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Coprecipitation of Arsenate with Metal Oxides: Nature, Mineralogy, and Reactivity of Aluminum Precipitates

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Arsenic mobilization in soils is mainly controlled by sorption/desorption processes, but arsenic also may be coprecipitated with aluminum and/or iron in natural environments. Although coprecipitation of arsenic with aluminum and iron oxides is an effective treatment process for arsenic removal from drinking water, the nature and reactivity of aluminum–iron–arsenic coprecipitates has received little attention. We studied the mineralogy, chemical composition, and surface properties of aluminum–arsenate coprecipitates, as well as the sorption of phosphate on and the loss of arsenate from these precipitates. Aluminum–arsenate coprecipitates were synthesized at pH 4.0, 7.0, or 10.0 and As/Al molar ratio (R) of 0, 0.01, or 0.1 and were aged 30 or 210 d at 50 °C. In the absence of arsenate, gibbsite (pH 4.0 or 7.0) and bayerite (pH 10.0) formed, whereas in the presence of arsenate, very poorly crystalline precipitates formed. Short-range ordered materials (mainly poorly crystalline boehmite) formed at pH 4.0 ($R = 0.01$ and 0.1), 7.0, and 10.0 ($R = 0.1$) and did not transform into $\text{Al}(\text{OH})_3$ polymorphs even after prolonged aging. The surface properties and chemical composition of the aluminum precipitates were affected by the initial pH, R , and aging. Chemical dissolution of the samples by 6 mol L^{-1} HCl and 0.2 mol L^{-1} oxalic acid/oxalate solution indicated that arsenate was present mainly in the short-range ordered precipitates. The sorption of phosphate onto the precipitates was influenced by the nature of the samples and the amounts of arsenate present in the precipitates. Large amounts of phosphate partially replaced arsenate only from the samples formed at $R = 0.1$. The quantities of arsenate desorbed from these coprecipitates by phosphate increased with increasing phosphate concentration, reaction time, and precipitate age but were always less than 30% of the amounts of arsenate present in the materials and were particularly low (<4%) from the sample prepared at pH 4.0. Arsenate appeared to be occluded within the network of short-range ordered materials and/or sorbed onto the external surfaces of the precipitates, but sorption on the external surfaces seemed to increase by increasing pH of sample preparation and aging. Furthermore, at pH 4.0 more than

in neutral or alkaline systems the formation of aluminum arsenate precipitates seemed to be favored. Finally, we have observed that greater amounts of phosphate were sorbed on an aluminum–arsenate coprecipitate than on a preformed aluminum oxide equilibrated with arsenate under the same conditions ($R = 0.1$, pH 7.0). In contrast, the opposite occurred for arsenate desorption, which was attributed to the larger amounts of arsenate occluded in the coprecipitate.

Introduction

Arsenic, a toxic element for humans, animals, and plants, is ubiquitous in the earth's crust with a mean concentration of 3 mg kg^{-1} (1–5). The presence of arsenic at elevated concentrations in natural environments is attributable to both natural and anthropogenic inputs. Arsenic-contaminated soils, sediments, and sludges are the major sources of arsenic contamination of the food chain, surface water, groundwater, and drinking water (2, 3).

In natural environments (soils, groundwaters, and surface waters) arsenic is most commonly present as arsenite ($\text{As}(\text{III})$) and arsenate ($\text{As}(\text{V})$). Arsenic mobility in soil is limited by its capacity to be sorbed on soil components, particularly metal oxides and short-range ordered aluminosilicates (allophane and imogolite) and at the edges of phyllosilicates. Many studies have demonstrated that arsenite is sorbed on Al-oxides, phyllosilicates, and calcite in a lesser extent than arsenate, whereas the opposite is true for iron oxides (3, 6–8). Arsenite and arsenate seem to form similar surface complexes, but arsenate is more strongly held onto these soil components (2, 7–9), so that arsenite is more mobile and toxic (25–60 times) than arsenate. Some methyl arsenic species can be more toxic than inorganic species but organic forms of arsenic are rarely present in soil at concentrations above 1 mg L^{-1} (10, 11).

Many studies have revealed that millions of people are at serious risk in many countries around the world, especially in Southeast Asia, due to their exposure to arsenic-contaminated drinking water. Tens of thousands of people already suffer from symptoms such as skin lesion, hyperkeratosis, melanosis, and liver, lung, and kidney/bladder cancer, in addition to skin cancer (3, 12, 13). Various treatment processes have been adopted to remove arsenic from polluted waters, such as (i) sorption onto metal oxides, (ii) sorption-coprecipitation using iron and aluminum, (iii) reverse osmosis, and (iv) ion exchange (3, 14, 15).

Coprecipitation of arsenic with iron and aluminum are practical and effective treatment processes used for removing arsenic from drinking waters. In fact, coprecipitation of arsenic with Fe or Al has been widely studied by hydro-metallurgists as a means of removing arsenic from processed wastewaters (12, 14–16). Furthermore, in natural environments arsenic may form precipitates or coprecipitates with Al, Fe, Mn, and Ca (17–20).

