



# Long-term phosphorus effects on evolving physicochemical properties of iron and aluminum hydroxides

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## Abstract

Iron (Fe) and aluminum (Al) hydroxides are highly reactive components in environmental processes, such as contaminant fate and transport. Phosphorus (P) sorption by these components can decrease environmental problems associated with excess accumulation of P in soils. The long-term stability of P sorbed by Fe/Al hydroxides is of major concern. Synthetic Fe and Al hydroxides coprecipitated with P (1:1 metal:P molar ratio) were incubated at 70 °C for 24 months to simulate natural long-term weathering processes that could influence the stability of sorbed P. Heat incubation (70 °C) of the untreated (no P) Al hydroxides resulted in drastic decreases (within the first month of incubation) in oxalate-Al extractability, specific surface area (SSA), and micropore volume with time. These changes were consistent with the formation of pseudoboehmite. Untreated Fe hydroxides showed no formation of crystalline components following heating (70 °C) for 24 months. Much smaller changes in oxalate-Al, P extractability, and SSA values were observed in the P-treated Al particles when compared with the untreated. Phosphorus treatment of both Fe and Al hydroxides stabilized the particle surfaces and prevented structural arrangements toward a long-range ordered phase. Slight reduction in SSA of the P-treated particles was related to dehydration phenomena during heating at 70 °C. Monitoring of physicochemical properties of the solids after heating at 70 °C for 2 years showed that sorbed P may be stable in the long-term. Understanding long term physicochemical properties may help engineers to optimize the Fe/Al hydroxides performance in several environmental/industrial applications.

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**Keywords:** Iron and Al hydroxides; Stability; Heat incubations; Microporosity; Specific surface area

## 1. Introduction

Iron (Fe) and aluminum (Al) hydroxides are ubiquitous in soils and play a key role in contaminant transport and reactivity. Iron and Al hydroxides are usually small in size (<2 µm), vary in crystallinity, and are often characterized by large specific surface areas (SSAs). In soils, Fe and Al hy-

droxides are the product of primary and secondary mineral weathering, and exist both as mineral coatings and discrete phases. Thermodynamic stabilities of Fe and Al hydroxides in soils regulate the fate and availability of macronutrients, like phosphorus (P). Iron or Al hydroxides may greatly increase a sandy soil's P sorption capacity, reducing off-site P losses that have been correlated with excess P amounts in water bodies [1].

Iron and Al hydroxides find use in environmental as well as industrial applications. Phosphorus-treated Al and Fe hydroxides have attracted much attention as catalysts, or ion exchangers for heavy metals [2]. Aluminum phosphates

**Abbreviations:** SSA, specific surface area; P, phosphorus; Fe/Al hydroxides, iron/aluminum hydroxides.

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have also been used to remove heavy metals (Co, Ni, and Cu) from aqueous solutions [3]. Amorphous Al phosphates (1:1 P:Al molar ratios) are used as adjuvants in licensed human vaccines as the stimulant for the immune response [4].

Amorphous Fe and Al hydroxides can be metastable, transforming with time to thermodynamically stable phases. A general rule is that crystal growth increases with increasing pH and temperature [5]. At pH < 5.1, gibbsite  $[Al(OH)_3]$  readily forms because conversion rates from boehmite  $[AlO(OH)]$  to bayerite  $[Al(OH)_3]$  to gibbsite are fast [5]. Amorphous Fe hydroxides transform to more crystalline phases either by dissolution/reprecipitation (to goethite,  $\alpha$ - $FeO(OH)$ ), or by structural rearrangements (to hematite,  $Fe_2O_3$ ) [6]. Goethite formation is usually favored under conditions of dissolution/reprecipitation phenomena. Hematite formation is favored by dehydration at pH values where the solid has the lowest solubility and the greatest potential for coagulation/aggregation [7]. In low water activity or dry systems, transformations occur, but at lower rates, since ion mobility is restricted. After 20.4 years, air-dried two-line ferrihydrite transformed to hematite at room temperature [6]. Internally adsorbed water facilitated the conversion process, even at low water content (100 to 150 g kg<sup>-1</sup> water). However, in dry systems, hematite will form in <20 years as temperatures increase to ~300 °C [6]. Hematite formation is more sensitive to temperature changes than goethite formation [8].

Amorphous Fe and Al hydroxides usually contain impurities, such as inorganic and organic ions that can influence particle stability. Specific adsorption of inorganic anions, such as phosphates, largely retarded the transformation of ferrihydrite to a more crystalline atomic arrangement [7]. Phosphate was the most important inorganic ligand in inhibiting crystallization of Al hydroxides followed by silicate > sulfate > chloride > nitrate > perchlorate [9]. Crystallization of ferrihydrite, as evidenced by oxalate extractions, proceeded normally at arsenate loads up to 29.5 g kg<sup>-1</sup> after 125-day incubation at 40 °C, and arsenate was stabilized into the goethite/hematite structure [10]. Greater arsenate loads retarded ferrihydrite crystallization [10]. In the absence of phosphate, ferrihydrite was transformed to hematite and goethite mixtures when incubated for 2 years at 25 °C, or 2 months at 50 °C [11]. When P was added, ferrihydrite transformation was largely retarded, and at P/Fe ratios > 1.5%, the oxalate-extractable Fe/total Fe ratio was ~1, suggesting no formation of a crystalline phase [11]. Similarly, dissolution rates of Fe hydroxides in the presence of sorbed phosphate were significantly reduced [12].

Contrasting theories deal with the stability of sorbed ions by Fe and Al hydroxides. The classic theory of aging supports the idea of structural reorganization of an amorphous solid phase by ion incorporation into the solid, forming a “solid solution” [13]. Solubility of long-range ordered oxides is usually orders-of-magnitude less than that of the amorphous solid and the vulnerability of these oxides to mi-

crobiologically induced Fe reduction is significantly less [14]. Ion partitioning is envisioned to be irreversible, unless dissolution of the host mineral occurs.

