

Article

Pb Mineral Precipitation in Solutions of Sulfate, Carbonate and Phosphate: Measured and Modeled Pb Solubility and Pb^{2+} Activity

Xinxin Li ^{1,2}, Behrooz Azimzadeh ¹ , Carmen Enid Martinez ¹  and Murray B. McBride ^{1,*}
¹ Section of Soil and Crop Sciences, Cornell University, Ithaca, NY 14850, USA; lixinxin2013@163.com (X.L.); ba324@cornell.edu (B.A.); cem20@cornell.edu (C.E.M.)

² School of Environmental Science and Engineering, Shandong University, Qingdao 266237, China

* Correspondence: mbm7@cornell.edu; Tel.: +1-607-255-1728; Fax: +1-607-255-2644

Abstract: Lead (Pb) solubility is commonly limited by dissolution–precipitation reactions of secondary mineral phases in contaminated soils and water. In the research described here, Pb solubility and free Pb^{2+} ion activities were measured following the precipitation of Pb minerals from aqueous solutions containing sulfate or carbonate in a 1:5 mole ratio in the absence and presence of phosphate over the pH range 4.0–9.0. Using X-ray diffraction and Fourier-transform infrared spectroscopic analysis, we identified anglesite formed in sulfate-containing solutions at low pH. At higher pH, Pb carbonate and carbonate-sulfate minerals, hydrocerussite and leadhillite, were formed in preference to anglesite. Precipitates formed in the Pb-carbonate systems over the pH range of 6 to 9 were composed of cerussite and hydrocerussite, with the latter favored only at the highest pH investigated. The addition of phosphate into the Pb-sulfate and Pb-carbonate systems resulted in the precipitation of $\text{Pb}_3(\text{PO}_4)_2$ and structurally related pyromorphite minerals and prevented Pb sulfate and carbonate mineral formation. Phosphate increased the efficiency of Pb removal from solution and decreased free Pb^{2+} ion activity, causing over 99.9% of Pb to be precipitated. Free Pb^{2+} ion activities measured using the ion-selective electrode revealed lower values than predicted from thermodynamic constants, indicating that the precipitated minerals may have lower K_{SP} values than generally reported in thermodynamic databases. Conversely, dissolved Pb was frequently greater than predicted based on a speciation model using accepted thermodynamic constants for Pb ion-pair formation in solution. The tendency of the thermodynamic models to underestimate Pb solubility while overestimating free Pb^{2+} activity in these systems, at least in the higher pH range, indicates that soluble Pb ion-pair formation constants and K_{SP} values need correction in the models.

Keywords: Pb solubility; Pb^{2+} activity; precipitation; ion pairs; thermodynamic models



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1. Introduction

The chemical speciation and mineral forms of Pb in soil and water are critically important in determining the solubility, bioavailability and potential toxicity of this metal [1–3]. The chemical environment—specifically the pH, dissolved inorganic carbon or CO_2 pressure and concentrations of sulfate and phosphate—largely determines the mineral forms of Pb likely to form and persist. In the case of soils severely contaminated by spoils from Pb mining activity, the original mineralogical composition of the mine waste is a key factor in determining the speciation of Pb by controlling the pH and soluble ion composition of the pore water in these waste materials [4]. Whether Pb carbonates (cerussite, hydrocerussite), Pb oxides, Pb sulfates (anglesite, lanarkite) or Pb phosphates (such as pyromorphite) are ultimately the weathering products from the Pb ore mineral, galena, is dependent on the initial ore rock composition. Thus, oxidative dissolution of galena (PbS) during weathering of waste rock releases aqueous Pb^{2+} and SO_4^{2-} , causing anglesite to be a prevalent mineral in acid environments associated with rocks containing high pyrite levels [1,5–8].

In the alkaline environment of carbonate-rich rocks, cerussite $[\text{PbCO}_3]$, hydrocerussite $[\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2]$ and occasionally shannonite $[\text{Pb}_2\text{OCO}_3]$ have been identified [8,9]. In addition to these minerals, lanarkite $[\text{Pb}_2\text{OSO}_4]$, leadhillite $[\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2]$ and plumbojarosite $[\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_2]$ have been identified in soils contaminated by Pb mine wastes [6,10]. The rare Pb phosphate mineral plumbogummite $[\text{PbAl}_3(\text{PO}_4)(\text{OH})_5]$ is also believed to have formed by oxidative weathering of Pb [11] in waste rock at old mining sites. Since the oxidative weathering of PbS to plumbojarosite or plumbogummite requires the availability of soluble Fe or Al, these latter minerals are most likely to be formed in acidic environments.

Thermodynamic principles have limitations in predicting the mineral phases of Pb actually encountered in the field. Numerous discrepancies and uncertainties have been noted where predicted mineral solubilities and stabilities are not consistent with observations. In the case of Pb sulfates in weathered environments contaminated by mine spoils, anglesite occurs commonly whereas lanarkite is only rarely encountered. Keim et al. [12] noted that while lanarkite is reported to be thermodynamically stable over a wide range of SO_4^{2-} concentrations at slightly alkaline pH, this Pb oxysulfate is much less frequently encountered in mine-spoil-contaminated sites than expected. This observation is in contradiction to expectations based on the laboratory-measured thermodynamic stability of lanarkite. However, the free energies of formation (ΔG_f^0) reported for lanarkite in various studies have ranged considerably, from -1071.9 to -1014.6 [10], with the latter value being more consistent with the scarcity of lanarkite occurrence in the field.

In slightly alkaline (calcareous) soil environments, metallic Pb corroded by centuries of exposure to soil environments is weathered to Pb carbonates (cerussite and hydrocerussite) as well as Pb oxide (litharge) [13]. These various forms of Pb are somewhat soluble and labile, so the addition of soluble phosphate to Pb-contaminated soils can transform more soluble minerals to much less soluble Pb phosphates [14–17]. However, there is uncertainty as to how complete a conversion from these more labile forms of Pb to the less labile Pb phosphate minerals (e.g., hydroxypyromorphite) actually occurs within a relevant time period under field conditions [18]. The kinetics of mineral dissolution and precipitation may limit the rate at which Pb in contaminated soils is converted to its thermodynamically most stable form [19,20]. Thus, less stable (more soluble) Pb mineral phases may persist and coexist with more stable (less soluble) minerals in soils for prolonged periods of time.