Until today no detailed information is available on the influence of arsenic on the nature of aluminum–iron–arsenic coprecipitates, whereas many studies have been carried out on the surface properties, chemical composition, mineralogy, and reactivity of aluminum or iron precipitates obtained by coprecipitating aluminum and/or iron with selected inorganic (phosphate, sulfate, silicate) and organic ligands (low molecular mass organic acids and humic and fulvic acids) (21–26 and references therein).

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TABLE 1. Synthesis Conditions, Mineralogy and Specific Surface Area (SSA) of the Samples Formed in the Absence or Presence of Arsenate after 30 or 210 d at 50 °C^a

sample	synthesis conditions		mineralogy	SSA (m ² g ⁻¹)	
	initial As/Al molar ratio (R)	initial pH	aged 210 d	aged 30 d	aged 210 d
4R0	0	4.0	—	—	—
4R0.01	0.01	4.0	vso	230 ± 16	51 ± 4
4R0.1	0.1	4.0	vso	135 ± 10	70 ± 5
7R0	0	7.0	G + (Boh)	100 ± 7	40 ± 3
7R0.01	0.01	7.0	G + [Boh] + [N]	145 ± 12	65 ± 5
7R0.1	0.1	7.0	Boh	135 ± 7	97 ± 8
7AR0.1 ^b	0.1	7.0	Boh	135 ± 5	—
10R0	0	10.0	B + (N)	25 ± 2	6 ± 0.3
10R0.01	0.01	10.0	B + (N)	37 ± 3	7 ± 0.5
10R0.1	0.1	10.0	Boh	150 ± 12	105 ± 8

^a B, bayerite; G, gibbsite; N, nordstrandite; Boh, poorly crystalline boehmite; vso, very short ordered materials; () small amounts; [] trace; —, no precipitate collected. ^b Arsenate was added immediately after the formation of Al precipitate at pH 7.0.

The effect of phosphate on the sorption/desorption of arsenic is of great importance, because application of phosphate fertilizers is a practice that may enhance arsenic mobility (2, 27–29). It has been established that the chemical behavior of arsenate is similar to that of phosphate (2, 3, 27–29). Many authors showed that arsenate may be partially removed from soil colloids by phosphate, but even large amounts of phosphate cannot desorb all the applied arsenate (2, 3, 29–31). However, whereas some studies have been carried out on the factors (surface coverage, residence time, pH) which influence the desorption of arsenate previously sorbed onto oxides, phyllosilicates, and soils by phosphate (5, 31–33), no information is available on the possible desorption of arsenate coprecipitated with Fe or Al by phosphate.

In this study we describe the mineralogy, surface properties, and reactivity toward phosphate of Al-oxides with which arsenate was coprecipitated at different As/Al molar ratios (*R*) of 0, 0.01, or 0.1, and different pH values (4.0, 7.0, or 10.0) after aging for 30 or 210 d at 50 °C and the removal of arsenate by phosphate from these precipitates. A comparison of desorption of arsenate coprecipitated with aluminum or added immediately after the formation of an aluminum precipitate is also made.

Methods and Materials

Preparation of Aluminum–Arsenate Coprecipitates and their Characterization. Solutions (1 L) of 0.05 mol L⁻¹ Al(NO₃)₃, both in the absence or presence of arsenate (Na₂HAsO₄) at initial arsenate/aluminum molar ratio (*R*) of 0, 0.01, or 0.1, were titrated with 0.5 mol L⁻¹ NaOH at a rate of 2 mL min⁻¹ to a final pH of 4.0, 7.0, or 10.0. During the titration the solutions were thoroughly stirred. The suspensions were kept in polypropylene containers and aged at 50 °C for 30 or 210 d. After every 7–15 days, the pH of the suspensions, which were previously equilibrated at 20 °C, was adjusted with 0.5 mol L⁻¹ NaOH or HNO₃ to the initial value. After aging, the samples were collected and washed five times with deionized water, followed by centrifugation at 10 000g for 30 min. The suspensions were then dialyzed [molecular weight (MW) cutoff of 15 000] in deionized water, freeze-dried, and lightly ground to pass through a 0.315 mm sieve. A sample (7AR0.1) was prepared by adding arsenate (*R* = 0.1) immediately after precipitation of aluminum at pH 7.0 and aged 30 d at 50 °C. The synthesis conditions and symbols of the samples are reported in Table 1.

The X-ray diffraction (XRD) patterns of randomly oriented samples were obtained using a Rigaku X-ray diffractometer (Rigaku Co., Tokyo) with Fe-filtered Co K α radiation generated at 40 kV and 30 mA and a scan speed of 2° 2 θ min⁻¹.

