transformation and arsenic mobilization

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ABSTRACT

It is well known that calcium arsenates may not be a good choice for arsenic removal and immobilization in hydrometallurgical practices. However, they are still produced at some plants in the world due to various reasons. Furthermore, calcium arsenates can also naturally precipitate under some specific environments. However, the transformation process of poorly crystalline calcium arsenates (PCCA) and the stability of these samples under atmospheric CO₂ are not yet well understood. This work investigated the transformation process of PCCA produced by using different neutralization reagents (CaO vs. NaOH) with various Ca/As molar ratios at pH 7–12 in the presence of atmospheric CO₂. After aging at room temperature for a period of time, for samples neutralized with NaOH and precipitated at pH 10 and 12, release of arsenic back into the liquid phase occurred. In contrast, for the samples precipitated at pH 8, the aqueous concentration of arsenic was observed to decrease. XRD, Raman, and SEM results suggested that the formation of various types of crystalline calcium carbonates and/or calcium arsenates controls the arsenic behavior. Moreover, the application of lime may enhance the stability of the generated PCCA. However, no matter what neutralization reagent is used, the stability of the generated PCCA is still of concern.

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Introduction

Arsenic (As) is a toxic metalloid that is commonly present in more than 300 minerals (Drahota and Filippi, 2009; Nazari et al., 2017; Riveros et al., 2001). As-containing wastewater can be generated from arsenic-bearing minerals or concentrates and enter into mineral processing solutions and effluents during the smelting of metals (Nazari et al., 2017; Riveros et al., 2001). Precipitation

is the preferred choice when a relatively high concentration of As has to be processed, such as those encountered in hydrometallurgical processes (Ke et al., 2017; Nazari et al., 2017; Riveros et al., 2001; Twidwell and McCloskey, 2011).

Fe^{III}–As^V coprecipitates, scorodite, and calcium arsenates are the typically produced As-bearing wastes (Bothe and Brown, 1999a; Demopoulos et al., 1995; Violante et al., 2007). The long-term stabilities of each of these As-bearing solids

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depends on the choice of operational conditions such as pH, metal/As molar ratio, neutralization reagent (CaO or NaOH) as well as the conditions of the storage environments, such as temperature, atmospheric CO₂, and oxic or anaerobic conditions (Das et al., 2011; Jia and Demopoulos, 2008; Jia et al., 2012; Moldovan and Hendry, 2005; Robins and Tozawa, 1982; Robins et al., 1988). Ferric arsenates are stable at low pH and are more suitable for iron-rich As-containing wastewaters. By contrast, calcium arsenates exhibit solubility minima at high pH and are a better choice for iron-deficient conditions (Lei et al., 2017; Swash and Monhemius, 1996; Robins et al., 1988). Hence, precipitation of As with lime is still widely practiced in metallurgical industries, and also used for the recovery of arsenic compounds (Riveros et al., 2001; Castro and Muñoz, 2000). Calcium arsenate compounds can also be formed at an industrial site from the interaction of run-off waters with As-bearing sulfidic wastes and underlying limestone (Juillot et al., 1999), or as a result of efflorescence on the walls of abandoned underground mines, such as deposits observed in the Czech Republic (Ondruš et al., 1997). Thousands of tons of calcium arsenate wastes are still being produced and stored in surface environments all over the world (Nazari et al., 2017; Riveros et al., 2001; Valenzuela, 2000).

Previous literature has reported the formation of crystalline calcium arsenates such as weillite, haidingerite, pharmacolite, saintfeldite, vladimirite, johnbaumite (Pierrot, 1964; Swash and Monhemius, 1996), Ca₄(OH)₂(AsO₄)₂·4H₂O, Ca₃(AsO₄)₂·3.67H₂O, and Ca₃(AsO₄)₂·4.25H₂O (Bothe and Brown, 1999b) under various conditions. The solubility and stability of a variety of calcium arsenates have also been evaluated (Nishimura and Robins, 1998; Swash and Monhemius, 1995). Furthermore, the solubility product constants and free energies of formation of various types of calcium arsenates were determined by Bothe and Brown (1999b). However, in spite of all these works, there still exists a lack of knowledge about the stability of poorly crystalline calcium arsenates during their long-term storage. The only study that considered the long-term stability (4 years of aging) of calcium arsenates at Ca/As molar ratio of 0.8–4.0 at room temperature and in the absence of atmospheric CO₂ was conducted by Bothe and Brown (1999a). The solid phases transformed into various types of calcium arsenates such as Ca₅(AsO₄)₃OH, Ca₃(AsO₄)₂·4.25H₂O, and Ca₄(OH)₂(AsO₄)₂·4H₂O under alkaline conditions. The final aqueous As concentration varied over a wide range of 0.01–710 mg/L depending upon the molar ratios of Ca/As, pH, and aging times used. The above experiments were conducted under the protection of N₂ atmosphere and the source of Ca was derived by calcining Ca(OH)₂ or CaCO₃ at 1000°C in order to avoid the interference of atmospheric CO₂ (Bothe and Brown, 1999a, 1999b; Nishimura and Robins, 1998; Swash and Monhemius, 1996). However, in industrial practice as well as under conditions that may occur naturally to produce calcium arsenate, atmospheric CO₂ cannot be excluded. It has been demonstrated that calcium arsenate compounds decompose slowly in contact with atmospheric CO₂ to form calcium carbonate, subsequently leading to strong As release into the liquid phase (Nishimura et al., 1983, 1985; Robins and Tozawa, 1982). However, the redistribution of As between liquid and solid phases during this transformation process has not yet been well established.

CaO is a commonly used neutralization reagent in various industrial practices (Conner, 1990; Lieberman et al., 2018; Nazari et al., 2017; Riveros et al., 2001; Yao et al., 2018, 2019), while samples generated by using NaOH were the control group in this work. In addition, it has been illustrated that the Ca–As solids formed are different if different neutralization reagents are used in the absence of atmospheric CO₂ (Bothe and Brown, 1999a). Therefore, it is necessary to systematically investigate the crystallization process of PCCA at a range of pH values and Ca/As molar ratios by using different neutralization reagents.

The aims of this study were to quantitatively investigate the release of As from calcium arsenate wastes during long-term storage processes and to discover the phase transformations that occur in Ca–As slurries at room temperature in the presence of atmospheric CO₂.

1. Materials and methods

All chemicals were used as received without further purification, and all solutions were prepared using deionized (DI) water. All glassware was cleaned by soaking in dilute HNO₃ (5%) overnight and rinsing thoroughly with DI water. The stock solutions of As and Ca were prepared from As₂O₅ and Ca(NO₃)₂·4H₂O sources, respectively. The reagents were purchased from Sigma–Aldrich and used without further purification. CO₂ in the air was not excluded from the stock solutions used for preparing the samples and the subsequent aging process in order to simulate the real environment where calcium arsenates are stored. Arsenic used in this investigation is assumed to be As^V unless otherwise specified. The meaning of the long-term stability of the calcium arsenates in our work refers to the As concentration in the liquid phase and whether this exceeds the maximum contaminant level (MCL) for As discharge (e.g., 5 mg/L) (Riveros et al., 2001).