Another discrepancy regarding Pb mineral stability is the fact that hydrocerussite is rare in soils, whereas the reported ΔG_f^0 values of hydrocerussite and cerussite indicate that the former mineral should be common in soils and natural waters [21]. Consequently, free energies of formation have been adjusted over time to be consistent with this observation [22]. However, solubility experiments conducted to measure these energies of formation are very difficult to carry out because the results are sensitive to the model of speciation used to interpret the Pb solubilities [22]. Specifically, the stabilities of the soluble Pb-hydroxy and Pb-carbonate complexes may not be sufficiently well known to allow the precise measurement of the ΔG_f^0 value of hydrocerussite [21]. For example, Marani et al. [23] found that the solubilities of Pb minerals precipitated from bicarbonate, carbonate and sulfate solutions were 2–3 orders of magnitude higher than predicted from a geochemical speciation model (MINTEQA2) in the alkaline range of pH (>7). In addition, there were important discrepancies between the mineral phases actually precipitated (e.g., anglesite, cerussite, hydrocerussite) and those expected (e.g., lanarkite, lead hydroxide) based on thermodynamic data.

Pb phosphates are substantially less soluble and less chemically labile than Pb hydroxides, carbonates or sulfates; thus, Pb transformation from the more soluble solid phases to highly insoluble Pb phosphates is thermodynamically favorable [16,17,24]. The introduction of phosphates into soils effectively reduces Pb bioavailability by converting soluble reactive Pb into insoluble pyromorphite-like minerals $[\text{Pb}_5(\text{PO}_4)_3(\text{F, Cl, Br, OH})]$ [25]. However, kinetics plays an important role as well as thermodynamics in this process of Pb stabilization. Sima et al. [26] investigated the remediation effect of phosphates

on Pb-contaminated soils spiked with $\text{Pb}(\text{NO}_3)_2$, PbSO_4 and PbCO_3 and found that the rate of Pb-phosphate mineral formation was limited by the dissolution kinetics of the original Pb compounds.

When considering human exposure to Pb in drinking water, Pb sulfates, carbonates and phosphates have all been implicated as potentially limiting solubility and providing some protection from corroding water pipes containing metallic Pb components [27]. Drinking water is intentionally treated with soluble phosphate to limit Pb solubility because of the much lower solubility of Pb and Ca-Pb phosphates (notably hydroxypyromorphite and phosphohedyphane) compared to Pb carbonates or sulfates [28,29]. Pb solubility can be limited to about $10\text{--}15\text{ }\mu\text{g L}^{-1}$ in slightly alkaline orthophosphate-treated water (pH 8.0) flowing through Pb pipes, consistent with the calculated expected solubility assuming equilibrium with hydroxypyromorphite as the stable solid phase [29]. Our preliminary research has shown similar solubilities of Pb ($29 \pm 11\text{ }\mu\text{g L}^{-1}$) in water equilibrated for up to 30 days with microcrystalline hydroxypyromorphite at near-neutral pH with phosphate added at 3 mg L^{-1} or greater. Without any added phosphate, Pb solubility in the same hydroxypyromorphite system is more than 10 times higher, averaging $435 \pm 122\text{ }\mu\text{g L}^{-1}$. In these systems open to atmospheric CO_2 , dissolved inorganic carbon raises the solubility of Pb due to the formation of soluble Pb-carbonate complexes in solution [23].

Numerous Pb phosphate precipitation and dissolution studies have reported solubilities of Pb substantially greater than those calculated using the generally assumed K_{SP} for hydroxypyromorphite or chloropyromorphite [30–33]. Discrepancies among studies and between measured and predicted Pb solubilities reflect the fact that the K_{SP} values of the insoluble Pb phosphate minerals are still not well defined despite their widespread usage in modeling. One impediment to establishing accurate solubility products is that Pb apatite structures such as hydroxypyromorphite dissolve incongruently at near-neutral pH, with the result that they have ill-defined and non-constant K_{SP} values [30,34]. Further challenges include the difficulties of accurately measuring very low Pb solubilities and even lower free Pb^{2+} ion activities in order to determine the K_{SP} and stability constants of soluble Pb complexes such as Pb-carbonate and Pb-phosphate ion pairs. Although the Pb-carbonate ion pair stabilities have been fairly well established [35], Pb-phosphate stabilities have not [36,37].

In summary, the pH and dissolved ionic composition (sulfate, bicarbonate/carbonate, phosphate) of pore water in mine waste and waste-contaminated soils are controlling chemical factors in determining the stable mineral forms and solubility of Pb created by weathering. From the standpoint of human and animal exposure to toxic Pb, the mineral forms of Pb are critically important because they display a wide range of solubilities and bioaccessibilities related to their variable dissolution kinetics [1,4,38]. For example, cerussite is much more soluble and bioaccessible than pyromorphite or galena under most conditions [39] and, therefore, is more likely to pose a hazard to humans and ecosystems. The presence of several anions in solution, which is normally the case for soils and natural waters, further complicates the chemistry of Pb precipitation reactions. For example, soluble phosphate ions can replace carbonate ions in the minerals PbCO_3 and $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ and cause the formation of $\text{Pb}_5(\text{PO}_4)_3\text{OH}$, reducing soluble Pb [15]. Conversely, the oxyanions CO_3^{2-} and SO_4^{2-} can substitute for structural PO_4^{3-} in the hydroxypyromorphite $[\text{Pb}_5(\text{PO}_4)_3\text{OH}]$ structure, although SO_4^{2-} substitution is believed to be more limited than CO_3^{2-} [40].

The solubility and stability of Pb mineral phases formed in multi-component systems created by sulfate-, carbonate- and phosphate-rich aqueous environments have not been fully described under controlled conditions. However, such knowledge is necessary to explain the pattern of Pb dissolution responsible for the mobilization and transport of Pb in more complex water and soil systems. To this end, the aim of the present study was to investigate the following:

(1) The effects of pH and environmentally ubiquitous sulfate, phosphate and carbonate anions on Pb^{2+} ion activity and on the solubility and bioavailability of Pb;

- (2) The effects of phosphate on the mechanisms of Pb precipitation and stable mineral phase formation from aqueous sulfate and carbonate solutions under variable pH conditions;
- (3) The discrepancies reported in previous studies relating to solubility products and thermodynamic stabilities of Pb minerals commonly formed in aqueous solutions.