The XRD traces were the results of eight summed signals. The FT-IR spectra of the samples were obtained using the diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy analysis. Sample preparation for DRIFT determinations was as follows: 0.2 mg of sample was mixed with 200 mg of KBr (FTIR grade, Aldrich, Chemical Co., Milwaukee, WI). The mixture was finely ground in an agate mortar and transferred to a sample holder. Its surface was smoothed with a microscope glass slide. The DRIFT spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrophotometer (Perkin-Elmer USA). The instrument had a spectral resolution of 1 cm⁻¹, which was used in all spectra determinations.

Specific surface area (in triplicate) was determined by H₂O sorption at 20% relative humidity according to the method described by Quirk (34).

Chemical Analyses. About 10 mg of the samples aged for 30 or 210 d at 50 °C, in triplicate, was treated with 10 mL of 0.2 mol L⁻¹ NH₄-oxalate/oxalic acid at pH 3.0 (29, 32) for 6 h or with 5 mL 6 mol L⁻¹ HCl for 24 h (29). Aluminum and arsenate solubilized by HCl or NH₄-oxalate/oxalic acid at pH 3.0 were determined, respectively, by atomic absorption spectroscopy on a Perkin-Elmer AA700 or by inductively coupled plasma (ICP-AES, Varian, Liberty 150). Coefficients of variation among the replicates ranged from 2% to 4% for aluminum and from 2% to 5% for arsenate.

Phosphate Sorption and Arsenate Desorption. A 20–50 mg aliquot of each sample, in duplicate, was equilibrated at 20 °C with 19 mL of 0.05 mol L⁻¹ KCl at pH 6.0. Suitable amounts of 0.01 mol L⁻¹ solutions containing KH₂PO₄ were then added in order to have initial phosphate concentration in the range 5 × 10⁻⁴ to 10⁻² mol L⁻¹. The pH of each suspension was kept constant for 24 h by adding 0.1 or 0.01 mol L⁻¹ HCl or NaOH. The final suspensions (20 mL) were centrifuged at 10 000g for 20 min and filtered through a 0.22- μ m membrane filter. Arsenate removed by different amounts of phosphate and phosphate was determined in the final solutions by ion chromatography, using a Dionex DX-300 ion chromatograph (Dionex Co, Sunnyvale, CA), an IonPac AS11 column (4.0 mm), an eluent of 0.05 mol L⁻¹ NaOH at a flow rate of 1 mL min⁻¹, and a CD20 conductivity detector combined with autosuppressor. The phosphate standard concentration was 0.1–2 mmol L⁻¹, and the arsenate standard concentration was 0.05–0.5 mmol L⁻¹. The amount of phosphate sorbed was determined by the difference between the initial and final concentrations. Coefficients of variation among the replicates ranged from 2 to 5%.

Effect of Time on Desorption of Arsenate by Phosphate. Experiments were carried out at pH 6.0 by adding a large amount of phosphate (2000 mmol kg⁻¹) to the aluminum–

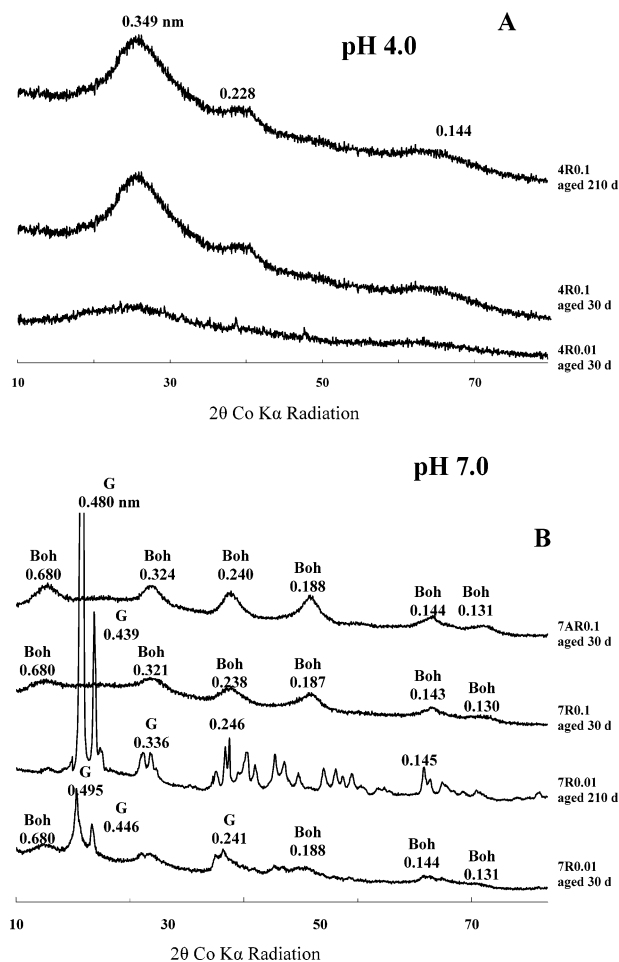


FIGURE 1. X-ray powder diffractograms of randomly oriented samples aged for 30 or 210 d at 50 °C. Boh stands for poorly crystalline boehmite, G is for gibbsite; spacings in nm, Co K α radiation. For sample symbols see Table 1.

arsenate coprecipitates prepared at $R = 0.1$ and aged for 30 or 210 d. The suspensions were then allowed to react for 5, 24, 48, and 170 h. The pH of the suspensions was kept constant for all the experiments with 0.1 or 0.01 mol L⁻¹ HCl or NaOH. The final suspensions were centrifuged at 10 000g for 20 min and filtered through a 0.22- μ m filter. Arsenate was determined in the supernatants by ion chromatography, as discussed before. Coefficients of variation among the replicates ranged from 2 to 6%.