1.1. Synthesis and aging treatment of Ca–As precipitates (neutralized by NaOH)

The precipitation procedure involved direct neutralization of the separately prepared Ca and As solutions at various pH values via simultaneous addition of 1 mol/L NaOH solution under vigorous mechanical stirring. Briefly, 200 mL DI water was poured into a 1000 mL beaker and then the As solution was added. The pH of the solution was adjusted to the pre-set value (e.g., 8, 10, and 12) with 1 and/or 0.1 mol/L NaOH solutions. Different amounts of the Ca solution prepared in another flask were introduced by peristaltic pump to the As solution to give final Ca/As molar ratios of 1, 2, and 4. Then the neutralization reagent (a NaOH solution) was added to the mixture (using a pipette) as soon as the Ca solution was dropped into the beaker. The flow velocity was controlled at 1.3 mL/min and the entire precipitation process lasted for about 1 hr. The pH of the slurry was kept constant by using 1 or 4 mol/L HNO₃ solution. After stabilization for 1 hr at room temperature, the slurry was transferred to tightly capped conical flasks and allowed to age at room temperature. The total volume of the slurry was 500 mL, with 1000 mg/L as the initial As concentration. These samples are designated as Ca–As₁ slurries.

The whole aging process was conducted for at least 120 days, and in order to determine the transformation products, some samples were aged up to 1100 days. The pH was checked and controlled at a constant value for each sample. The slurries (30 mL) were collected at pre-determined time intervals. After centrifugation at 4500 r/min for 5 min, the supernatant was filtered through a 0.22- μm membrane and then analyzed for aqueous As and Ca concentrations. The solid residue was rinsed with 120 mL DI water under magnetic stirring for at least 1 hr, repeated at least 4 times, air-dried and stored at room temperature for further characterization.

The long-term stability evaluation method used in our work is reasonable because we wanted to mimic the transformation process for the calcium arsenates when they are disposed of in tailings, and this method has already been used for evaluating the long-term stability of other As-bearing waste solids which also stored in tailings (Jia and Demopoulos, 2008; Jia et al., 2012).

1.2. Synthesis and aging treatment of Ca–As precipitates (neutralized by CaO)

The acidic As solution was neutralized by slaked lime (CaO) to pH 12 in a 2500 mL beaker with the final volume of 1500 mL. Before the neutralization process, dilute H_2SO_4 solution was also added to the acidic As solution to give a final H_2SO_4 concentration of 1 mol/L in order to simulate the waste solids generated from hydrometallurgical practices (Nazari et al., 2017; Riveros et al., 2001). After having been stabilized for 2 days under vigorous mechanical stirring (pH maintained constant by using slaked lime), equal volumes (400 mL) of the Ca–As slurry were transferred into three beakers separately. The pH of these samples was adjusted to 8, 10, and 12, respectively, with 5 mol/L H_2SO_4 solution or slaked lime, and the final volume of these samples was 500 mL at a total As concentration of 1600 mg/L. The samples are designated as Ca–As₂ slurries. These slurries were aged at room temperature for at least 1120 days and afterwards centrifuged, washed, and air-dried. The concentration of As and Ca in the supernatant was analyzed and the solid phase was subjected to material characterization.

Reference compounds used for material characterization were PCCA and calcite. For the synthesis of PCCA, the stock solutions of As and Ca were introduced simultaneously into a 100 mL beaker by a peristaltic pump at a molar ratio of 1 with an initial As concentration of 1000 mg/L, and the pH was maintained at 12 by 1 mol/L NaOH solution. After being allowed to stabilize for 1 hr, the solid was washed and air-dried. Calcite was also purchased from Sigma–Aldrich and used without further purification.

1.3. Solid characterization

X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM) were employed to identify the nature of the aged solids. XRD analysis was performed on a Rigaku D/max 2400 X-ray diffractometer equipped with a rotating anode, copper target (λ Cu $K_{\alpha 1}$ = 1.5418 Å), crystal graphite monochromator and scintillation detector. The equipment was run at 56 kV and 182 mA by step scanning

from 10° to 90° 2 θ with increments of 0.04° 2 θ and a scan step time of 1.2 sec.

Raman spectra were collected on a Thermo DXR Raman microscope equipped with a solid laser diode operating at 780 nm and a 400 lines/mm grating. The data were obtained in the range of 60–2000 cm^{-1} with an energy resolution of 4 cm^{-1} . The laser beam produced a spot size of 3 μm in diameter using the 10 \times short-distance objective. The scans were collected at 3.33% (0.8 mW) power of the laser output at the microscope exit to avoid phase transformation.

The morphologies and elemental composition in selected areas of the solid samples were analyzed on a FEI Quanta 250 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDS). All the samples were mounted on pin stubs by use of double-sided carbon tape, sputter-coated with gold and imaged at 30 kV.

1.4. Determination of As and Ca concentrations in the liquid phase

Aqueous As concentrations were determined on an atomic fluorescence spectrophotometer coupled with a hydride generator (HG-AFS) (Xu et al., 2011; Zhao et al., 2011). The concentration of Ca was determined by using inductively coupled plasma–atomic emission spectroscopy (ICP-AES, Thermo-6300). The detection limits of the instruments for As and Ca were 0.01 $\mu\text{g/L}$ and 0.02 mg/L, respectively.

2. Results and discussion

2.1. The release of As during the aging of the Ca–As₁ precipitates

The concentration of As in the liquid phase over the course of aging of the Ca–As₁ slurries (NaOH as neutralization reagent) was monitored and presented in Fig. 1. The results indicated that for the sample prepared at pH 7 with a Ca/As = 4, almost all of the As still remained in the liquid phase, and there was no solid formed under these experimental conditions even after aging at room temperature for 380 days. This was also the case for samples prepared at pH 8 with Ca/As molar ratios of 2 and 4. The solubility of the various forms of calcium arsenates controls this precipitation process (Bothe and Brown, 1999b). The relatively low initial As concentration and near-neutral pH value as well as the room temperature used in this work may be the reasons why no solid was observed for these samples (Bothe and Brown, 1999b; Nishimura and Robins, 1998; Swash and Monhemius, 1996). Therefore, no solid characterization was done for these samples. For the samples precipitated at pH 12 with Ca/As molar ratios of 1, 2, and 4, the As concentration in the liquid phase first decreased and then increased during the aging process at room temperature. For example, the aqueous As concentration decreased from 7.5 to 4.6 mg/L after being aged for 80 days for the Ca/As = 4 sample, and then increased to 13.3 mg/L if the solid continued to age for 380 days at room temperature. This phenomenon was more evident for the Ca/As = 2 solid, where the As aqueous concentration decreased from 15.2 to 11.8 mg/L after aging for 7 days and slightly