Artificial aging may occur by heat input, which increases the translational energy of atoms, and thus, transformation rates toward a lower free energy system. Heat incubation of amorphous metal hydroxides could hasten transformation reaction rates and heat treatment has been used as an experimental technique to study long-term structural and physical changes of solids [15,16]. Aging (200 days) and subsequent incubation at 70 °C for 2 months of Cd, Cu, and Zn coprecipitates with amorphous Fe hydroxides resulted in decreased Cd and Zn solubility [15]. Despite Cu movement toward the surface with increasing aging time (up to 2 years at 23 °C), decreased Cu solubility resulted from the coprecipitation of Cu with alumina [17]. Aging induced the transformation of an initially noncrystalline alumina to more crystalline phases, including gibbsite [17].

The classic theory of decreasing metal solubility in aged metal hydroxides does not apply to all metals. Heat incubations at 50 °C resulted in SSA reductions due to increasing crystallinity of Fe hydroxides [16,18]. Further heating at temperatures up to 900 °C transformed amorphous Fe (hydr)oxides to hematite. Despite the formation of the more stable hematite, elevated temperatures significantly reduced Cd and Pb retention capacity of the hematite [16]. Aging (1.5 years) at 70 °C of suspensions of a Brazilian Oxisol soil containing large quantities of Fe oxides resulted in increasing Pb solubility as the Fe amorphous phases crystallized toward goethite [16]. Ferrihydrite in contact with Pb solutions at 40–70 °C for 0.5 to 1.5 months resulted in Pb exclusion from the solid because of reduced sorption sites, due to formation of goethite [19].

Phosphorus interactions with hydrolysis products of Al and Fe are important in controlling the fate of P in the environment (e.g., soils and sediments [20,21]); in industrial and engineering processes (e.g., water purification [22]); in medicine (e.g., as adjuvants in licensed human vaccines [4]). Waste products of the drinking water purification are enriched in Fe or Al hydroxides and have been tested as cost-effective amendments to reduce soluble P concentrations in poorly P-sorbing sandy soils in an effort to prevent transport of agricultural P to water bodies [23].

Much research has been conducted on the nature of P sorption by metal oxides, but little is understood about the mutual interactions of metals and P when P is present in the formative stage of metal hydrolysis, as in the case of soil mineral weathering in P-rich soils, or in drinking-water or wastewater treatment coagulation processes. Long-term changes in physicochemical properties of the evolved Al/Fe hydroxides due to presence of high soluble-P levels, as well as the stability of P associated with natural and artificial metal hydroxides are not well understood. This study was conducted to (i) evaluate changes in physicochemical properties during the heat-accelerated aging (up to 2 years) of Fe and Al hydroxides, in the presence or absence of P; and

(ii) interpret the findings with respect to implications for long-term stability of P associated with the Fe/Al hydroxides.

## 2. Materials and methods

All reagents were of analytical grade and were used without further purification. Solutions were prepared in double-distilled water using Pyrex glass vessels. Amorphous gels of Fe and Al were prepared, with and without P [24]. Briefly, P was added to metal chloride solutions ( $\text{FeCl}_3$ , or  $\text{AlCl}_3$ ) to achieve 1:1 (P:metal) molar ratio in the final suspension. Mixtures were reacted for 1 h at 23 °C with continuous stirring. Suspensions were brought up to pH 8 with the aid of 1.08 N NaOH. This process enabled the metals to form hydroxide gels that precipitated out of solution. The resulting gels were separated by centrifugation at 3000g for 15 min, and washed with deionized water. Double-distilled water was used to bring all suspensions to the same volume; the suspensions were covered with Al foil, and placed in incubators at 70 °C. Bulk moisture was not controlled, and all physisorbed water was evaporated within 3 weeks of incubation.

Subsamples were collected from the incubated samples over 24 months. Before all analyses, aggregates were gently crushed with mortar and pestle. Oxalate (5 and 200 mM) extractions were performed according to the procedures of McKeague et al. [25]. Oxalate-extractable P, Al, and Fe were unaffected by changes in the solid:solution ratio (1:60 versus 1:300) or filter size (0.45 versus 0.1 μm) (data not shown); thus, a 1:300 ratio, and 0.45 μm filter size were chosen for further use. Following oxalate extraction, suspensions were centrifuged at 3000g for 15 min, filtered, and analyzed for P, Al, and Fe by a Perkin–Elmer Plasma 3200 inductively coupled plasma spectrometer (ICP).

Powder XRD analyses were conducted using monochromatic  $\text{CuK}\alpha$  radiation at 35 kV and 20 mA. The  $2\theta$  diffraction angle (2° to 50 or 70°) was scanned at a rate of 2° ( $2\theta$ )  $\text{min}^{-1}$ . Specific surface areas of the particles were measured at 77 and 273 K using  $\text{N}_2$  and  $\text{CO}_2$ , respectively, as the adsorbates in a volumetric apparatus (Quantachrome Autosorb-1, Quantachrome Corporation). Dinitrogen and  $\text{CO}_2$  gas sorption experiments were performed in liquid  $\text{N}_2$  (77 K), and ethylene glycol baths at 273 K, respectively, using a thermostat (Fisher Isotemp 3017). Prior to gas sorption/desorption, all samples were outgassed at 70 °C for 4 h using He as the eluent.

Based on the BET- $\text{N}_2$  gas sorption data, the quantification of micropores in the metal hydroxides was accomplished using the Saito–Foley model (SF model) [26] that accounts for large interaction potentials involved between pore walls in close proximity (<1.5 nm). The SF model assumes cylindrical pores with structure similar to zeolites, or molecular sieves [26].