2. Materials and Methods

2.1. Establishment of Reaction Systems

Precipitation reactions of Pb were conducted in 50-milliliter tubes containing aqueous solutions of 1 mM $\text{Pb}(\text{NO}_3)_2$ and 5 mM of either Na_2SO_4 , Na_2CO_3 , Na_2HPO_4 , Na_2SO_4 - Na_2HPO_4 or Na_2CO_3 - Na_2HPO_4 , with pH adjusted over a wide range. In order to avoid pre-emptive precipitation of Pb as a hydroxide or oxide mineral, the stock solutions were pre-adjusted to a pH of 4.0, 5.0, 6.0, 7.0 and 8.0 for sulfate (SO_4), phosphate (PO_4) and sulfate-phosphate (SO_4 - PO_4) systems and 6.0, 7.0, 8.0 and 9.0 for carbonate (CO_3) and carbonate-phosphate (CO_3 - PO_4) systems using 0.01 M HNO_3 or 0.01 M NaOH . Then, $\text{Pb}(\text{NO}_3)_2$ solution was added to create a final Pb concentration of 1 mM and initiate precipitation, with each oxyanion-to-Pb mole ratio initially set at 5:1. The reaction mixtures were capped and continuously shaken for 30 days. During equilibration, pH was readjusted frequently to maintain the initial target values using 0.01 M HNO_3 and 0.01 M NaOH addition. Carbon dioxide exchange with the atmosphere was not prevented in the experimental procedure used, but pH measurements indicated that quasi-equilibrium conditions among soluble species, solid phases and the atmosphere were achieved within a few days of combining the reagents. Each treatment was replicated three times.

2.2. Determination of Pb Solubility and Pb^{2+} Activity

The free Pb^{2+} activity in the solutions was determined by the solid-state ion-selective Pb electrode at days 0, 10, 20 and 30. The Pb electrode was calibrated by measuring millivolt response in 10^{-4} M $\text{Pb}(\text{NO}_3)_2$ solutions containing concentrations of Na oxalate between 0 and 0.01 M and buffered at pH 5.0 with 0.01 M Na acetate. The activities of free Pb^{2+} ions in these buffer solutions were calculated using the chemical speciation program Visual MINTEQ (version 3.1) with the adjusted Pb-oxalate complexation constant determined from a previous study [30], and a calibration curve of $\log(\text{Pb}^{2+})$ vs. millivolt reading was obtained over the log activity range of -4 to -9 . The equilibrated solutions at day 30 were centrifuged to separate precipitates from the solution phases. The precipitates collected after centrifugation were air-dried after washing in deionized water to remove salts and then kept refrigerated prior to further analysis. Samples of the supernatants were acidified using concentrated HNO_3 to achieve a final concentration of 1.0 M HNO_3 before determining the dissolved Pb concentrations using inductively coupled plasma optical emission spectrometry (ICP-OES). The Visual MINTEQ program was used to identify expected precipitated mineral phases as well as to predict Pb solubilities over the specific pH range tested.

2.3. Mineralogical Analyses of Pb Precipitates

Fourier-transform infrared (FTIR) spectra of Pb precipitates were collected using a Bruker Vertex 70 spectrometer (Bruker Optics Inc., Billerica, MA, USA) equipped with a Pike GladiATR accessory (Pike Technologies, Madison, WI, USA). Solid samples were analyzed using a single reflection diamond internal reflection element. Spectra were collected from 4500 to 150 cm^{-1} with a resolution of 4 cm^{-1} , with each spectrum representing an average of 200 co-added scans. Post hoc smoothing (Savitzky-Golay, 5 point) and normalization were performed with OPUS 7.2 (Bruker Optics Inc.) software.

X-ray diffraction (XRD) patterns were acquired using a Bruker D8 Advance powder X-ray diffractometer operated at 40 kV and 25 mA with $\text{CuK}\alpha$ radiation and a photon energy of 8.04 keV. Measurements were made using a step-scanning mode with a fixed 0.02° 2θ step and a counting time of 1 s/step over the 10 – 80° 2θ $\text{CuK}\alpha$ angular range ($\lambda = 1.54060\text{ \AA}$). The acquired diffractograms were analyzed using the JADE software package (version 8.1)

and compared to databases from the International Centre for Diffraction Data to estimate the relative abundance of crystalline mineral phases in the precipitates.

The morphology of the precipitated Pb mineral crystallites was observed using an optical microscope at $400\times$ magnification as further confirmation of mineral identification based on XRD and FTIR.

2.4. Data Analysis

All solution measurements (pH, dissolved Pb, Pb activity) are presented as an average of triplicates with standard deviation. The treatment effects were determined by analysis of variance according to Tukey's test using SPSS 20.0. Significance was tested at the 0.05 probability level.

3. Results and Discussion

3.1. Effects of Sulfate, Carbonate and Phosphate on Pb Solubility

The experimental data (Table 1 and Figure 1) showed that more than 98% of Pb in all aqueous systems precipitated over a wide range of pH. In the case of the SO_4 system, 1–2% of the Pb remained soluble in the acidic range of pH, but this decreased to less than 0.1% in the alkaline pH range. However, in the SO_4 - PO_4 system, Pb solubility was lowered over the entire pH range of 4 to 8 when compared with the SO_4 system (Figure 1A) and was comparable to that of the pure PO_4 system. Similarly, although the CO_3 system limited the Pb solubility to less than 0.2% of the initial concentration, the presence of phosphate in the CO_3 - PO_4 system lowered the solubility even further (Figure 1B). Thus, Pb solubilities were similar in the SO_4 - PO_4 , CO_3 - PO_4 and PO_4 systems when compared over the pH range of 6 to 8, indicating that the formation of insoluble Pb phosphate minerals limited solubility whether PO_4 was present alone or in combination with CO_3 or SO_4 . This result is consistent with the known very low solubility of Pb phosphate minerals relative to the solubilities of Pb sulfates and carbonates [37].

Table 1. Percentage (%) of Pb remaining in solution after 30 days of reaction.

System	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9
SO_4	$1.42 \pm 0.63\text{a}$	$1.71 \pm 0.35\text{a}$	$1.55 \pm 0.60\text{a}$	$0.07 \pm 0.02\text{b}$	$0.05 \pm 0.01\text{b}$	ND
CO_3	ND	ND	$0.19 \pm 0.08\text{a}$	$0.11 \pm 0.01\text{ab}$	$0.049 \pm 0.02\text{b}$	$0.047 \pm 0.01\text{b}$
PO_4	$0.018 \pm 0.003\text{a}$	$0.010 \pm 0.005\text{ab}$	$0.006 \pm 0.007\text{ab}$	$0.005 \pm 0.004\text{b}$	$0.010 \pm 0.004\text{ab}$	ND
SO_4 - PO_4	$0.12 \pm 0.02\text{a}$	$0.011 \pm 0.004\text{b}$	$0.008 \pm 0.002\text{b}$	$0.007 \pm 0.002\text{b}$	$0.008 \pm 0.002\text{b}$	ND
CO_3 - PO_4	ND	ND	$0.011 \pm 0.003\text{a}$	$0.009 \pm 0.003\text{ab}$	$0.005 \pm 0.003\text{ab}$	ND

Data expressed as mean $\pm$ standard deviation ($n = 3$). Means with the same letters in the same row were not significantly different at $p < 0.05$. ND = not determined.