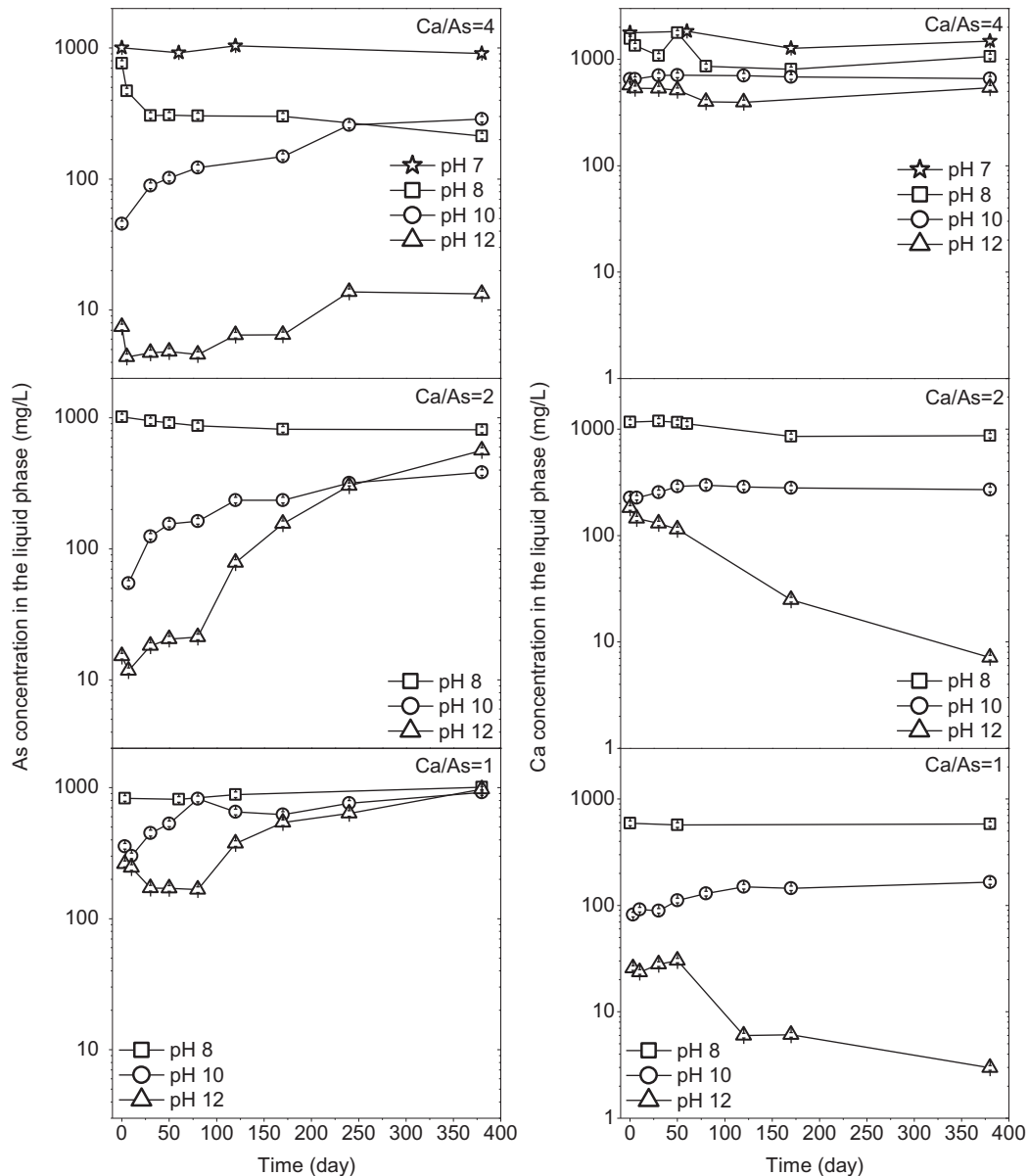


Fig. 1 – As and Ca concentration in the liquid phase over the course of aging of Ca–As₁ slurries (initial As concentration 1000 mg/L, Ca/As = 1, 2, and 4) at various pH values, 25°C.

increased to 21.3 mg/L after being aged for 80 days; however, this value sharply increased to 565 mg/L when after further aging for 380 days. As for the samples precipitated at pH 10, generally speaking, the As concentration increased with increasing aging time. For the Ca/As = 2 sample, the As concentration in the liquid phase increased from 54.6 to 383 mg/L after it was aged for 380 days; whereas for the sample precipitated at pH 8 with a Ca/As molar ratio of 4, the aqueous As concentration decreased from 765 to 213 mg/L over the course of the aging period. Based on previous works (Bothe and Brown, 1999a), it is widely accepted that the As concentration in the liquid phase increases with decreasing pH and Ca/As molar ratio, which is also what we observed in this work.

The corresponding aqueous Ca concentration was also monitored throughout the whole aging process (Fig. 1). As can be observed, the concentration of Ca in the liquid phase for the sample precipitated at pH 7 with a Ca/As molar ratio of 4 remained nearly unchanged when aged for 380 days. Similar results can also be seen for the samples precipitated at pH 8 with a molar ratio of 1 and 2, and this is in agreement with the observed trend of aqueous As concentration because no solid formed for these samples during the aging process in this work. For those samples precipitated at pH 12 with Ca/As molar ratios of 1, 2, and 4, the Ca concentration in the liquid phase decreased throughout the whole aging process. However, for samples precipitated at pH 10, the aqueous Ca concentration slightly increased and stabilized at 160, 300,

and 700 mg/L for the Ca/As = 1, 2, and 4 samples. The different transformation products, such as various forms of crystalline calcium arsenates as well as carbonates (atmospheric CO₂ was not excluded in this work) control the As and Ca behavior between the liquid and solid phase, which will be discussed in the following section.

2.2. Characterization of the aged Ca–As₁ precipitates

2.2.1. Raman and XRD results

The Raman spectra of the Ca–As solids precipitated at various pH values with different Ca/As molar ratios and aged at room temperature are compared with those of reference materials in Fig. 2. Only the frequency region of interest (100–1200 cm⁻¹) is displayed, where the stretching and bending vibrations of As–O bonds and carbonate group show characteristic Raman bands (Myneni et al., 1998; Sánchez-Pastor et al., 2016). The broad band positioned at 831 cm⁻¹ represents the As–O asymmetric stretching vibration and is comparable with some published results (Gomez et al., 2010; Müller et al., 2010). This band did not split or shift for the samples precipitated at pH 10 and 12 with a Ca/As molar ratio of 1 if they were aged at room temperature for less than 10 days, which suggested the poorly crystalline nature of these solids. However, for the Ca/As = 1 sample precipitated at pH 10 and aged for 380 days, additional peaks positioned at 691, 713, 865,

and 1059 cm⁻¹ appeared besides the As–O vibration peak, and the data corresponded to the four fundamental vibrations of the free carbonate group in monohydrocalcite (MHC) (Coleyshaw et al., 2003). In fact, some type of crystalline calcium carbonate had already been formed for this solid after aging for 240 days, as evidenced by the appearance of the peak located at 1059/cm, although this peak was not as strong as for that aged for 380 days. When the precipitation pH increased to 12 for the Ca/As = 1 solid, similar peaks appeared after aging for 240 days, which can also be ascribed to MHC, as that sample precipitated at pH 10 after 380 days of aging. However, if this sample continued to age at this pH for 380 days, peaks centered at 154 cm⁻¹ (lattice mode), 281 cm⁻¹ (lattice mode), 711 cm⁻¹ (internal in-plane antisymmetric bending of carbonate group), and 1085/cm (symmetric stretching of carbonate group) appeared, which is consistent with the peaks of calcite. In addition, some lattice mode vibrations (148, 206, 262, 274, and 297 cm⁻¹) and internal in-plane antisymmetric bending of carbonate groups (678, 733, and 745 cm⁻¹) belonging to vaterite also appeared (Sánchez-Pastor et al., 2016). The corresponding XRD results for these Ca–As₁ solids are presented in Appendix A Fig. S1 and the results were consistent with the Raman spectra, which corroborate the identity of the transformation products present after aging for 380 days at room temperature. It has been demonstrated that in the Ca–As–CO₂–H₂O system, the