## 3. Results and discussion

### 3.1. Oxalate extractions and XRD analyses

Stability transformations of incubated (70 °C) Al hydroxides coprecipitated with and without P were monitored via oxalate extractions. The rapid initial decrease in Al extractability (over the first week of incubation) was followed by a slower decrease up to 3 months of incubation at 70 °C, and thereafter leveled off (up to 2 years) (Fig. 1). When P was coprecipitated with Al at a 1:1 molar ratio and incubated at 70 °C, there were no significant changes in oxalate (200 mM)-extractable Al or P concentrations with time (Fig. 1). No significant effect of incubation time was observed for the Fe hydroxides treated with or without P.

Aluminum extractability with oxalate (200 mM) increased with P treatment (from ~50 for the untreated versus 150  $\text{g kg}^{-1}$  for the P-treated samples) (Fig. 1). Phosphorus treatment has possibly opened up the structure of the amorphous solid, thus facilitating the ligand-mediated dissolution process. On the contrary, oxalate (200 mM)-extractable Fe of the untreated (no P) samples was greater (~500  $\text{g kg}^{-1}$ ) than the P-treated (~200  $\text{g kg}^{-1}$ ), suggesting a negative effect of

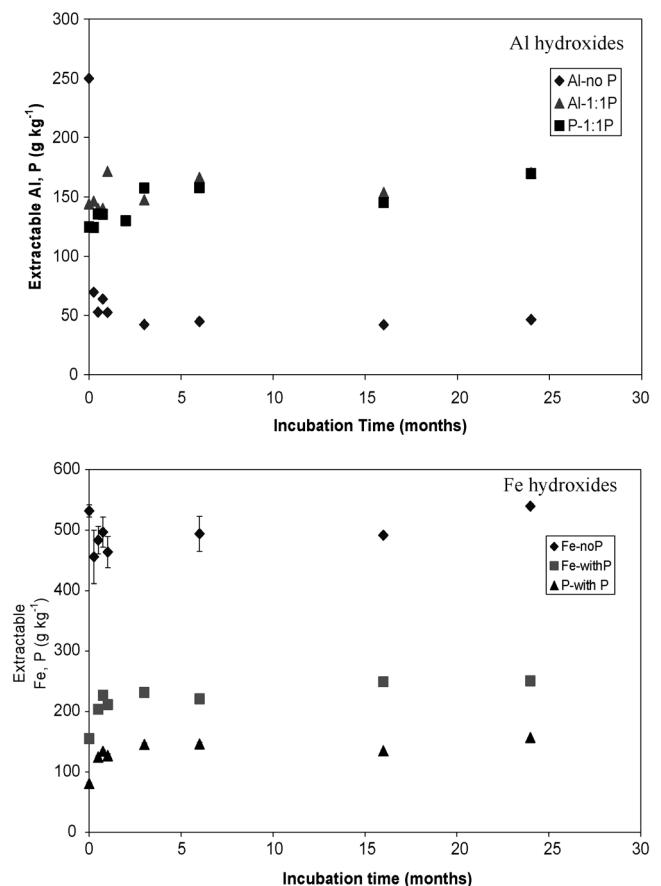


Fig. 1. Changes in oxalate (200 mM)-extractable Al or Fe and P of P-treated and untreated Al and Fe hydroxides incubated for 24 months at 70 °C. Error bars denote one standard deviation of the mean ( $n = 2$ ), and their size may be smaller than in the legend.

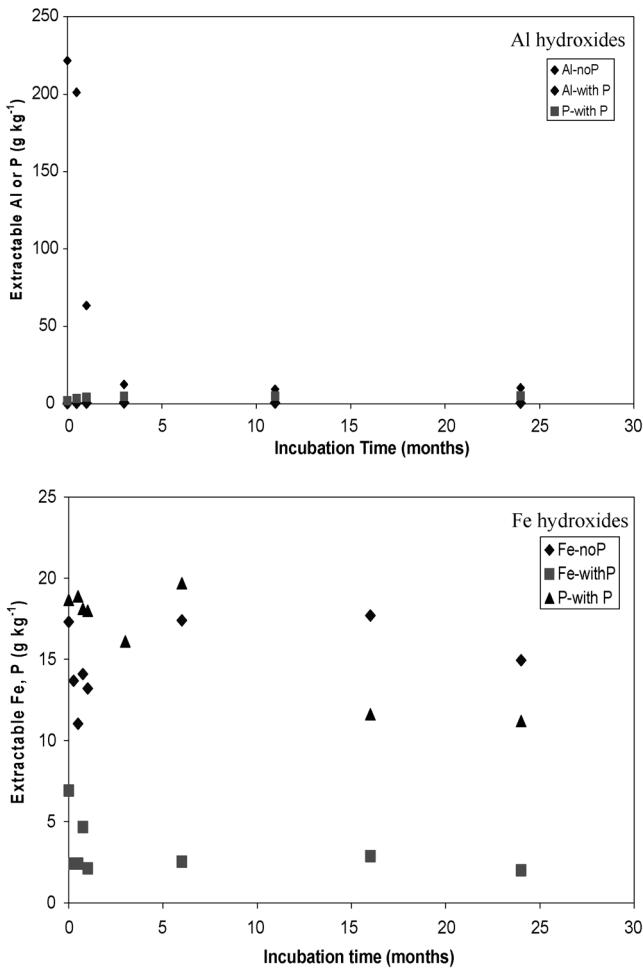


Fig. 2. Changes in oxalate (5 mM)-extractable Al, or Fe, or P of P-treated and untreated Al hydroxides incubated for 24 months at 70 °C.