Results and Discussions

Mineralogy of the Precipitates. The mineralogy of the aluminum precipitation products was affected by the initial pH, As/Al molar ratio (R), and aging (Figure 1; Table 1; Figure S1 in the Supporting Information). For the sample synthesized at pH 4.0 in the absence of arsenate (4R0) it was difficult to collect a precipitate for mineralogical and chemical analyses, because at low pH values the initially formed soluble monomers and polymers of Al did not convert easily into solid species (26, 35). Only after prolonged aging (about one year at 50 °C) was the presence of gibbsite observed (data not shown). The presence of arsenate facilitated the formation of precipitates, which appeared to be very short range ordered materials even after 210 d of aging at 50 °C (Figure 1A). The samples formed at $R = 0.01$ and 0.1 showed only diffuse and/or very broad peaks at about 0.349, 0.228, and 0.144 nm, which appeared much more evident in the sample 4R0.1. The exact nature of these materials is not known, but they could be attributed to the presence of very poorly crystalline

and highly defective Al-oxyhydroxides of boehmitic character probably mixed with noncrystalline precipitates. In fact, these samples resemble the precipitates obtained by Colombo et al. (36) formed in the presence of tannate (tannate/Al molar ratio of 0.05 or 0.1) which showed very broad peaks centered around at 0.400–0.345, 0.217–0.220 nm after aging for 300 d at 50 °C and 5 years at room temperature. Only after a further aging of 15 days at 140 °C in a hydrothermal Teflon vessel did these materials show the characteristic broad peaks centered around 0.680–0.620, 0.325, 0.240, 0.188, 0.145, and 0.130 (as observed in the samples formed at $R = 0.1$ and at pH 7.0 [Figure 1] or 10.0) of very poorly crystalline boehmite, the so-called “pseudoboehmite” (26, 36 and references therein). However, the presence of aluminum arsenate precipitates in the sample formed at $R = 0.1$ cannot be ruled out (Figures S2 and S3).

The precipitate formed at pH 7.0 in the absence of arsenate (7R0) showed presence of well crystallized gibbsite (Table 1). In the presence of arsenate ($R = 0.01$) gibbsite formed but the formation of very poorly crystalline boehmite appeared evident mainly in the sample aged for 30 d (Figure 1B). The XRD pattern of this material clearly showed that the amount of gibbsite strongly increased after 210 d of aging. At pH 10.0, bayerite with small amounts of nordstrandite formed at $R = 0$ and 0.01. At $R = 0.1$ poorly crystalline boehmite formed and remained unchanged even after aging for 210 d both at pH 7.0 and 10.0 (Table 1; Figure S1).

The crystallinity of the Al-oxyhydroxides synthesized at $R = 0.1$ increased by increasing the initial pH and aging time, as evident from their XRD patterns (not shown). In fact, it is well-known that the greater the shift of the reflections of poorly crystalline boehmites to lower 2θ values, as referred to well crystallized boehmite) and the greater their full width at half-maximum (FWHM) the smaller the structural order and/or the crystallite size of their particles (26, 36 and references therein).

FT-IR spectra of the samples formed at $R = 0.1$ are shown in Table S1. The presence of a band in the 840 to 865 cm⁻¹ region was attributed to symmetric stretching of As–O bond of the inner-sphere As–O–Al species (8). The position of the ν (As–O) bond decreased in frequency from 864 to 850 cm⁻¹ upon increasing the pH from 4.0 to 10.0 and remained unchanged (pH 4.0) or decreased (pH 7.0 and 10.0) with aging. According to Goldberg and Johnston (8) the increase in frequency upon decreasing the pH indicates that the As–O bond strengthens upon lowering the pH, a behavior of arsenate observed also in aqueous solutions. Our results show changes in frequencies upon aging for the samples formed at pH 7.0 or 10.0.

Specific Surface Area (SSA). The specific surface area of the aluminum precipitation products formed in the absence or presence of arsenate was affected by the pH, R , and aging (Table 1). After 30 d of aging, the samples that showed presence of poorly crystalline materials or low amounts of Al (OH)₃ polymorphs (Figure 1, Table 1; e. g., samples 4R0.01, 4R0.1, 7R0.01, 7R0.1 and 10R0.1) had a large SSA ranging from 230 to 135 m² g⁻¹. By contrast, the precipitates in which well crystallized Al-hydroxides were predominant (samples 10R0 and 10R0.01) showed a surface area particularly low.