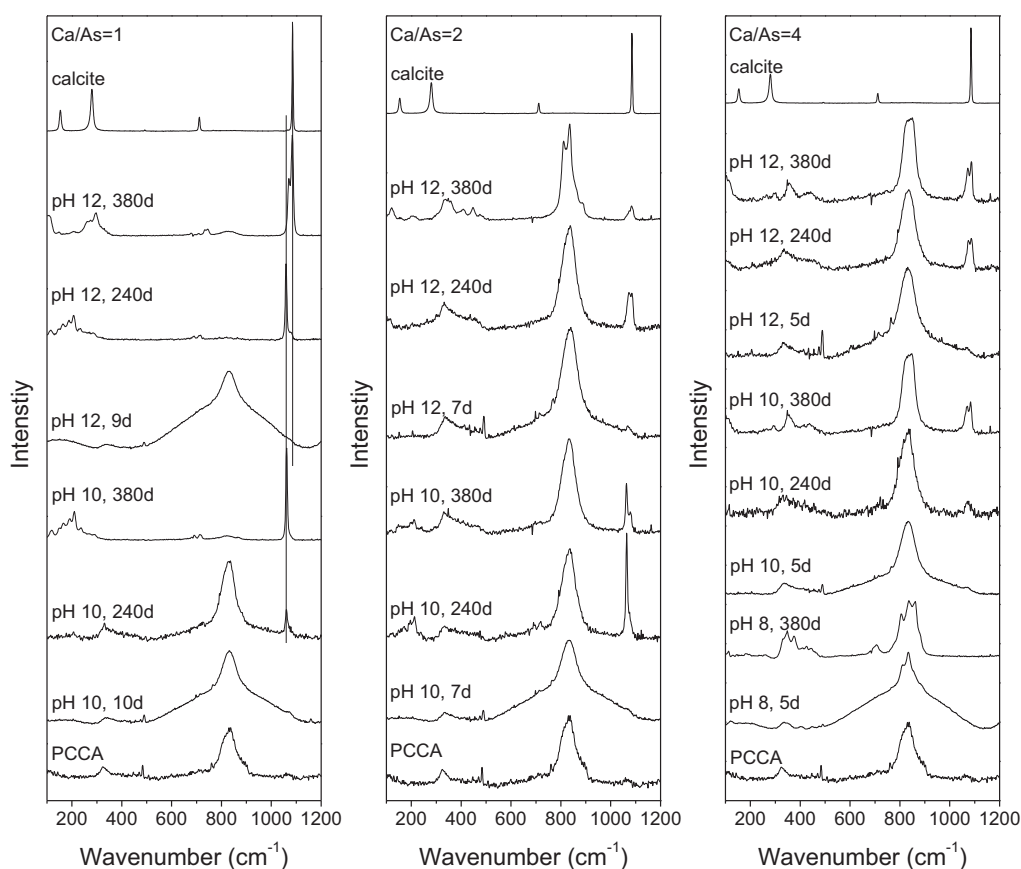


Fig. 2 – Raman spectra of aged Ca–As₁ solids (initial As concentration 1000 mg/L, Ca/As = 1, 2, and 4) at various pH values, 25°C. “PCCA” stands for poorly crystalline calcium arsenate.

formation of calcite will increase the release of As from the solid phase (Nishimura et al., 1983, 1985; Robins and Tozawa, 1982). Similar results were also observed in this work (Fig. 1). In addition, our data suggested that MHC is the intermediate phase during the transformation process of PCCA to calcite and/or aragonite, as suggested by some other investigations without the presence of As (Coleyshaw et al., 2003; Nishiyama et al., 2013). The aqueous As concentration was larger than 900 mg/L for the Ca/As = 1 samples after aging for 380 days, which means that almost all of the solid As phase was released back into the liquid phase during the crystallization process of various types of calcium carbonates.

For the samples precipitated at a Ca/As molar ratio of 2, similar results were observed for the sample precipitated at pH 10 as that of the Ca/As = 1 sample. After it was aged for 240 days, the appearance of the peak at 1064/cm in the Raman spectrum indicated that MHC is the transformation product (Fig. 2). XRD results suggested that after aging for 380 days, there still exists a large amount of PCCA in the solid phase in addition to crystalline MHC (Fig. 3). The aqueous concentration of As was 383 mg/L, which is quite a bit lower than the corresponding Ca/As = 1 sample as discussed above (921 mg/L) (Fig. 1). The overall data indicated that the amount of As

released back into the liquid phase decreased with increasing molar ratio of Ca/As if the precipitation pH was constant. When the precipitation pH increased to 12 for the Ca/As = 2 sample, the carbonate group symmetric stretching split into two peaks located at 1074 and 1085/cm, which indicated the formation of vaterite after aging for 240 days (Sánchez-Pastor et al., 2016) (Fig. 3). If the sample continued to age after 380 days, splitting of the asymmetric stretching vibrations occurred, producing peaks at 886, 835, and 811 cm^{-1} . XRD results verified that this As-bearing solid is johnbaumite ($\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$) (Fig. 2). The appearance of peaks in the Raman spectra belonging to the lattice modes (151 and 208 cm^{-1}) and the symmetric stretching of the carbonate group (1075 and 1083 cm^{-1}) from vaterite indicated that it was still present in this sample (Wehrmeister et al., 2010). In addition, a new type of calcium carbonate phase, calcium carbonate hemihydrate (CCHH) was recently discovered by Zou et al. (2019), and some of the peaks in our XRD data may be attributable to CCHH, as indicated by the blue arrows in Fig. 3. The results indicated that the transformation process of PCCA to crystalline phases was more complicated than previously expected, and that more than one type of intermediate (CCHH and/or MHC) can exist during this process. The aqueous As concentration was