P treatment on Fe extractability. The oxalate treatment almost completely dissolved Fe and Al particles and extracted >90% of the total P and metal (data not shown). Particle transformations are probably difficult to detect using a high concentration of oxalate (200 mM).

The insensitivity of the 200 mM oxalate treatment in monitoring sorbed P stability led us to use a milder extractant (5 mM oxalate). Phosphorus coprecipitation with the Al hydroxides decreased Al extractability with a 5 mM oxalate ligand to very low concentration ( $\sim 0.6 \text{ g kg}^{-1}$ ) when compared with the untreated Al hydroxide (Fig. 2). Similarly to the Al system, oxalate (5 mM)-extractable Fe of the P-treated Fe hydroxides was significantly lower than the untreated Fe particles (Fig. 2). Phosphorus addition stabilized the metal hydroxide surfaces by lowering oxalate (5 mM)-extractable P and Al concentrations when compared with the untreated (no P added) samples (Fig. 2). Decreased dissolution rates of Fe hydroxides have been reported in the presence of sorbed phosphate [12].

There was no long-term (up to 2 years) effect of incubation (70 °C) on oxalate (5 mM) extractability of metal and P concentrations in the Al hydroxides, since only slight

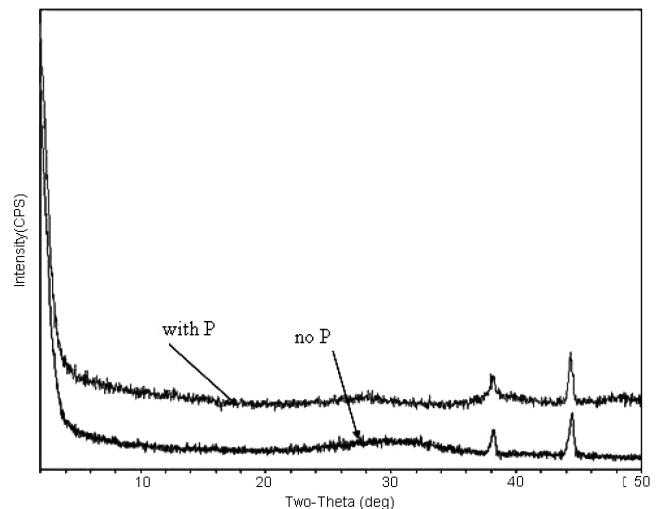


Fig. 3. X-ray diffraction analysis of P-treated and untreated Al hydroxides before placing them into incubators (time zero). Both treatments (P-treated and untreated) were amorphous. The two sharp peaks around 40° 2θ came from the mount.

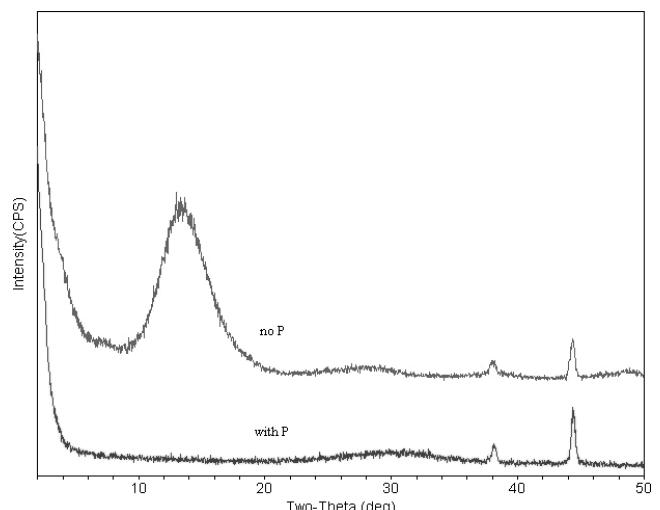


Fig. 4. X-ray diffraction analysis of P-treated and untreated Al hydroxides 1 month after incubation at 70 °C. Untreated samples showed the formation of pseudoboehmite. Further incubation at 70 °C for 24 months did not result in major changes to the peaks shown here. The two sharp peaks around 40° 2θ came from the mount.

changes were initially observed (the first 2–3 months of incubation). In the case of the Fe hydroxides, there seems to be a decreasing effect of aging on the oxalate (5 mM)-extractable P levels after the first 6 months of incubation. Based on the 5 mM oxalate extraction data, there seems to be little fear of increasing P extractability with time, suggesting P stabilization into the particles.

Although small in magnitude, changes in oxalate (200 and 5 mM)-extractable metal and P concentrations led us to suspect changes in particle crystallinity due to heat incubation (70 °C). X-ray diffraction analyses showed that at time zero, both P-treated and untreated Al hydroxides were amorphous (Fig. 3). Incubation at 70 °C of the untreated Al

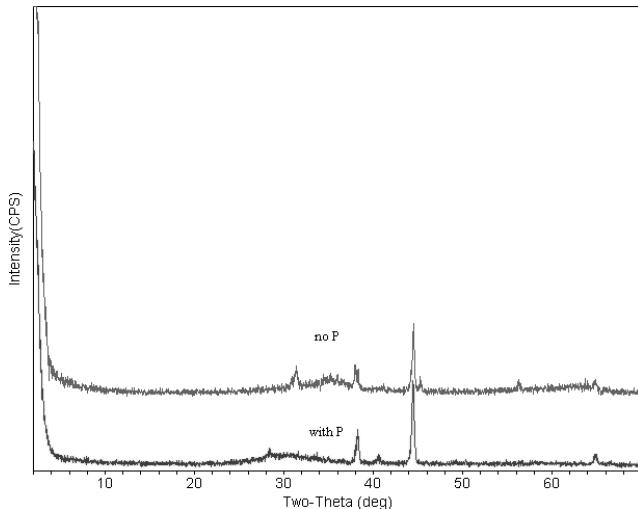


Fig. 5. X-ray diffraction analysis of P-treated and untreated Fe hydroxides one month after incubation at 70 °C. Both untreated and P-treated samples were amorphous. Further incubation at 70 °C for 24 months did not result in major changes of the peaks shown here. The two sharp peaks around 40° 2θ come from the mount. Sharp peak of the untreated sample around 32° 2θ comes from remaining salt (NaCl).