As shown in Figure 1A, the measured Pb solubility in solutions containing SO_4^{2-} was essentially constant between pH 4 and 6, but decreased by about 1.4 log units as the pH increased from 6.0 to 8.0. In the CO_3 system (Figure 1B), dissolved Pb decreased gradually by 0.55 log units as the pH was increased from 6.0 to 9.0. This relative insensitivity of Pb solubility to pH change is attributed to the formation of the stable aqueous ion pairs $\text{PbCO}_3(\text{aq})$ and $\text{Pb}(\text{CO}_3)_2^{2-}$, predicted by Visual MINTEQ to dominate the speciation of soluble Pb at pH 8 and higher (Figure S1, Table S1). With phosphate present, pH showed little influence on Pb solubility in the SO_4 - PO_4 and CO_3 - PO_4 systems between pH 5 and 8, as precipitation of Pb removed more than 99.9% of the total Pb from solution over this entire pH range. The presence of PO_4^{3-} with SO_4^{2-} or CO_3^{2-} reduced soluble Pb by approximately 1 to 2 log units compared to soluble Pb in the absence of PO_4^{3-} , attributable to Pb phosphate precipitation. An abrupt decrease in Pb solubility took place at the highest pH of 9.0 in the CO_3 - PO_4 system, resulting in the dissolved Pb concentration falling below the ICP-OES analytical detection limit ($<5 \mu\text{g L}^{-1}$). To put these soluble Pb concentrations in perspective, the horizontal broken line (at $15 \mu\text{g L}^{-1}$ concentration) denoting EPA's action level for drinking water reveals that all systems at pH 5 and higher containing

phosphate were close to or below this level (Figure 1A,B). These results are explained by the thermodynamically favorable precipitation of insoluble Pb phosphates in the presence of other anions. The specific mineral formed from these solutions was predicted by Visual MINTEQ to be hydroxypyromorphite $[\text{Pb}_5(\text{PO}_4)_3\text{OH}]$ on the basis of the saturation indices of the solutions [15,17,27].

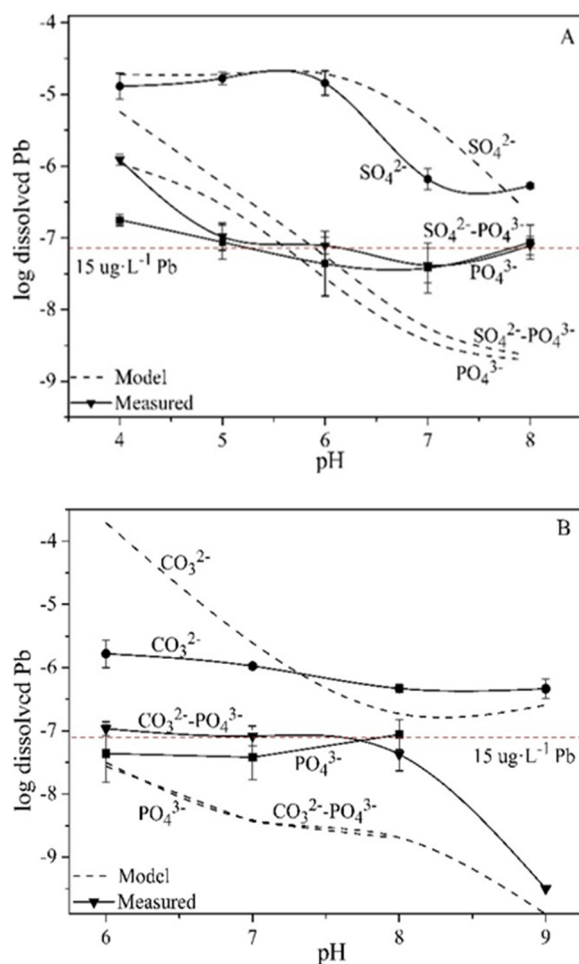


Figure 1. Measured dissolved concentrations of Pb (in log molarity units) in Pb solutions containing sulfate with and without phosphate (A) and carbonate with and without phosphate (B) as a function of pH. The phosphate-only Pb solubilities are included for comparison. Model dissolved concentrations of Pb using Visual MINTEQ (assuming equilibrium with atmospheric CO₂ = 400 ppmv) are shown for comparison. Error bars represent the standard deviation of three replicates.

Although the Visual MINTEQ model predicted the observed trends in measured Pb solubilities qualitatively in the case of the CO₃ and CO₃-PO₄ systems, it overestimated Pb solubility at low pH and underestimated solubility at pH > 6 in the PO₄ and SO₄-PO₄ systems (Figure 1A). Similarly, the model underestimated actual Pb solubility in the CO₃-PO₄ system. Discrepancies between the experimental and modeling results for Pb solubility at higher pH may be attributable to stronger ion-pair formation of Pb with anions in aqueous solution than has been generally assumed based on past estimates of the stability constants of these soluble species [30]. Specifically, greater formation of the ion pairs $\text{PbHPO}_4(\text{aq})$ and $\text{PbH}_2\text{PO}_4^+(\text{aq})$ than predicted by Visual MINTEQ (Table S1) would have the effect of increasing total soluble Pb at equilibrium with a mineral phase, particularly at pH > 6 where these ion pairs are most stable. This ion-pair effect could explain the higher-than-predicted solubility of Pb in the PO₄ and SO₄-PO₄ systems at pH > 6 in Figure 1A, but the generally lower Pb solubility than predicted at lower pH

cannot be due to this effect and may reflect the failure of reported solubility products for Pb phosphate minerals to remain constant over a wide range of pH [36].

In summary, the presence of SO_4 in solution at a concentration equal to PO_4 had little to no effect on either Pb solubility or the efficiency of Pb precipitation, except possibly at the lowest pH (Figure 1A).

Dissolved Pb measured in aqueous solutions containing only carbonate was somewhat greater than predicted by Visual MINTEQ in the alkaline pH range (Figure 1B). With PO_4 present in addition to CO_3 , Pb solubility was decreased markedly but was still greater than predicted by Visual MINTEQ over the entire pH range (6–9). Possible explanations for these discrepancies could be the slow kinetics of bicarbonate-carbonic acid equilibrium with atmospheric CO_2 leading to greater formation of Pb-carbonate ion pairs [41], or greater soluble ion-pair formation of PO_4 and CO_3 with Pb than predicted based on stability constants in the Visual MINTEQ thermodynamic database.