The Al precipitation products formed at $R = 0.1$ but at different pH values (4R0.1, 7R0.1, and 10R0.1), which showed only presence of short-range ordered Al-oxyhydroxides, had a similar surface area. Surprisingly, the samples 4R0.01 and 4R0.1, which showed similar XRD patterns (Figure 1), had a different surface area, respectively of 230 and 135 m² g⁻¹. Evidently the larger amount of arsenate in the sample 4R0.1 (Table 2) promoted strong aggregation among the particles. In fact, as demonstrated by Violante and Huang (21, 22) ligands with a strong affinity for aluminum may promote strong aggregation among the particles of the precipitates

TABLE 2. Amounts (mmol kg⁻¹) of Aluminum and Arsenic Solubilized by 6 mol L⁻¹ HCl (Al_{HCl}, As_{HCl}) or 0.2 mol L⁻¹ Oxalic Acid/NH₄ Oxalate at pH 3.0 (Al_{ox}, As_{ox}) from the Samples

sample	Al _{ox}	As _{HCl}	As _{ox}	As _{ox} /As _{HCl}
Aged for 30 d				
pH 4.0				
4R0	—	—	—	—
4R0.01	8.4 (62) ^b	0.24	0.15	0.62
4R0.1	5.1 (40)	2.35	2.20	0.94
pH 7.0				
7R0	7.5 (56)	—	—	—
7R0.01	7.8 (63)	0.13	0.12	0.92
7R0.1	8.9 (69)	1.18	1.24	1.05
pH 10.0				
10R0	0.6 (5)	—	—	—
10R0.01	0.8 (6)	0.11	0.08	0.73
10R0.1	6.2 (46)	0.95	0.87	0.92
Aged for 210 d				
pH 4.0				
4R0	—	—	—	—
4R0.01	N.D. ^c	N.D.	N.D.	N.D.
4R0.1	6.5 (52)	2.26	2.21	0.98
pH 7.0				
7R0	3.4 (26)	—	—	—
7R0.01	5.3 (43)	0.14	0.13	0.93
7R0.1	8.9 (71)	1.13	1.15	1.02
pH 10.0				
10R0	N.D.	—	—	—
10R0.01	1.0 (8)	0.10	0.08	0.80
10R0.1	3.5 (28)	0.63	0.50	0.79

^a Al_{HCl} range from 12.5 to 13.5 mmol kg⁻¹. ^b The data in parentheses indicate the percentages of Al_{ox} as referred to the total aluminum solubilized by HCl (Al_{HCl}). ^c Not determined.

with a consequent decrease of the apparent surface area (22, 24, 26). These authors (21, 22) demonstrated that the specific surface area of aluminum precipitation products formed in the presence of tannate or tartrate increased in the presence of low amounts of organic ligands and then decreased by increasing their concentration above certain values. According to these authors (21, 22) polydentate ligands play an important role in both perturbing the crystallization of Al(OH)₃ polymorphs and promoting the aggregation of the reaction products. Probably structural distortion and aggregation occur simultaneously but aggregation may be more prominent when the amount of certain ligands in the solid phase is sufficiently high.

The surface area of the samples decreased with aging. In the samples where the mineralogy of the aluminum precipitation products did not change (e.g., formation of poorly crystalline boehmite) the decrease of surface area must be attributed to an increase of the structural order and/or size of the crystals of the Al-oxyhydroxides (25, 26, 36).

Chemical Composition of the Precipitates. The precipitates aged for 30 or 210 d at 50 °C were solubilized either by 6 mol L⁻¹ HCl, which solubilizes both the poorly crystalline and well crystallized aluminum precipitation products, or 0.2 mol L⁻¹ NH₄-oxalate/oxalic acid at pH 3.0, which is used for determining the amount of noncrystalline or short range ordered materials in soil samples (23, 36).

The amounts of aluminum solubilized by NH₄-oxalate/oxalic acid (Al_{ox}) and, in parentheses, their percentages as referred to the total aluminum solubilized by HCl, the content of arsenate in the precipitates after solubilization with HCl (As_{HCl}) or NH₄-oxalate/oxalic acid (As_{ox}), and, finally the As_{ox}/As_{HCl} molar ratio, which gives useful information on the possible distribution of arsenate between precipitates of different crystallinity, are reported in Table 2.