hydroxides for a month was sufficient to induce changes in crystallinity, as evidenced by a broad peak (Fig. 4) that was tentatively assigned to pseudoboehmite [5]. There was no further increase in crystallinity even after 24 months of incubation at 70 °C. Phosphorus-treated (1:1 P:Al molar ratio) Al hydroxides remained amorphous throughout the incubation period of 24 months (data not shown), suggesting that P addition poisoned particle crystallization. At P/Fe molar ratios less than 3%, crystallization of ferrihydrite proceeded normally, whereas at ratios greater than 3% phosphate inhibited the crystallization of Fe hydroxide [11]. The high Al:P molar ratio (1:1 P/metal molar ratio) of the Al hydroxides used here inhibited the structural transformations that were observed in the absence of P.

Similarly to oxalate extraction data, XRD patterns suggested no effect of incubation time on crystal growth for either P-treated, or untreated Fe hydroxides; particles remained amorphous throughout the incubation period (Fig. 5). The X-ray pattern of the untreated Fe hydroxides resembled a six-line ferrihydrite and was highly amorphous, similarly to what Stanjek and Weidler [27] found for another ferrihydrite that was incubated at 100 °C. The method used in our study was initially designed for the synthesis of Al hydroxides, but should work for Fe hydroxides, as well [14]. However, preparation conditions were different than the typical two- and six-line ferrihydrite methods [6].

### 3.2. Surface area and porosity of the Al and Fe hydroxides

At time zero (right before incubation at 70 °C), untreated (no P added) Al hydroxides were fully hydrated and characterized by large BET-N<sub>2</sub> SSA ( $607 \text{ m}^2 \text{ g}^{-1}$ ) (Fig. 6). Dinitrogen gas adsorption isotherms showed increased N<sub>2</sub> sorption

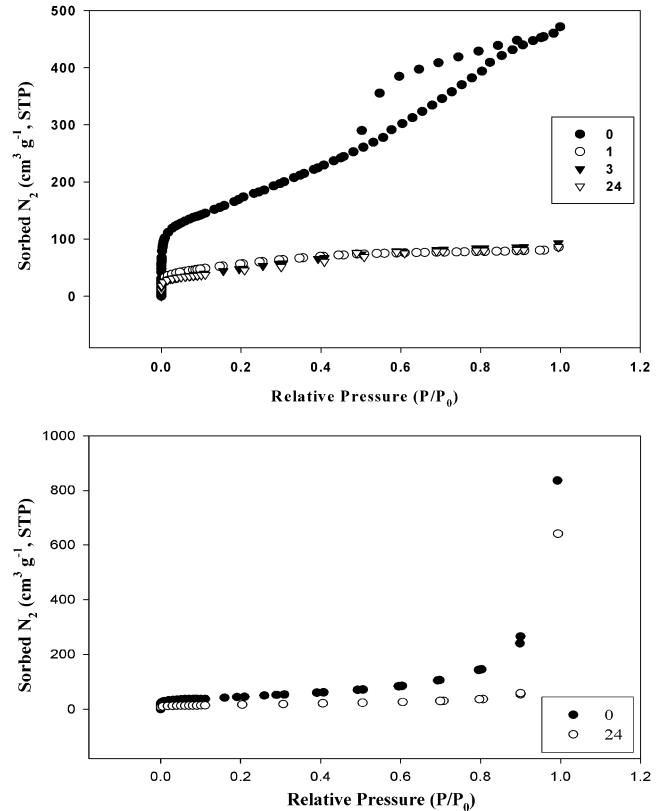


Fig. 6. Changes in N<sub>2</sub> gas adsorption/desorption isotherms ( $-196^\circ\text{C}$ ) of the Al hydroxides performed at different incubation times (0 to 24 months) at 70 °C. The first graph shows the untreated, and the second shows the P-treated particles. Hysteretic desorption was observed only for time zero (first graph), where sorption data did not coincide with desorption points. For all other incubation times, adsorption points fell on top of desorption data points.

at low relative pressures (less than  $0.1 \text{ P}/\text{P}_0$ ), indicative of microporosity (<2 nm) [28]. When subjected to N<sub>2</sub> gas desorption, the isotherm revealed a hysteretic behavior for the untreated Al hydroxides. The hysteresis observed at higher relative pressures ( $>0.5$ ) suggested the abundance of mesopores in the untreated Al hydroxides that formed during the coprecipitation process [28].

Incubation (70 °C) of the untreated Al hydroxides resulted in significant BET-N<sub>2</sub> SSA decreases (Fig. 6). After 1 month of incubation (70 °C), there was a drastic reduction in the SSA of the untreated Al hydroxides (from  $607$  to  $168 \text{ m}^2 \text{ g}^{-1}$ ) (Fig. 6). Further incubation for 24 months resulted in minor SSA decreases. This trend is corroborated by similar kinetic trends observed with oxalate extractions, as well as XRD data, for the untreated Al hydroxides. Decreases in SSA of the untreated Al hydroxides may have resulted from the combination of physisorbed water losses with structural rearrangements toward a more ordered phase, due to heat input (70 °C). Interestingly, the initial mesoporosity of the untreated Al hydroxides before incubation (time zero) disappeared after 1 month of incubation, since N<sub>2</sub> desorption was no longer hysteretic (evidenced by the overlap of adsorption and desorption points) (Fig. 6).