3.2. Effects of Sulfate, Carbonate and Phosphate on Pb^{2+} Activity

As shown in Figure 2, the free Pb^{2+} ion activities were more sensitive than Pb solubilities to pH in all of the systems, decreasing by 2–4 log units with the increase in pH from 4.0 to 8.0 (PO_4 , SO_4 and SO_4 - PO_4 systems) and 6.0 to 9.0 (CO_3 and CO_3 - PO_4 systems). Pb activities were not, however, very sensitive to system equilibration time. Thus, Figure 2 shows the activity for the 30-day equilibrations only, with similar results for shorter reaction times not shown. The lowered Pb^{2+} activities at higher pH result from the precipitation of carbonates, phosphates and possibly hydroxides/oxides. However, for the SO_4 system without PO_4 present, the insensitivity of Pb^{2+} activity and Pb solubility to pH in the lower pH range (4–6) is an expected feature of anglesite (PbSO_4) precipitation (Figures 1A and 2A). At higher pH, increased OH^- and carbonate in solution cause lowered Pb^{2+} activity and Pb solubility as Pb minerals less soluble than anglesite precipitate.

The speciation of dissolved Pb was also very sensitive to pH. At low pH, soluble Pb in the presence of the SO_4^{2-} , HCO_3^- and H_2PO_4^- oxyanions was primarily in the free Pb^{2+} ion form (Table S1). However, in the more alkaline pH range (7–9), free Pb^{2+} made up a much smaller fraction of the dissolved Pb concentration, as the main species present were predicted by thermodynamic modeling to be Pb-hydroxy, Pb-phosphate, Pb-carbonate and Pb-sulfate complexes (Figure S1, Table S1).

At any given pH, free Pb^{2+} activity in solutions containing the anionic species tested followed the order CO_3^{2-} - $\text{PO}_4^{3-} < \text{SO}_4^{2-}$ - $\text{PO}_4^{3-} < \text{PO}_4^{2-} < \text{CO}_3^{2-} < \text{SO}_4^{2-}$. Thus, CO_3^{2-} added to solution was more effective than SO_4^{2-} in reducing free Pb activity when compared over the same pH range of 6.0 to 8.0. The presence of added PO_4^{3-} further enhanced the reduction in free Pb activity, and the greatest reduction by phosphate (by about 3 log units) was found at pH 6.

As shown in Figure 2, thermodynamic modeling predicted the general trends observed in Pb^{2+} ion activities as affected by pH and the presence of the different anions, but consistently predicted much higher Pb^{2+} activities than measured by the Pb ion-selective electrode. The lower measured Pb^{2+} activities relative to those predicted by the Visual MINTEQ model (which uses generally accepted solubility products for Pb sulfate, carbonate and phosphate minerals) suggest that the commonly employed K_{SP} values overestimate the solubility of minerals such as anglesite, cerussite and hydroxypyromorphite. It is important to note that the solubility products of many of these minerals were determined decades ago by dissolution experiments that require free Pb^{2+} activity to be estimated at equilibrium. This was generally attempted by the process of modeling soluble Pb speciation [21,42], but substantial uncertainties in soluble Pb ion-pair (Pb-hydroxy, Pb-carbonate, Pb-phosphate) stabilities presented a serious obstacle to calculating accurate K_{SP} values by this method [43].

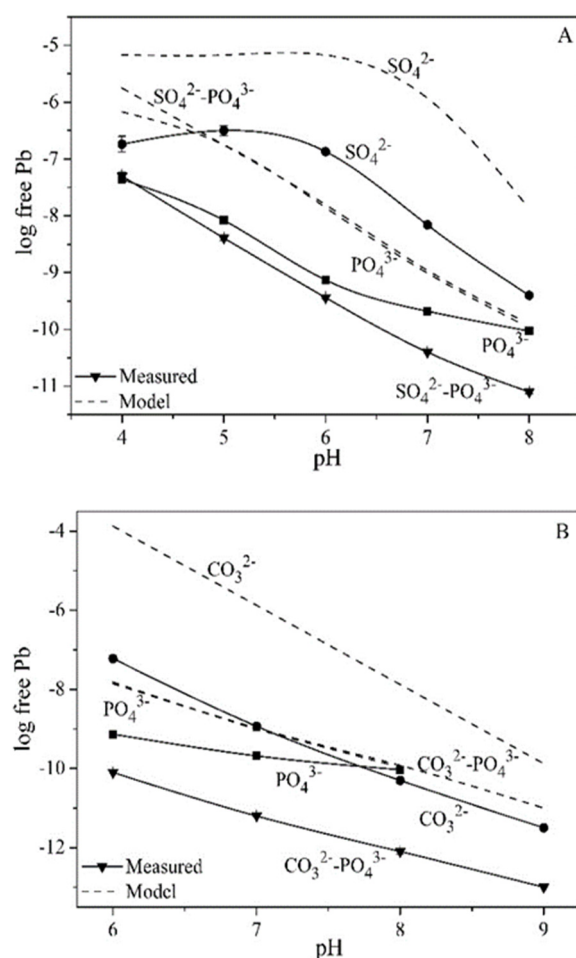
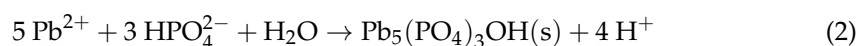
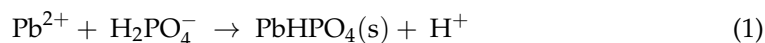


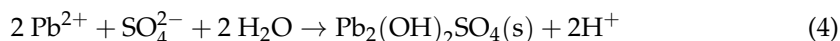
Figure 2. Measured activities of free Pb^{2+} (in log molarity units) in Pb solutions containing sulfate with and without phosphate (A) and carbonate with and without phosphate (B) as a function of pH. The phosphate-only Pb activities are included for comparison. Model activities of free Pb using Visual MINTEQ (assuming equilibrium with atmospheric $\text{CO}_2 = 400$ ppmv) are shown for comparison. Error bars represent the standard deviation of three replicates.

3.3. Effects of Pb Precipitation on Solution pH

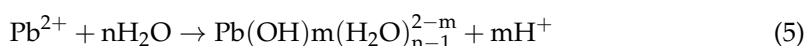
The aqueous suspensions containing Pb minerals were equilibrated and re-adjusted periodically to the initial target pH, but spontaneous shifts in pH to more acidic values were observed upon the addition of Pb to the solutions. This effect was most pronounced in the first 24 h after the initial Pb precipitation events (see Figure S2), particularly for the higher target pH values of the CO_3 and SO_4 systems without phosphate present. In the $\text{SO}_4\text{-PO}_4$ system, a pH shift was evident only at lower pH (4–5), whereas the pH was relatively stable over 30 days at higher pH, attributable to strong buffering by dissolved phosphate. In the $\text{CO}_3\text{-PO}_4$ system, a pH shift occurred initially over the entire pH range of 6–9, but was stable after the first 24 h. The presence of phosphate acting as a buffer in the solutions tended to shorten the time required to stabilize the solution pH at the target value.