The percentage of Al_{ox} decreased with aging and increased by increasing the content of arsenate but for the coprecipi-

tates formed at pH 4.0, with Al_{ox} being greater in the sample 4R0.01 than in the sample 4R0.1. This behavior must be attributed to the strong aggregation of the particles in the latter material (as discussed before, Table 1), which evidently partially prevented the solubilization of this sample. In the precipitates, which showed only presence of poorly crystalline boehmite, the percentage of Al_{ox} ranged from 71% for the sample 7R0.1 aged for 30 d to 28% for the sample 10R0.1 aged for 210 d. Oxalic acid/NH₄oxalate solution at pH 3.0 could not completely solubilize the short-range ordered precipitates of aluminum even after 6–10 h of reaction, showing clearly that this solution is not specific for poorly crystalline aluminum precipitates. For this reason, the percentages of Al_{ox} give only a relative indication of the quantity of short-range ordered and easily solubilized material in the samples. The partial solubilization of poorly crystalline materials may be also due, at least in part, to the presence of arsenate on the surfaces of the precipitates. According to Cornell and Schwertmann (23) the presence of sorbed additives may inhibit dissolution of Fe oxides.

As_{ox} was only slightly lower than As_{HCl} and the As_{ox}/As_{HCl} molar ratio was then usually near to 1, indicating that arsenate was present mainly in the short-range ordered precipitates. In the precipitates obtained at *R* = 0.1 (4R0.1, 7R0.1, and 10R0.1) As_{HCl} or As_{ox} decreased by increasing pH and aging. The presence of greater amounts of arsenate in the precipitates formed at lower pH is not surprising because arsenate sorption increases by decreasing pH (5, 6, 8, 30, 31). The slight decrease of arsenate present in the samples after prolonged aging, particularly those formed at pH 7.0 or 10.0, must be due to the crystallization process of the hydrolytic products of aluminum with a consequent greater crystallinity and/or size of the particles of the samples after aging. Likely, during the reorganization and crystallization of the precipitates arsenate present in the initially formed aluminum precipitation products was partially removed into solution and was, at least in part, sorbed onto the external surfaces of the precipitates depending on the size and crystallinity of the particles. Probably, the surface coverage of arsenate on the external surfaces increased with aging much more on the sample formed at pH 10.0 than on that formed at pH 7.0 or 4.0 as the crystallization processes are faster in the former than in the latter (as will be discussed later; Table 3, Figure 4).

Sorption of Phosphate onto Al-Oxides. The isotherms of sorption of phosphate at pH 6.0 onto selected Al precipitation products formed at pH 7.0 and 10.0 and aged 30 or 210 d are shown in Figure 2. For the lack of material only some experiments were carried out for the samples formed at pH 4.0 (as discussed below; Figure 4).

The sample formed at pH 7.0 and at *R* = 0 (7R0) sorbed lower amounts of phosphate than the samples formed at *R* = 0.01 or 0.1 (7R0.01 and 7R0.1). This behavior must be attributed to the presence of well crystallized Al(OH)₃ (gibbsite) in the precipitate formed at *R* = 0 and to the consequent lower surface area (Table 1). In the samples at *R* = 0.01 or 0.1, the presence of large amounts of poorly crystalline materials (Figure 1 and Tables 1 and 2) favored the sorption of phosphate (Figure 2A). The sorption of phosphate onto the same samples aged for 210 d at 50 °C strongly decreased [mainly on the sample at *R* = 0 (not shown) and 0.01] due to the greater crystallinity of the materials present in the precipitates after prolonged aging (Figure 2B).

It is particularly interesting to note that the samples 7R0.1 and 10R0.1 showed only presence of poorly crystalline boehmite (Figure 1), similar surface area (Table 1) but different capacity in fixing phosphate. Greater amounts of phosphate were sorbed on the sample formed at pH 7.0 than on that formed at pH 10 (Figure 2). A possible explanation of these findings is that the sorption of phosphate onto

TABLE 3. Amounts (mmol kg^{-1}) of Arsenate Removed from Aluminum–Arsenate Coprecipitates Formed at pH 7.0 or 10.0 and at Initial As/Al Molar Ratio (R) of 0.1 after the Addition of Increasing Quantities of Phosphate and after 24 h of Reaction^a

sample	aging	P added (mmol kg^{-1})					
		100	200	500	600	900	1000
7R0.1	30 d	n.d. ^b (∞) ^c	n.d. (∞)	29.0 (17.2)	45.6 (13.1)	97.4 (8.9)	105.6 (8.2)
7R0.1	210 d	n.d. (∞)	43.0 (4.65)	74.3 (6.3)	95.1 (5.8)	128.5 (5.1)	136.5 (5.1)
7AR0.1 ^c	30 d	31.3 (3.1)	48.2 (3.8)	142.0 (2.3)	172.7 (2.1)	248.9 (1.7)	-
10R0.1	30 d	n.d. (∞)	n.d. (∞)	70.8 (5.8)	78.0 (6.1)	87 (7.3)	101 (7.3)
10R0.1	210 d	22.7 (3.9)	42.7 (4.1)	85.7 (4.5)	101.4 (4.1)	136.6 (3.3)	171.4 (2.6)

^a Numbers in parentheses indicate the final P sorbed/As desorbed molar ratios. ^b n.d. stands for not detectable. ^c Arsenate was added after precipitation of Al at pH 7.0.