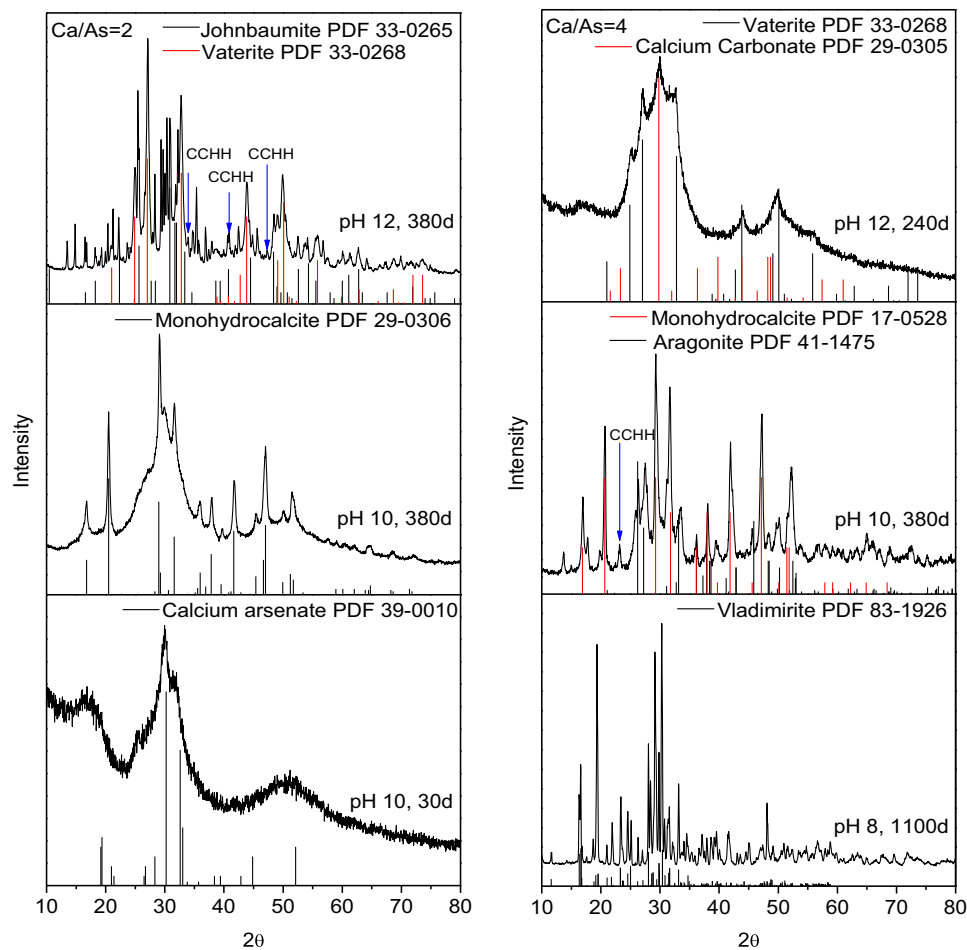


Fig. 3 – XRD spectra of aged Ca-As₁ solids (initial As concentration 1000 mg/L, Ca/As = 2 and 4) at various pH values, 25°C. “CCHH” stands for calcium carbonate hemihydrate.

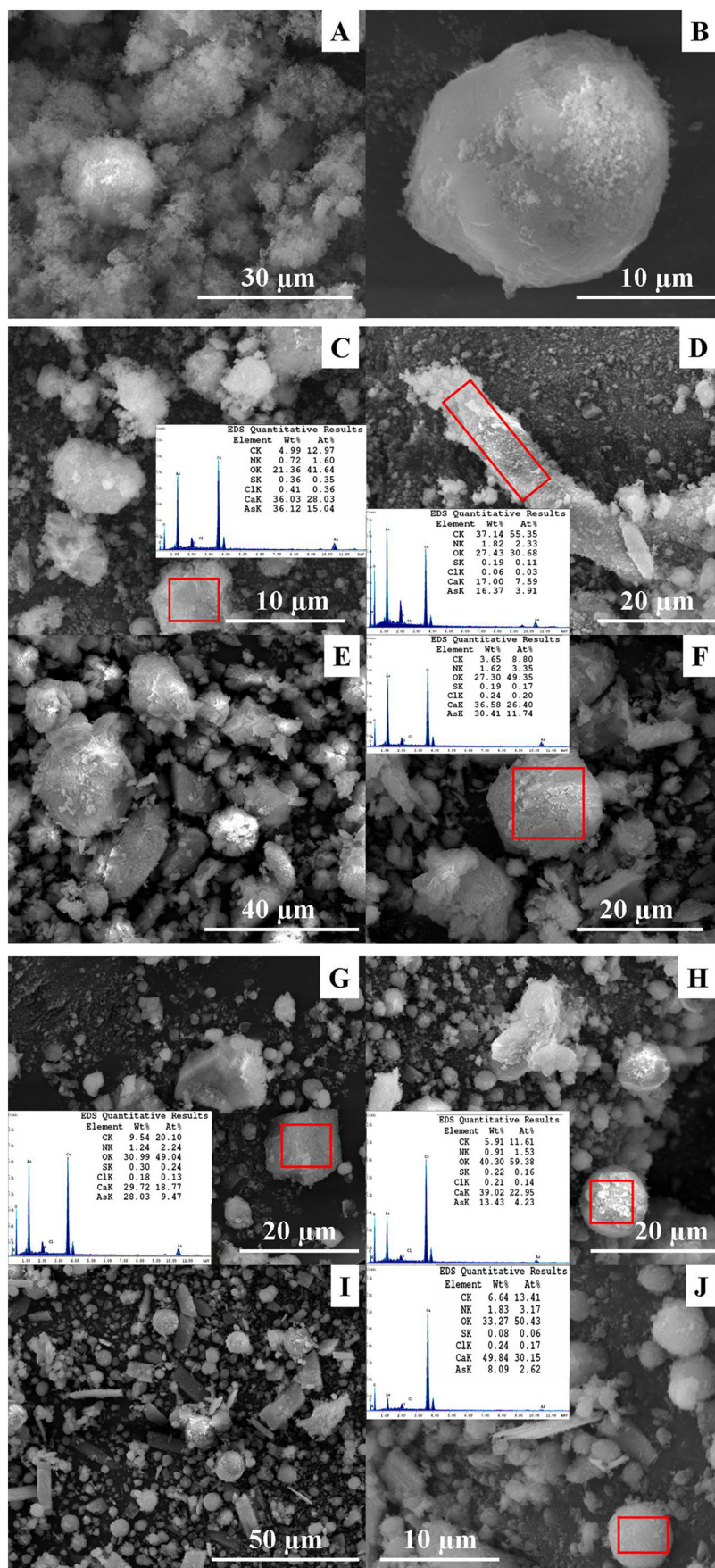


Fig. 4 – SEM images of aged Ca-As₁ solids (Ca/As = 2) precipitated at pH 10 after aging for 30 days (A, B), 240 days (C, D) and 380 days (E, F) as well as solids precipitated at pH 12 after aging for 240 days (G, H) and 380 days (I, J).