The downward shift in solution pH could be the direct result of proton release by the precipitation of Pb minerals, including PbHPO_4 , hydroxypyromorphite, hydrocerussite and lanarkite:





Specifically, the initial pH decrease in the SO_4 system is most reasonably explained by the precipitation of lanarkite (reaction (4)), as anglesite precipitation should have no effect on pH. For the solutions initially adjusted to alkaline pH values, a number of other reactions could contribute to a pH decrease. The dissolution of atmospheric CO_2 into alkaline solutions would lower the pH as H_2CO_3 reacts with hydroxyl and carbonate. Moreover, the hydrolysis of Pb in solution at higher pH also could contribute to the pH decrease as follows ($n > m$):



Pb hydrolysis becomes significant for dilute solutions of Pb^{2+} at pH 6 and higher [44].

In summary, although initial shifts in pH were suggestive of the precipitation of certain Pb minerals, identification of the actual minerals formed after 30 days of equilibration relied upon FTIR spectroscopy and XRD, as described in the next sections.

3.4. FTIR Analysis of Precipitated Pb Minerals

The FTIR spectra of the precipitates formed by the reaction of soluble Pb with sulfate, carbonate and phosphate over a wide pH range are shown in Figure 3. For the SO_4 system at low pH (4.0–6.0), diagnostic absorption bands of the PbSO_4 mineral anglesite were observed. These bands at 993 and 959 and at 586 and 620 cm^{-1} are attributed to stretching (ν_1) and antisymmetric bending (ν_4) vibrations of SO_4^{2-} , respectively [45]. Additional bands at 1050 and 596 cm^{-1} are also characteristic of sulfate bend vibrations in this mineral. At higher solution pH conditions, marked changes in the spectra revealed the formation of new mineral phases replacing those formed at low pH. Specifically, new peaks appeared near 673 and 1370 cm^{-1} at higher pH, indicating the greater presence of carbonate relative to that of sulfate in the precipitates. A band near 3447 cm^{-1} indicative of structural OH (not shown) was also present at higher pH [42]. Although carbonate ions were not initially added to the SO_4 and $\text{SO}_4\text{-PO}_4$ systems, FTIR detected CO_3^{2-} ions in the precipitates formed from the sulfate solutions, as evidenced by a broad peak centered at 1370 cm^{-1} and a sharp peak at 673 cm^{-1} that had greater intensity at higher pH. This carbonate in the precipitates was produced from atmospheric CO_2 that dissolved into the aqueous systems during the 30-day equilibration. These observations indicate that low levels of dissolved bicarbonate compete effectively with high concentrations of soluble sulfate in forming carbonate-containing Pb minerals at pH 6 and higher.

The introduction of phosphate into the SO_4 system greatly changed the spectra, with new FTIR bands in the 3200–3600 cm^{-1} region and changes in the 400–600 cm^{-1} frequency region attributable to the stretching modes of structural O-H and the asymmetric bending vibrations of P-O from PO_4^{3-} groups, respectively [46]. At pH 4, the diagnostic bands characteristic of Pb-O-P and P-O groups at 960 and 1130 cm^{-1} were also present [30]. At higher pH (7.0–8.0), the strong carbonate bands at 673 and 1370 cm^{-1} observed in the absence of phosphate were diminished and single peaks at 1047 and 834 cm^{-1} merged into a doublet, apparently reflecting phosphate substitution for sulfate in the precipitate formed at high pH. The absence of carbonate absorption bands in the precipitated Pb mineral is an indication that phosphate, unlike sulfate, strongly suppressed formation of Pb carbonate minerals over the entire pH range.

In the CO_3 system, the IR spectra were essentially the same in the pH range between pH 6 and 8, displaying a broad band centered at 1373 cm^{-1} with a weaker shoulder at 1424 cm^{-1} consistent with the ν_3 vibrational mode of the carbonate anion [47]. The FTIR bands located at 1107 and 1051 cm^{-1} are assigned to the characteristic C-O symmetric stretching vibration, while two sharp bands at 677 and 837 cm^{-1} are diagnostic peaks of cerussite [48]. However, at pH 9, these two sharp bands were lost, and new features in the spectrum indicated that hydrocerussite had formed in place of cerussite at high pH.