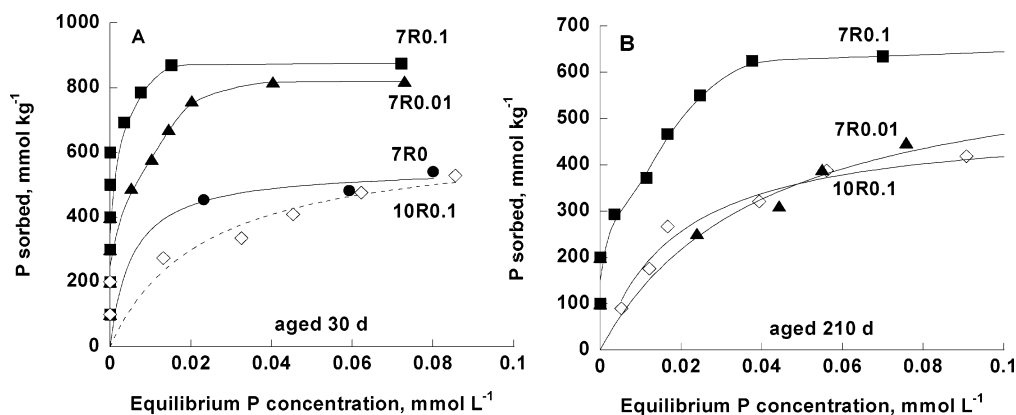


FIGURE 2. Sorption isotherms of phosphate at pH 6.0 onto the samples formed at pH 7.0 and at R of 0, 0.01, or 0.1 or at pH 10.0 and at R of 0.1 after aging for 30 d (A) or for 210 d (B). For sample symbols see Table 1.

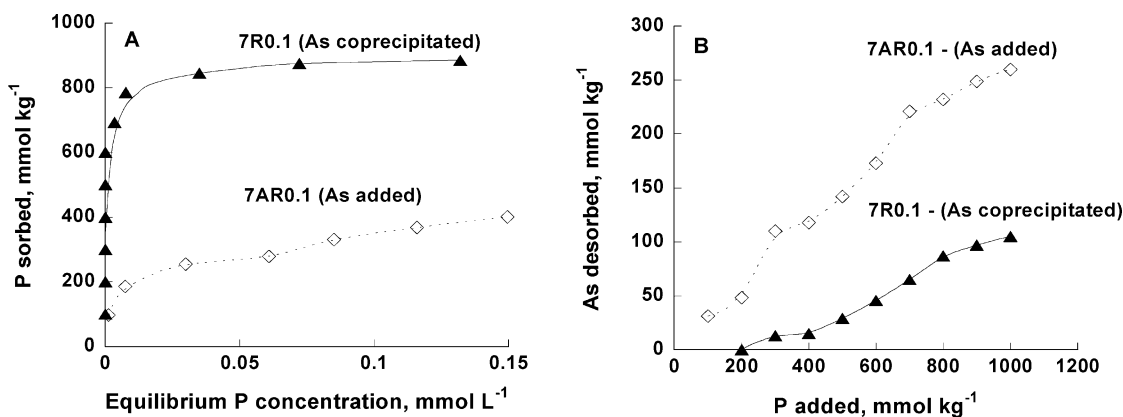


FIGURE 3. Sorption isotherms of phosphate at pH 6.0 on aluminum–arsenate coprecipitates obtained respectively by coprecipitating at pH 7.0 arsenate with aluminum (7R0.1) or by adding arsenate to a preformed Al precipitate (7AR0.1) (A); arsenate desorbed by phosphate from 7R0.1 and 7AR0.1 as a function of increasing amounts of phosphate added (B).

aluminum–arsenate coprecipitates is not only affected by the mineralogy and SSA of the samples, but also by the distribution of arsenate occluded in the precipitate and/or present on the external surfaces (e.g., surface coverage of the anion on the external surfaces). Arsenate may strongly prevent the sorption of phosphate occupying many sorption sites (5, 30, 31, 33, 37). This hypothesis is strengthened by the experiments carried out on the sorption of phosphate (and desorption of arsenate, as discussed below) onto the two samples formed at pH 7.0 and $R = 0.1$, obtained by coprecipitating aluminum and arsenate (7R0.1) or by adding arsenate immediately after the precipitation of aluminum (7AR0.1; Figure 3A). These samples showed similar surface area (Table 1), but the sorption of phosphate onto 7AR0.1 sample was more than two times lower than that on 7R0.1 sample (Figure 3A). Evidently, in the 7AR0.1 sample arsenate anions, added to a preformed aluminum precipitate, were

sorbed on the external surfaces and occupied many sorption sites and, consequently, prevented the fixation of phosphate more efficiently than 7R0.1 sample where many arsenate anions were occluded into the network of the precipitate.