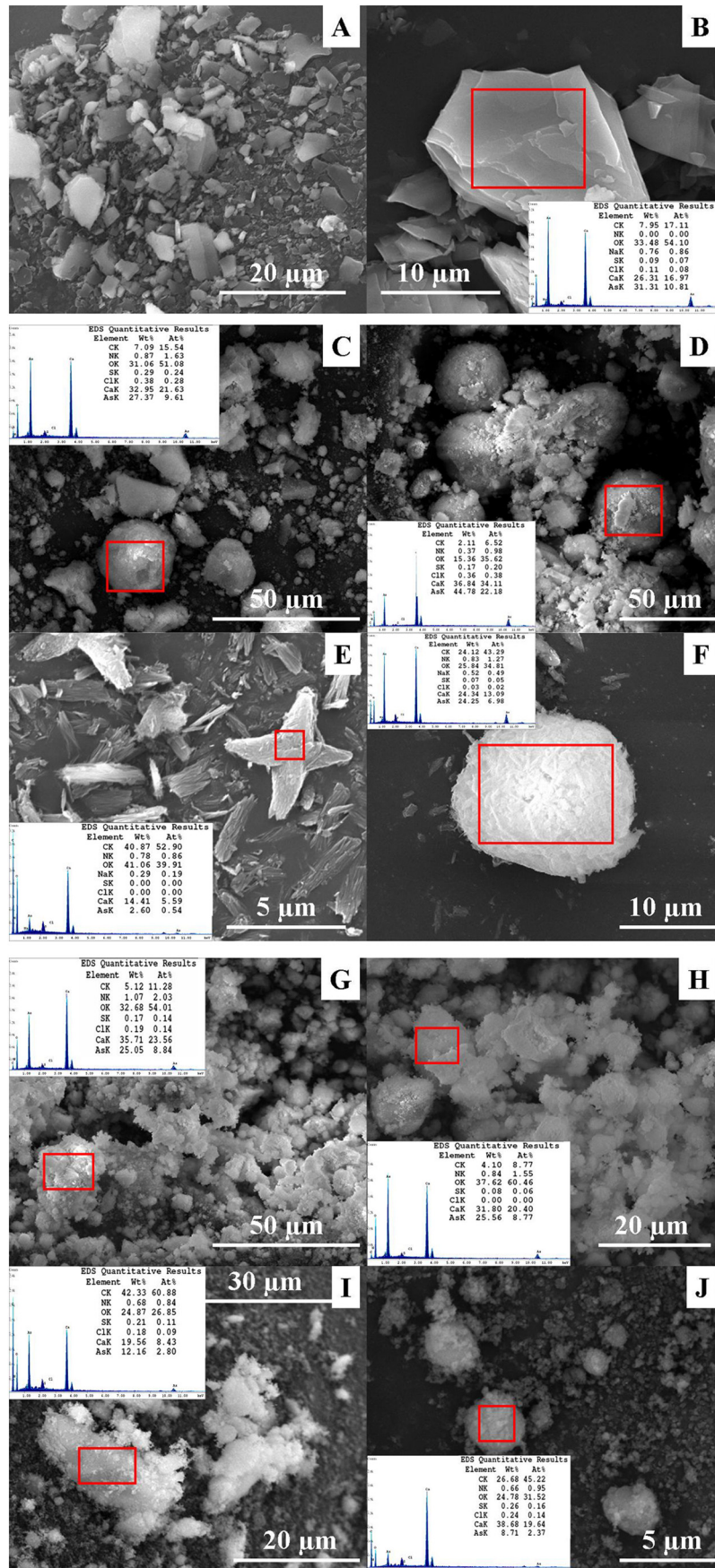


Fig. 5 – SEM images of aged Ca-As₁ solids (Ca/As = 4) precipitated at pH 8 after aging for 30 days (A) and 380 days (B) and those precipitated at pH 10 after aging for 240 days (C, D) and 380 days (E, F) as well as solids precipitated at pH 12 after aging for 240 days (G, H) and 380 days (I, J).

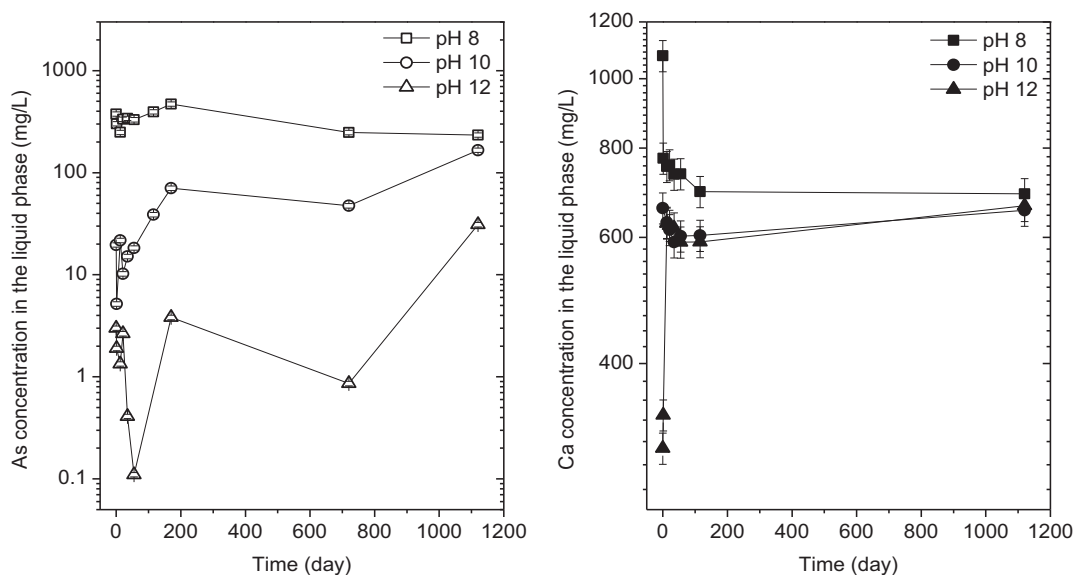


Fig. 6 – As and Ca concentration in the liquid phase over the course of aging of the Ca–As₂ slurries (initial As concentration 2000 mg/L, CaO as neutralization agent) at various pH values, 25°C.

only 565 mg/L, compared to 973 mg/L for the Ca/As = 1 sample precipitated at the same pH (Fig. 1). This result is in agreement with the transformation products of these two samples (crystalline calcium arsenate and carbonate for the Ca/As = 2 slurry vs. only crystalline calcium carbonate for the Ca/As = 1 slurry).

As for the samples precipitated at a Ca/As molar ratio of 4, a different result was obtained for the Ca–As₁ slurry when it was precipitated at pH 8. No solid was precipitated at this pH for the samples with Ca/As molar ratios of 1 and 2 as discussed above, but if the molar ratio was raised to 4, a type of crystalline calcium arsenate, vladimirite (Ca₄(HAsO₄)₂(AsO₃OH)₂·4H₂O) was formed, as suggested by the XRD data (Fig. 3). The Raman spectrum for this sample also indicated that some types of crystalline calcium arsenates were formed (Fig. 2). The peaks located at 861, 836, 805, and 706 cm⁻¹ can be distinguished, which can be ascribed to the asymmetric and symmetric stretching vibrations of As–O, As–OH, and/or As–O–Ca bonds, and this result can be compared to previous reports to some extent (Makreski et al., 2018; Myneni et al., 1998; Yang et al., 2011). In addition, crystalline calcium carbonate was not found for this sample, and the overall results can be used to explain why the aqueous As concentration decreased throughout the whole aging process for this specific sample (Fig. 1); whereas, if the Ca–As₁ sample was precipitated at pH 10, peaks located at 1071 and 1083 cm⁻¹ appeared in the Raman spectrum, indicating the formation of crystalline calcium carbonate. XRD results verified that the transformation products for this sample after aging for 380 days at room temperature are MHC, CCHH, and aragonite (Fig. 3). No crystalline calcium arsenate was precipitated for this sample, and the corresponding aqueous As concentration increased during the whole aging process. Similar phenomena could also be found for the Ca/As = 1 and 2 slurries if the samples were precipitated at pH 10 as discussed above. If the

precipitation pH increased to 12, it was observed that this sample had a similar Raman spectrum to that of the sample precipitated at pH 10 when the Ca/As molar ratio was 4 (Fig. 2). One of the transformation products was identified as crystalline calcium carbonate, as suggested by the XRD data (Fig. 3), and the concentration of As in the liquid phase also increased over the course of the aging process (Fig. 1). The results further confirmed that the amount of As release was dependent on the precipitation pH if the Ca/As molar ratio was constant (Bothe and Brown, 1999a).