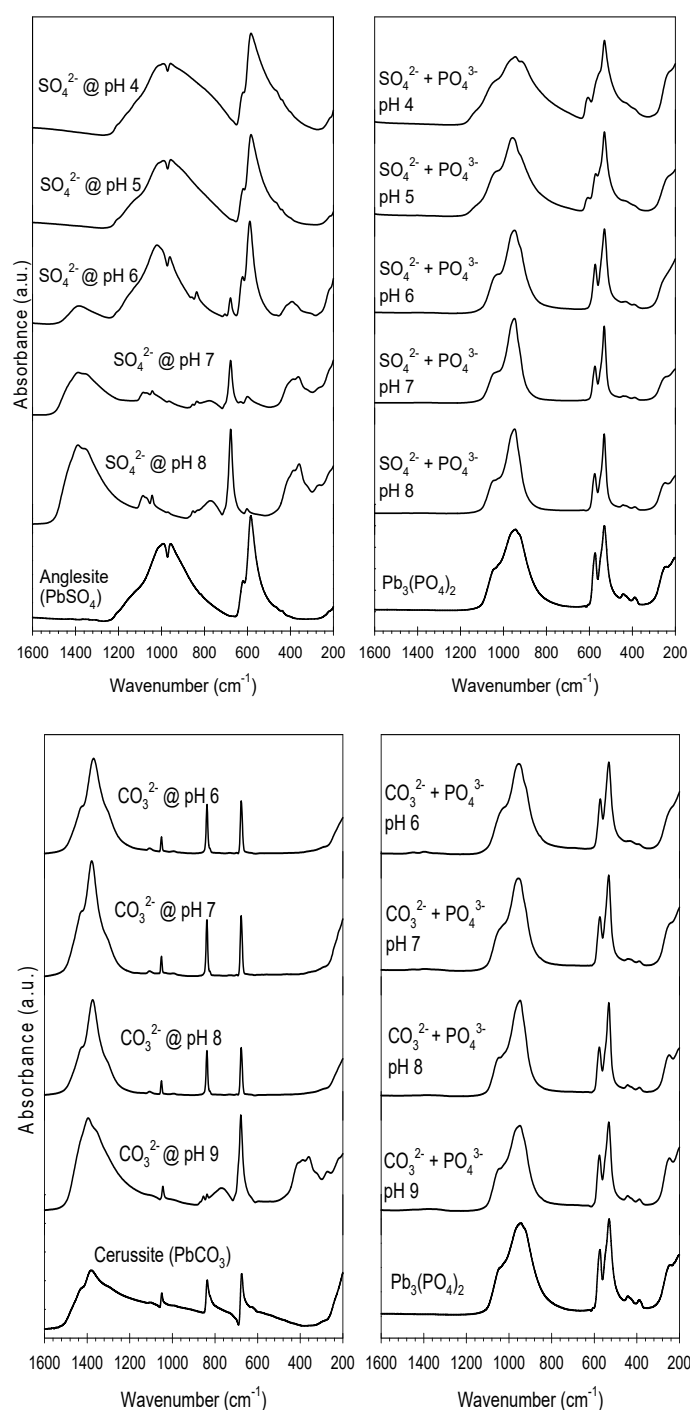


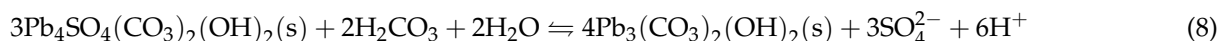
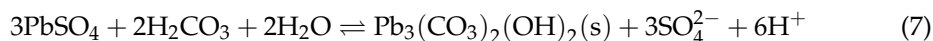
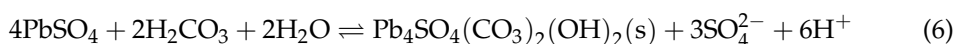
Figure 3. FTIR spectra of precipitates from experiments with Pb-sulfate (pH = 4.0–8.0) and Pb-carbonate (pH = 6.0–9.0) in the absence and presence of phosphate. The bottom spectra are those of relevant standard minerals.

The introduction of phosphate to the CO_3 system essentially eliminated the hydrocerussite and cerussite peaks at 1424 and 1378 and at 837 and 677 cm^{-1} . The broad band at 948 cm^{-1} with a low-intensity band at 1023 cm^{-1} and the doublet peaks at 575 and 531 cm^{-1} are assigned to stretching (ν_3) and bending (ν_4) vibrations of P-O groups [46]. Peaks that appear near 434, 395 and 236 cm^{-1} and become stronger at higher pH are attributed to the C-O stretching vibration for hydrocerussite [49]. These are greatly reduced with phosphate present in the CO_3 system, a further indication that phosphate is much more capable than sulfate in suppressing carbonate mineral formation. Finally, an

absorption band near 3364 cm^{-1} (not shown) is assigned to the in-plane vibration of O-H in hydroxyl. In comparing the CO_3 system with and without phosphate, it is clear that the precipitates formed are largely determined by the presence of phosphate rather than pH.

3.5. XRD Analysis of Pb Precipitates

The XRD patterns of the Pb mineral precipitates, shown in Figure 4, were analyzed using the JADE software to obtain quantitative estimates of the specific minerals formed. Table 2 lists the minerals identified by XRD compared to the minerals predicted to form based on saturation indices calculated for the solutions. In the SO_4 system without phosphate present, the precipitates at pH 4.0 and 5.0 were identified as 100% anglesite (PbSO_4). At pH 6.0 and 7.0, however, in addition to anglesite, leadhillite [$\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2$] was identified by the appearance of reflections at 24.9 and 30.9 degrees 2θ , although this mineral was not predicted as the most likely to precipitate based on its saturation index (Table 2). Hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] was formed under the most alkaline conditions tested (pH 7.0 and 8.0) as revealed by reflections at 24.7, 27.2 and 34.1 degrees 2θ , consistent with its predicted stability at higher pH (Table 2). The appearance of leadhillite and hydrocerussite at higher pH is explained by the transfer of atmospheric CO_2 into the suspensions over the 30 days of equilibration. However, lanarkite [$\text{Pb}_2(\text{OH})_2\text{SO}_4$] was not detected by XRD at any pH in the SO_4 system, despite being predicted as the most stable mineral at pH 6.0 (Table 2). Overestimation of lanarkite stability has been noted in past studies [10]. The XRD evidence for carbonate minerals becoming increasingly prevalent at higher pH corroborates the FTIR evidence for the presence of carbonate anions in the Pb precipitates. As described by Abdul-Samad et al. [10], the stability boundaries among anglesite, leadhillite and hydrocerussite are all dependent upon the activity of dissolved carbonic acid, $a_{\text{H}_2\text{CO}_3}$:



For the CO_3 system without phosphate present, an XRD peak at 24.8 degrees 2θ confirmed the Pb precipitates to be 100% cerussite over the pH range of 6.0 to 8.0. As the solution pH increased to 9.0, the XRD pattern indicative of cerussite was replaced by that of hydrocerussite (an intense reflection at 34.1 and weaker reflections at 24.7 and 27.2 degrees 2θ). However, the Visual MINTEQ simulations consistently predicted hydrocerussite to be more stable than cerussite in the pH range of 6 to 9, suggesting that the thermodynamic data for these two minerals need correction, as implied by earlier studies [21,22].

Compared to the SO_4 and CO_3 systems without phosphate, the presence of PO_4^{3-} completely altered the chemical and mineralogical composition of the Pb precipitates, with phosphate replacing sulfate and carbonate ions in the minerals formed from solution. The XRD patterns were virtually identical at pH 6 and higher for both the SO_4 - PO_4 system and the CO_3 - PO_4 system (Figure 4). Analysis of these XRD patterns using the JADE XRD software identified the predominant mineral to be $\text{Pb}_3(\text{PO}_4)_2$, although hydroxypyromorphite and $\text{Pb}_{10}(\text{PO}_4)_6\text{O}$ may also have been present. The minerals precipitated were those expected to form based upon the initial saturation indices (Table 2). All three of these Pb phosphates are structurally isomorphous as members of the apatite mineral group and, as such, have similar but distinguishable X-ray patterns [50]. The relatively broad XRD peaks of these Pb phosphate minerals indicate poor crystallinity and very small particle size compared to the Pb sulfate and carbonate minerals formed in this study, a supposition confirmed by the much smaller crystallite size of the Pb phosphates formed at higher pH as revealed using optical microscopy. However, at low pH (4–5) in the SO_4 - PO_4 system, a completely different XRD pattern that was not identifiable using the JADE XRD database suggested the formation of an unknown mineral under the acidic conditions less favorable

Table 2. Observed and predicted minerals precipitated in the aqueous Pb systems containing sulfate, phosphate and carbonate over a range of pH in equilibrium with atmospheric CO₂ (P_{CO2} = 400 ppmv). Predicted minerals are those with the highest saturation index, while minerals in brackets have saturation indices closest to the predicted mineral.