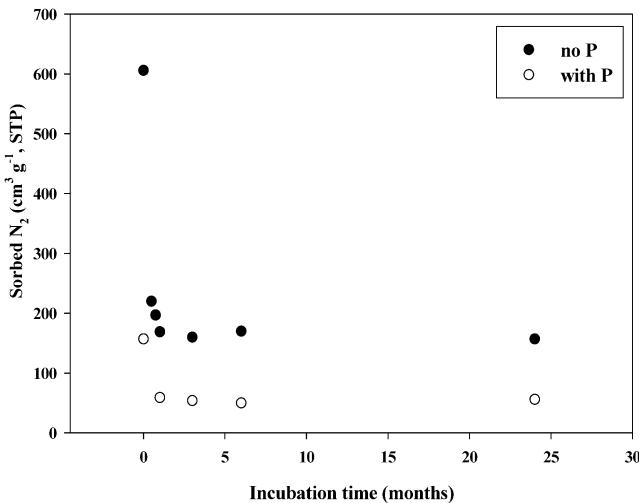


Fig. 7. Changes in BET-SSAs with time of the Al hydroxides coprecipitated with (1:1 P:Al ratio) or without P, and incubated at 70 °C.

Phosphorus treatment resulted in lowering SSA values when compared with the untreated (no P) samples (Figs. 6 and 7). Isotherms showed lower microporosity but greater macroporosity, as evidenced by the large upward direction of the curve at relative pressures 0.8–1  $P/P_0$ . Hysteretic N<sub>2</sub> gas desorption was absent in P-treated samples, suggesting the absence of mesopores (Fig. 6). Coprecipitation of P with the metal apparently resulted in meso- and/or micropore blocking by phosphates, and distortion of the structure toward greater macropore content (Figs. 6 and 7).

Except for the initial drop (within the first 1–2 months), there was no effect of incubation time on SSAs of the Al hydroxides (Fig. 7). Typical interpretation of such decreases in SSA is usually correlated with increasing crystallinity. This was the case for the untreated Al hydroxides, but not for the P-treated particles (Fig. 7). Decreases in SSA of a material do not necessarily reflect increases in crystallinity. Phenomena such as pore shrinkage due to dehydration could be responsible for the observed SSA decrease in the amorphous P-treated particles.

Meso- and micropore size distributions using the SF model are useful in assessing pores shrinkage phenomena. The SF pore size distribution of the untreated Al hydroxides revealed the predominance of micropore diameters around 10 Å (1 nm = 10 Å) (Fig. 8). At time zero, micropores were abundant, but were significantly reduced after 1 month of incubation at 70 °C, and remained unchanged thereafter (Fig. 8). This trend is consistent with oxalate extractions, SSA, and crystallinity (XRD analyses) measurements of the untreated Al hydroxides. As crystallite size increases, SSA decreases, and micropore volume decreases at the apparent expense of crystal growth.

Phosphorus-treated micropore volume measured by the SF method was much smaller than the untreated Al hydroxides (maximum differential pore volumes of 0.009 and 0.032, respectively) (Fig. 8). Phosphorus-treated micropore

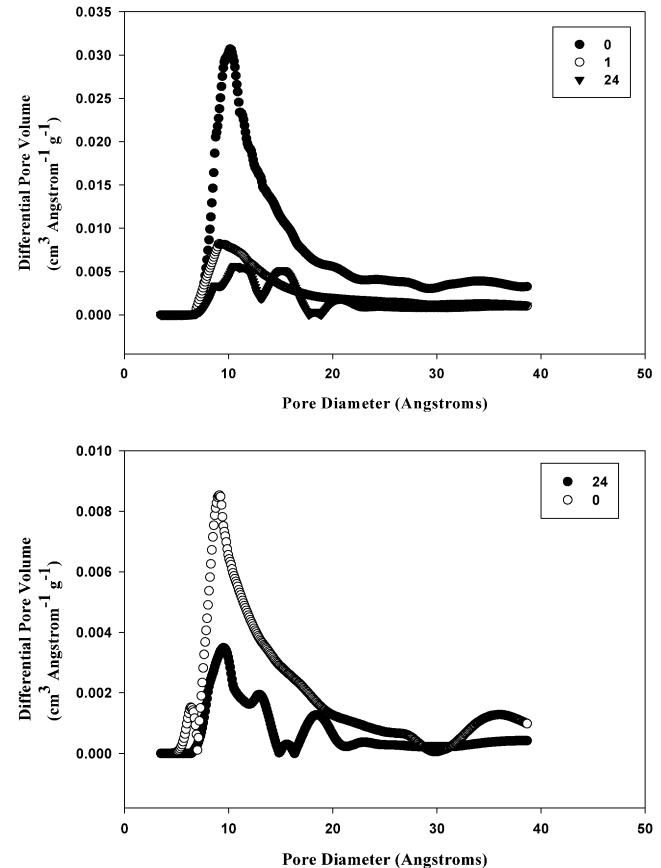


Fig. 8. Pore size distribution of the untreated (first graph) and the P-treated (second graph) Al hydroxides incubated at 70 °C for 0 to 24 months.

size distributions also exhibited a predominant size ~1 nm, similarly to the untreated pore size distributions.

Similar SSA and porosity analyses were conducted for the Fe hydroxides. Results from the N<sub>2</sub> gas adsorption isotherms of the untreated Fe hydroxides showed a large micropore volume content relative to the total pore volume and hysteretic desorption, suggesting the presence of mesopores (Fig. 9). Hysteretic desorption was observed at all incubation times (from time zero to 24 months of incubation at 70 °C). The amount of N<sub>2</sub> gas adsorbed decreased within 1 month of incubation, but not as drastically as in the case of the untreated Al hydroxides.