All of these results indicated that due to the influence of atmospheric CO₂, crystalline calcium carbonates appeared in the solid phase and thus triggered the release of As from its carriers. Furthermore, it could be observed that As was still released back into the liquid phase even when crystalline calcium arsenates were formed in the solid phase in addition to the crystalline calcium carbonate, as observed for the samples precipitated at pH 12 with a Ca/As molar ratio of 2. The corresponding decreasing trend of the aqueous Ca concentration for samples precipitated at pH 12 indicated that for these samples, during the transformation process of PCCA to some types of crystalline calcium arsenates, crystalline calcium carbonate will also form to control the aqueous Ca concentration. The liquid phase concentrations of both As and Ca decreased for the Ca–As₁ samples precipitated at pH 8, thus indicating that the transformation of PCCA to crystalline calcium arsenate will not trigger the release of As when conditions are not favorable for the precipitation of crystalline calcium carbonate. However, for the samples precipitated at pH 10, the dramatically increasing trend of aqueous As concentration and the slight increase in Ca concentration indicated that for these samples, the formation of crystalline calcium carbonate and the decomposition of PCCA may be in equilibrium at this pH. The decomposition of PCCA was more favored at lower pH, and this may be one of the reasons why a

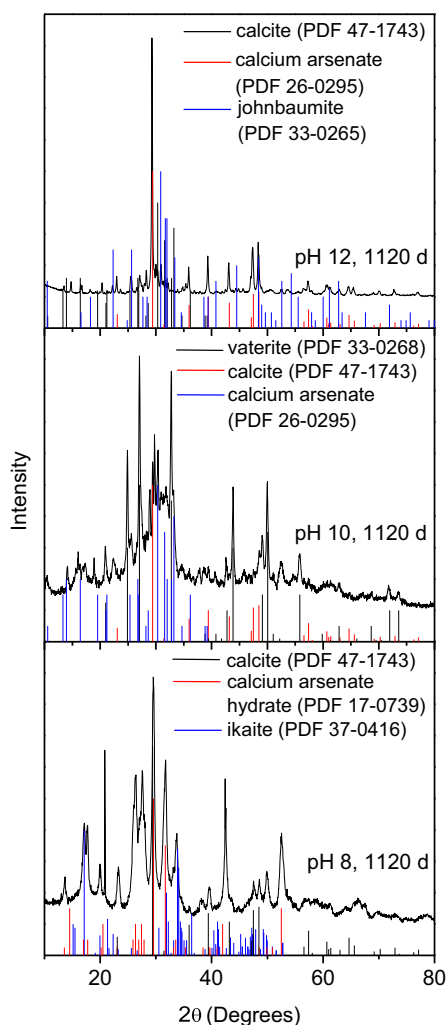


Fig. 7 – XRD spectra of the aged Ca–As₂ slurries precipitated at pH 8, 10, and 12, 25°C.

slightly increasing trend of aqueous Ca concentration was observed for samples precipitated at pH 10.

2.2.2. SEM analysis

The SEM images of the aged Ca–As₁ samples precipitated at various pH values with different Ca/As molar ratios are presented in Figs. 4–5 and Appendix A Fig. S2. Irregular bulk aggregates can be observed for the sample precipitated at pH 10 with a Ca/As molar ratio of 1 and aged for 240 days, which indicated its poorly crystalline nature (Appendix A Figs. S2A and S2B). The Ca/As molar ratio was not uniform, as indicated by the SEM-EDS results (1.9 in image A, while 3.9 in image B), however, at least the results showed that PCCA was one of the components of this aged Ca–As₁ sample. This result was consistent with the Raman spectra shown in Fig. 2. In contrast, different morphologies were obtained if this sample continued to age at room temperature for 380 days. Most of the particles were aggregates of needles of different sizes. In addition, some spherical particles were also observed (Appendix A Figs. S2C and S2D). According to the Ca/As molar ratio indicated by SEM-EDS, little As can be found in these

particles, and this is in agreement with XRD and Raman data showing that MHC is the transformation product for this sample, and almost all of the added As was in the liquid phase. The morphologies of this metastable crystalline calcium carbonate can be compared to those of samples formed from CaCl₂–MgCl₂–Na₂CO₃ solutions, as reported previously by Nishiyama et al. (2013). Appendix A Figs. S2E and S2F show the SEM images of the transformation products of the sample precipitated at pH 12 with Ca/As molar ratio of 1 and aged for 240 days. The increase of pH from 10 to 12 resulted in the formation of spherical and short rod-like aggregate particles. Vaterite spheres, layered and rhombohedral calcite, and a few needle-like MHC crystals (Tong et al., 2004) can be seen from the images of this sample when it was aged after 380 days at this pH and room temperature, confirming the results of XRD (Appendix A Figs. S2G and S2H).

As for the morphologies of the samples precipitated at a Ca/As molar ratio of 2 with different pH, it can be seen that if the precipitation pH is 10, no sharp changes of the morphologies of the sample occurred during the aging process. Irregular loose cotton-like aggregates appeared after this sample was aged for 30 days, confirming its poorly crystalline nature (Fig. 4A and B). The Ca/As molar ratio for the sample after aging for 240 days is 2 as calculated from the SEM-EDS results, no matter what shape or size particles were present, and a similar result was also observed for the sample after aging for 380 days (Figs. 4C–4F). The particles belonging to MHC (needle-like aggregates) were not found by SEM. This phase may have formed at the surface of the PCCA, or possibly it is too scattered and the amount of these crystals is quite low for this sample. These results are consistent with the XRD data, which indicated that in addition to the crystalline transformation product MHC, the solid phase of this sample is also composed of PCCA. As can be seen in Fig. 4G and H, spherical aggregated particles and some other aggregates with different shapes were the morphologies observed in the sample precipitated at pH 12 and aged for 240 days. The morphologies and aggregates of the sample did not undergo dramatic changes when this sample was aged for 380 days (Fig. 4I and J). Needle-like, spherical and plate-like aggregate particles appeared, and XRD results verified that the transformation product of this sample was a mixture of CCHH, vaterite and johnbaumite, as discussed above (Fig. 3). However, when the Ca/As molar ratio increased to 4, solids precipitated from the Ca–As solution at pH 8 and appeared as tabular-like aggregated particles when the sample was aged for 30 days, and the morphology of this sample was independent of the aging process (Fig. 5A and B). Only crystalline calcium arsenate (vladimirite) was produced for this sample, as suggested by XRD results. The increase of pH from 8 to 10 resulted in the formation of spherical and other aggregated particles with irregular shapes (Fig. 5C and D), which had similar morphologies to those in the sample precipitated at the same pH with a Ca/As molar ratio of 2 (Fig. 4E and F). Some needle-like (cross and rosette form or rod form) aggregate particles appeared separately or were deposited on the originally formed spherical aggregates after this sample had been aged for 380 days (Fig. 5E and F) and this is consistent with the XRD results showing that the transformation products were metastable calcium carbonate (CCHH,

MHC, and aragonite). The morphologies of the formed aragonite (cross and rosette form) and CCHH (rod form) showed similarities with previous reports (Guo and Riding, 1992; Zou et al., 2019). When the precipitation pH increased to 12, irregular aggregated particles with different sizes and shapes appeared (Figs. 5G–5J), and this phenomenon was similar to those observed in samples that had also been precipitated at pH 12 with different Ca/As molar ratios.