System	pH	Predicted by Visual MINTEQ ^a	Identified by XRD
SO ₄	4.0	PbSO ₄	PbSO ₄
	5.0	PbSO ₄ [Pb ₂ (OH) ₂ SO ₄]	PbSO ₄
	6.0	PbSO ₄ [Pb ₂ (OH) ₂ SO ₄]	PbSO ₄ , Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂
	7.0	Pb ₂ (OH) ₂ SO ₄ [Pb ₃ (OH) ₂ (CO ₃) ₂]	Pb ₃ (CO ₃) ₂ (OH) ₂ , Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂
	8.0	Pb ₃ (OH) ₂ (CO ₃) ₂ [Pb ₄ (OH) ₆ SO ₄]	Pb ₃ (CO ₃) ₂ (OH) ₂ , Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂
SO ₄ -PO ₄	4.0	PbHPO ₄ [Pb ₃ (PO ₄) ₂]	Unidentified mineral, Pb ₃ (PO ₄) ₂ , Pb ₅ (PO ₄) ₃ (OH)
	5.0	PbHPO ₄ [Pb ₃ (PO ₄) ₂]	Unidentified mineral, Pb ₃ (PO ₄) ₂ , Pb ₅ (PO ₄) ₃ (OH)
	6.0	Pb ₃ (PO ₄) ₂ [Pb ₅ (PO ₄) ₃ OH]	Pb ₃ (PO ₄) ₂ , Pb ₁₀ (PO ₄) ₆ O, Pb ₅ (PO ₄) ₃ (OH)
	7.0	Pb ₅ (PO ₄) ₃ OH [Pb ₃ (PO ₄) ₂]	Pb ₃ (PO ₄) ₂ , Pb ₁₀ (PO ₄) ₆ O, Pb ₅ (PO ₄) ₃ (OH)
	8.0	Pb ₅ (PO ₄) ₃ OH [Pb ₃ (PO ₄) ₂]	Pb ₃ (PO ₄) ₂ , Pb ₁₀ (PO ₄) ₆ O
CO ₃	6.0	Pb ₃ (OH) ₂ (CO ₃) ₂ [PbCO ₃]	PbCO ₃
	7.0	Pb ₃ (OH) ₂ (CO ₃) ₂ [PbCO ₃]	PbCO ₃
	8.0	Pb ₃ (OH) ₂ (CO ₃) ₂ [PbCO ₃]	PbCO ₃
	9.0	Pb ₃ (OH) ₂ (CO ₃) ₂ [Pb(OH) ₂]	Pb ₃ (CO ₃) ₂ (OH) ₂ , PbCO ₃
	6.0	Pb ₃ (PO ₄) ₂ [Pb ₅ (PO ₄) ₃ OH]	Pb ₁₀ (PO ₄) ₆ O, Pb ₃ (PO ₄) ₂
CO ₃ -PO ₄	7.0	Pb ₅ (PO ₄) ₃ OH [Pb ₃ (PO ₄) ₂]	Pb ₃ (PO ₄) ₂ , Pb ₁₀ (PO ₄) ₆ O
	8.0	Pb ₅ (PO ₄) ₃ OH [Pb ₃ (PO ₄) ₂]	Pb ₃ (PO ₄) ₂ , Pb ₁₀ (PO ₄) ₆ O, Pb ₅ (PO ₄) ₃ (OH)
	9.0	Pb ₅ (PO ₄) ₃ OH [Pb ₃ (PO ₄) ₂]	Pb ₃ (PO ₄) ₂ , Pb ₁₀ (PO ₄) ₆ O, Pb ₅ (PO ₄) ₃ (OH)

^a The predicted minerals are those with the highest (second highest in brackets) calculated saturation indices.

In summary, the XRD data revealed that no detectable Pb sulfates or carbonates formed after reacting Pb with SO₄^{2−} or CO₃^{2−} solutions in the presence of PO₄^{3−}. Thus, Pb phosphates, primarily Pb₃(PO₄)₂ and hydroxypyromorphite, prevailed as the stable phases over a wide range of pH (≥6) in all systems containing phosphate, despite the presence of sulfate or carbonate at initially high concentrations. The results confirm that the ability of phosphate to immobilize Pb is much stronger than that of carbonate and sulfate, an important feature of aqueous Pb chemistry useful in limiting Pb solubility in the treatment of contaminated water.

4. Conclusions

Our research revealed that, while sulfate and carbonate can greatly reduce Pb solubility over a wide pH range, the Pb immobilization effect of carbonate is significantly greater than that of sulfate. The presence of phosphate further stabilizes Pb by precipitation (>99.9% of total Pb), resulting in lower solubility of Pb. Based on the FTIR and XRD studies of precipitates formed from aqueous solutions open to the atmosphere, anglesite, leadhillite and hydrocerussite were formed from Pb sulfate solutions, while cerussite and hydrocerussite were formed from Pb carbonate solutions. The introduction of phosphate into these solutions resulted in the formation of highly insoluble Pb phosphates. The presence of sulfate or carbonate at comparable solution concentrations to phosphate did not significantly inhibit the precipitation of Pb phosphate, although the precise Pb phosphate mineral formed may have been altered by the presence of sulfate at low pH. The Visual MINTEQ model predicted the actual mineral compositions of the precipitates with reasonable accuracy, with the exceptions that the model overestimated hydrocerussite stability relative to cerussite and lanarkite stability relative to anglesite and underestimated leadhillite stability. However, the model generally underestimated the actual Pb solubility, indicating that soluble ion pairs of Pb with phosphate in particular were more stable than predicted. The speciation model also overestimated free Pb²⁺ activities in all of the equilibrated Pb reaction systems, suggesting that the widely used K_{SP} values for Pb sulfates, carbonates and phosphates may need adjustment. This research demonstrates the importance of pH and solution anion composition in determining the Pb mineral phases formed and the

effectiveness of Pb immobilization by targeted precipitation reactions, useful information in developing an effective remediation technology for environmental pollution cleanup.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11060620/s1>, Figure S1: Percentage of Pb species in Pb solution containing sulfate, carbonate, sulfate-phosphate and carbonate-phosphate as a function of pH. The speciation data were created using the Visual MINTEQ model assuming equilibrium with 400 ppmv CO₂; Figure S2: Variation of pH in Pb solution containing sulfate, carbonate, sulfate-phosphate and carbonate-phosphate as a function of reaction time. Error bars represent the standard deviation of three replicates; Table S1: Percentage distribution among dissolved Pb species in the four systems at equilibrium with atmospheric CO₂ as a function of pH using Visual MINTEQ program.

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