When P was coprecipitated with Fe, the formed Fe hydroxides were highly amorphous and showed less microporosity than the untreated, based on the lower amount of N<sub>2</sub> sorbed at relative pressures <0.1  $P/P_0$  (Fig. 9). Isotherms suggested a large proportion of macropores (relative pressures of 0.8–1). Specific surface areas were reduced with incubation time and macropores disappeared after 6 months of incubation.

Disappearance of macropores coincided with diminishing SSA with time for both P-treated and untreated Fe hydroxide particles (Fig. 10). Kinetics of SSA decrease, due to heat input, was independent of P treatment and was not accompanied by increases in crystallinity. Stabilization of SSA values

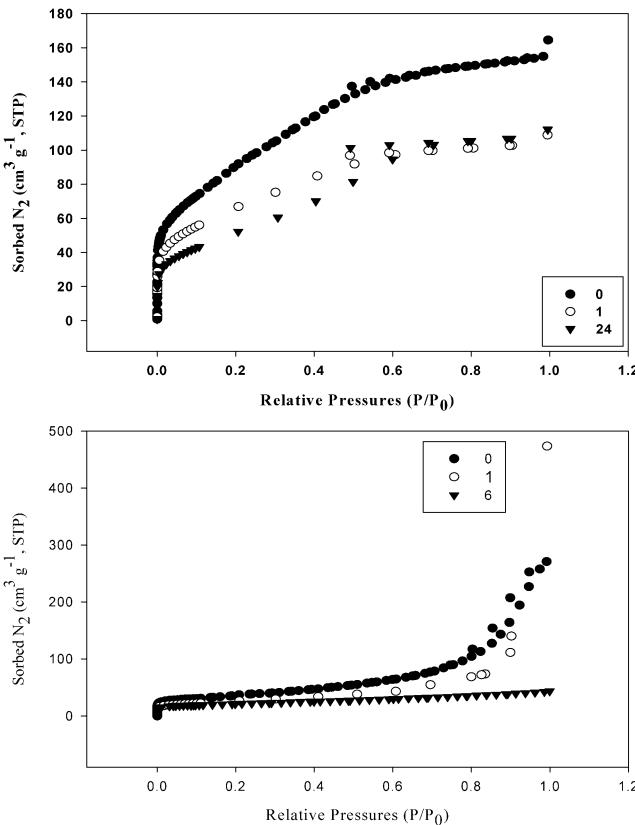


Fig. 9. Changes in N<sub>2</sub> gas adsorption/desorption isotherms of the untreated (first graph) and P-treated (second graph) Fe hydroxides after different incubation times (0 to 24 months) at 70 °C. Hysteretic desorption was observed for all incubation times, where sorption data did not coincide with desorption points. For the P-treated particles, there was no difference between the 6- and 24-month time intervals.

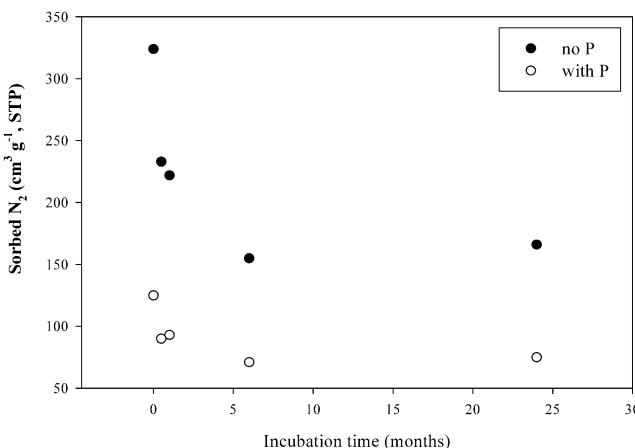


Fig. 10. Changes in BET-SSAs with time of synthetic Fe hydroxides coprecipitated with (1:1 P:Al ratio) or without P, and incubated at 70 °C.

for the Fe hydroxides took longer (~6 months) than with the Al hydroxides (1 month). However, stabilization of SSA values did not coincide with formation of crystalline Fe components, as was the case for the Al system.

Pore size distributions of the untreated Fe hydroxides were also determined based on the SF model (Fig. 11).

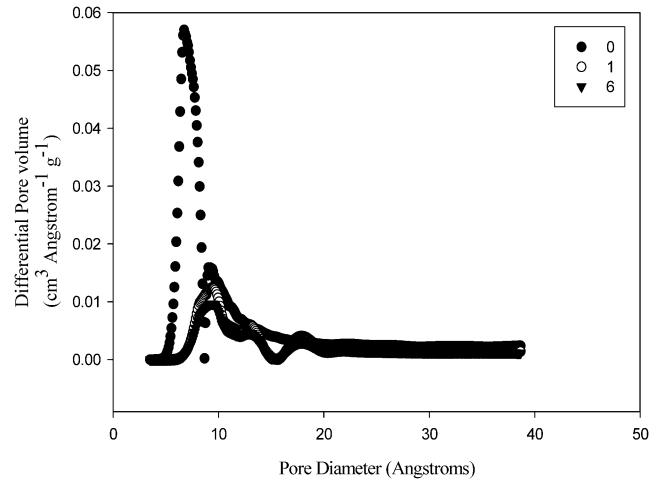


Fig. 11. Pore size distribution of the untreated Fe hydroxides incubated at 70 °C for 24 months. Only up to 6 months of incubation are shown here since there was no difference between 6- and 24-month treatments.