The characterization of the solid phase as well as the As concentration in the liquid phase indicated that the stability of the Ca–As slurries was rather low, especially in the presence of atmospheric CO₂, which could not be excluded when they were stored. Therefore, unless it is sealed with cement or other materials, this kind of As-bearing waste solid may not be a suitable As carrier due to safety considerations (Riveros et al., 2001; Robins et al., 2001).

2.3. Comparison of the stability of the Ca–As₁ and Ca–As₂ precipitates

Slaked lime is commonly used as a neutralization reagent in various industrial practices for generating industrial wastes (Conner, 1990; Lieberman et al., 2018; Riveros et al., 2001; Yao et al., 2018, 2019). Therefore, it was used as a reagent to neutralize the H₂SO₄-acidified As solution in order to simulate the As treatment in hydrometallurgical practice, while at the same time the concentrations of As and Ca in the liquid phase were monitored (Fig. 6). At pH 8, the aqueous As concentration fluctuated from 380 to 400 mg/L for the Ca–As₂ precipitates after aging for 115 days at room temperature, and the value was 234 mg/L if the aging time increased to 1120 days (Fig. 6). As discussed above, the concentration was 213 mg/L for the Ca–As₁ precipitates after aging for 380 days (Fig. 1). This result indicated that there is no discernable difference between these two samples in terms of the stability of the generated As-bearing solids at this pH value. The corresponding aqueous Ca concentration is also presented in Fig. 6, and it can be observed that its concentration decreased during the whole aging process. The Raman spectrum showed a characteristic broad As–O asymmetric vibration located at 839 cm⁻¹ for this Ca–As₂ precipitate after it had been aged for 190 days (Appendix A Fig. S3). In addition, a peak centered at 1084 cm⁻¹ appeared, which is indicative of the formation of some type of crystalline calcium carbonate, as discussed above. The Raman spectrum showed similarity with that of PCCA, thus indicating the poorly crystalline nature of this sample. However, after aging for 1120 days at room temperature, different Raman spectra could be observed for this sample. The peak located at 1072 cm⁻¹ can be ascribed to the symmetric stretching of ikaite, and some other unassigned peaks (332, 360, 415, 446, and 470 cm⁻¹) also appeared. The transformation products for this sample were a heterogeneous mixture consisting of ikaite, calcite, and crystalline calcium arsenate as indicated by the XRD results (Fig. 7). For the Ca–As₁ sample precipitated at pH 8, vladimirite appeared after aging for 1100 days at room temperature, as discussed above (Fig. 3). The reasons why different transformation products formed for these two samples may be due to the fact that a large amount of gypsum also formed for the Ca–As₂ samples. It is easy to understand that crystalline calcium carbonate was

more favorable to form if more Ca ion was present in the solution, and this may exert some influence on the crystallization process of PCCA to form crystalline calcium arsenate.

However, when the aging pH increased to 10 and 12, different results were obtained. The Ca–As₂ precipitates had higher stability than the corresponding Ca–As₁ samples. The aqueous As concentration was 167 mg/L for the Ca–As₂ sample aged at pH 10 for 1120 days. In contrast, the value was higher than 280 mg/L for the Ca–As₁ sample aged at the same pH for only 380 days, even when the molar ratio of Ca/As was 4. This was also the case for samples aged at pH 12 (0.9 mg/L for the Ca–As₂ sample after aging for 720 days vs. 13.3 mg/L for the Ca–As₁ sample after aging for 380 days). In addition, the aqueous As concentration first decreased and then increased for a period of time; after that, the value decreased again. The changes in the aqueous As concentration were similar for these three Ca–As₂ samples. However, for the samples aged at pH 10 and 12, the aqueous As concentration increased again if they continued to age for 1120 days and this fluctuation of As concentration may be due to the competing tendencies of Ca ions to form crystalline calcium arsenate and/or carbonate. The results from Raman spectra showed that crystalline calcium carbonates may also form during the aging process as observed for the Ca–As₁ precipitates (Appendix A Fig. S3). For the Ca–As₂ sample precipitated at pH 12 and aged for 190 days, the appearance of the peaks at 1081, 149, and 280 cm⁻¹ indicated the formation of calcite for this sample. The splitting of the asymmetric stretching vibrations of As in this sample showed similarity with the results of the Ca–As₁ samples precipitated at pH 12 with Ca/As molar ratios of 2 and 4. After aging for 1120 days, XRD results indicated that calcite, crystalline calcium arsenate (Ca₃(AsO₄)₂, Ca₅(AsO₄)₃(OH)) were the transformation products (Fig. 7), and this is consistent with the Raman spectrum. The results further confirmed that As will be released into the liquid phase during the transformation of PCCA to calcite, while PCCA may also transform to crystalline calcium arsenate, and this may be one of the reasons why the aqueous As concentration decreased after aging for a relatively long time. The aqueous Ca concentration was stabilized at 650 mg/L for both the Ca–As₂ samples precipitated at pH 10 and 12. The Raman spectra for the Ca–As₂ sample precipitated at pH 10 and aged for 190 and 1120 days also showed some similarities with those of the corresponding Ca–As₂ sample precipitated at pH 12. High pH and a relatively large amount of Ca ions may favor the formation of calcium carbonates and this was also the case in this work, no matter which neutralization reagents were applied. Furthermore, it has been demonstrated that Ca has the ability to retard the crystallization process of 2-line ferrihydrite under alkaline conditions (Zhang et al., 2018). In this work, the transformation process from PCCA to any type of crystalline solid was retarded by the presence of additional Ca ions (introduced by CaO as the neutralization reagent), leading to less As being released back into the liquid phase when compared with the results of the samples neutralized by NaOH.

A schematic diagram is presented in the Graphical Abstract to illustrate what occurs for the Ca–As slurries in the presence of atmospheric CO₂, and a table related to the transformation products and the trend of As concentration in

the liquid phase for all the aged samples in our work can also be seen in Appendix A Table S1.

3. Conclusions

The transformation process of PCCA generated from samples with various Ca/As molar ratios in the neutral to alkaline pH range (7–12) by using NaOH or CaO as the neutralization reagents in the presence of atmospheric CO₂ was investigated in this work. The results indicated that, for the NaOH-neutralized Ca–As samples, the release of As continued to occur if crystalline calcium carbonate appeared in the solid phase, and this had no relationship with whether a crystalline calcium arsenate formed or not. The formation of various types of crystalline calcium carbonates as well as calcium arsenates were identified, which control the fate of As. The findings of this work imply that the neutralization of acidic As wastewaters with lime may enhance the stability of the generated Ca–As wastes to some extent; however, they can still transform to crystalline calcium carbonates and trigger the release of As. The results of this work further suggest that the precipitation pH, the presence of atmospheric CO₂, as well as the neutralization reagent, are the factors that may exert some influence on the long-term stabilities of the calcium arsenates at room temperature. It is also worth noting that in real industrial practice, some other anions such as sulfate and chloride may also be present in the acidic As-bearing wastewaters (Zhang et al., 2018), and hence the long-term stability of Ca–As solids in the presence of such ions still needs further research.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jes.2019.04.017>.

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