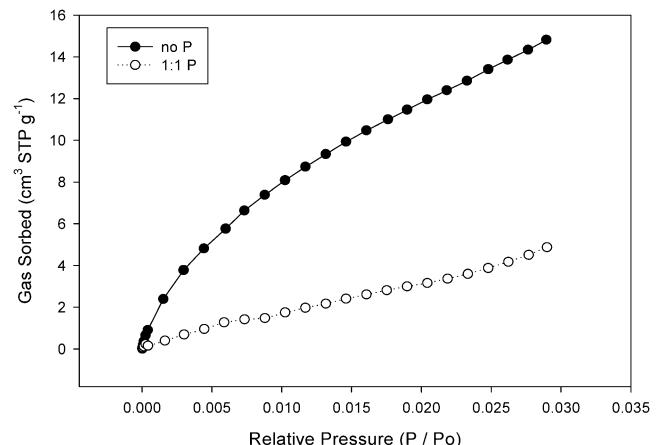


Fig. 12. CO<sub>2</sub> gas sorption isotherm (0 °C) of the Al hydroxides treated with and without P, and heated for 6 months at 70 °C.

At time zero, untreated Fe hydroxide particles showed a predominant micropore size distribution, which was significantly reduced within 1 month of incubation. Micropore volume reduction was stabilized 6 months after incubation at 70 °C with no changes thereafter. Data were similar for the P-treated Fe hydroxides (data not shown).

To further confirm the presence of phosphate in micropores of the hydroxides, CO<sub>2</sub> gas sorption experiments were performed. Micropores less than 1.5 nm in diameter that encounter diffusional restrictions can be determined by CO<sub>2</sub> adsorption at 0 °C [29]. Phosphorus treatment (1:1 P/Al molar ratio) resulted in a significant decrease in the amount of gas sorbed, and thus the CO<sub>2</sub>-based SSA (Fig. 12). This result further supports the idea of micropore blockage by phosphates. Pore blocking by phosphates probably hindered the movement of N<sub>2</sub> molecules within these pores, thus lowering SSA values [30]. The presence of phosphates in micropore openings suggests that P will be irreversibly bound to the

solid phase under ambient conditions. Micropore-bound P may be stable and immobilized in the long term.

#### 4. Discussion

A prerequisite for structural transformations of amorphous metal hydroxides toward crystalline phases is dehydration/rearrangement of atoms toward a lower free energy state. Decreases in SSA may be concurrent, or follow after dehydration/rearrangement processes. Therefore, changes in SSA do not prove de facto formation of crystalline components, but may simply denote dehydration phenomena from sites that can be afterward accessed by N<sub>2</sub> molecules during the SSA measurements.

For example, despite the decreased SSA values, heat-incubated (70 °C) amorphous Fe hydroxides did not develop long-range ordered components. Decreases in SSA of the untreated Fe hydroxides could have been the result of pore dehydration. Temperature is an important parameter controlling the transformation of amorphous to crystalline solid phases. Hematite formation is optimal at temperatures >90 °C, whereas goethite can be optimally synthesized at temperatures <40 °C [8]. The temperature used in this study (70 °C) seems to be outside the optimum range of hematite formation in the untreated Fe hydroxide system.

Phosphorus coprecipitation with Fe or Al resulted in significant alterations in the physicochemical properties of the evolved hydroxides. Oxalate (5 mM) extractions showed that the lower P extractability was not the result of increased crystallinity in the heat-treated (70 °C) Fe and Al particles. Increasing bonding strength between Al/Fe and phosphates may have occurred as evaporated water decreased interatomic distances, creating new and stronger metal–P bonds. Incubation data showed P inclusion into the metastable structure as it evolved toward a lower free energy equilibrium state. Manganese and Ni were incorporated into goethite when ferrihydrite–Mn or –Ni coprecipitates were aged at 70 °C for 17 days [31].

Lower P extractability as manifested by oxalate (5 mM) extractions has implications for the long-term stability of P occluded in the particle structure. In the long term (up to 2 years), P may be tenaciously retained in the micro- and mesopores of the solid, even at high P loads used in this study (1:1 P:Al molar ratio).

Phosphorus treatment had a significant negative effect on the N<sub>2</sub>- and CO<sub>2</sub>-based SSAs of the solids. Coprecipitated phosphate with Fe (up to 2% molar PO<sub>4</sub>/Fe ratio) heated between 100 and 300 °C showed that the SSA of the solid increased, as PO<sub>4</sub> was added to the system [32]. The increase in SSA was attributed to the formation of micropores during the coprecipitation process. Our study showed the opposite; P apparently blocked micropores or inhibited their formation, reducing the access of these pores by N<sub>2</sub> gas molecules. Also, our system used a higher P load (1:1 P/metal molar ra-

tio) and lower temperature (70 °C) than what Kandori et al. [32] used.

#### 5. Summary

This study focused on the long-term stability of P bound to evolving amorphous Fe and Al hydroxides coprecipitated with P. Metal hydrolysis products, with or without P, were characterized by large SSAs in the meso- and micropore size range. Heat incubations (70 °C) resulted in drastic changes in physicochemical properties (formation of pseudoboehmite, large reduction in SSA) of the untreated Al system, but changes were less drastic for the untreated Fe system.

Decreases in SSA and micropore volume with time were most evident in the untreated samples (within the first 1–2 months, and stabilized thereafter), and much less in the P-treated samples. Phosphate coprecipitation with the metal salt stabilized the particle surfaces, possibly by increasing the bonding strength between metal and P, but solids remained amorphous even after 2 years. Increased stability of P bound to the hydroxides was also demonstrated by the reduced 5 mM oxalate-extractable P concentrations, suggesting that sorbed P may be stable for at least 2 years (duration of the study).

These data may be very useful to address the long-term stability of these metal hydroxides when used as catalysts, heavy metal exchangers, or adjuvants in human vaccines. In addition, these data are pertinent to the stability of sorbed P by drinking-water treatment residuals (high in amorphous Fe/Al hydroxides) that are currently used to reduce soluble P concentrations in P-enriched systems [23].

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