In conclusion, the sorption of phosphate onto the aluminum oxides prepared in the absence or presence of arsenate is influenced by various factors such as the mineralogy of the samples, their surface properties, and the amounts of arsenate present in the precipitates. Some of these factors promote phosphate sorption (e.g., the presence of poorly crystalline materials), whereas others prevent it (e.g., the surface area, the aggregation of the particles, the presence of arsenate, the decrease of pzc (8)).

Desorption of Arsenate by Phosphate from Aluminum–Arsenate Coprecipitates. Negligible amounts of arsenate were replaced after 24–48 h of reaction by large amounts of phosphate from the samples formed at $R = 0.01$; by contrast,

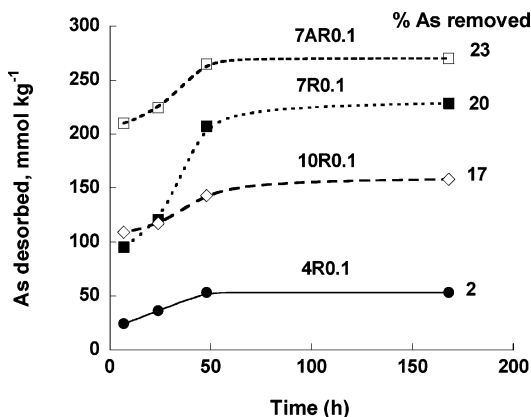


FIGURE 4. Effect of time on the desorption of arsenate by phosphate (2000 mmol phosphate kg^{-1}) from the samples 4R0.1, 7R0.1, 7AR0.1, and 10R0.1 after 30 d of aging at 50 °C. For sample symbols see Table 1.

the aluminum precipitates formed at $R = 0.1$ partially released arsenate by adding increasing amounts of phosphate (Table 3).

The amounts of arsenate desorbed by a given quantity of phosphate added were usually greater from the sample prepared at pH 10.0 than from that formed at pH 7.0 aged for 30 or 210 d (Table 3), although greater amounts of arsenate were present in the latter than in the former (Table 2). Only by adding large amounts of phosphate ($> 1000 \text{ mmol kg}^{-1}$) and increasing the reaction time ($> 24 \text{ h}$) more arsenate was desorbed from the sample formed at pH 7.0 than at pH 10.0 (Figure 4). A possible explanation of these findings is that the precipitates of boehmitic character formed at lower pH values had a lower crystallinity (Figure 1), a much lower size of the particles, and a higher percentage of arsenate occluded into the network of the precipitates. In other words, the surface coverage of arsenate onto the surfaces of the sample obtained at pH 10.0 was greater than that of the sample formed at pH 7.0 or 4.0. This explanation may also justify the observation that usually greater amounts of arsenate were desorbed from the samples aged for 210 d than from those aged for 30 d when the same quantity of phosphate was added. In fact, during the aging process the crystallinity of the Al-oxyhydroxides increased, the surface area decreased (Table 1) and, consequently, some arsenate anions initially present in the network of the precipitates were released into the external solutions and then, being sorbed onto the external surfaces, were more easily replaced by phosphate anions. In fact, from the sample formed at pH 10.0 and aged for 30 d (10R0.1) no arsenate was desorbed by adding up to 300 mmol of phosphate kg^{-1} , whereas on the same sample aged for 210 d arsenate could be partially desorbed by adding only 100 mmol kg^{-1} of phosphate (Table 3). These findings indicate that not only the sites available for phosphate decreased after aging but that the percentage of sites previously occupied by arsenate increased. The P sorbed/As desorbed molar ratios, which decreased by increasing the aging of the coprecipitates (Table 3), also confirm these observations.

The influence of the distribution of arsenate anions into the network of the precipitates and/or onto the external surfaces on their removal by phosphate appears evident in the experiments depicted in the Figure 3B which shows the desorption of arsenate by phosphate from the samples 7R0.1 and 7AR0.1 formed at pH 7.0 and $R = 0.1$, respectively, by coprecipitating aluminum and arsenate or by adding arsenate to a preformed aluminum precipitate. The 7AR0.1 sample, which showed a capacity to sorb phosphate lower than 7R0.1 sample (Figure 3A), released greater amounts of arsenate because arsenate in this sample was mainly present on the

external surfaces, occupying many sites which have a great affinity for phosphate.

Effect of Time on the Desorption of Arsenate by Phosphate. The effect of the reaction time on desorption of arsenate at pH 6.0 in the presence of a high concentration of phosphate (2000 mmol kg^{-1}) from the samples formed at $R = 0.1$ and pH 4.0, 7.0, or 10.0 and aged 30 d (Figure 4) or 210 d (data not shown) was also studied. The amounts of arsenate desorbed from the aluminum–arsenate coprecipitates increased with reaction time, but greater amounts were desorbed from the samples synthesized at pH 7.0 or 10.0 than from the sample obtained at pH 4.0. The percentages of arsenate desorbable by phosphate after 170 h of reaction, as referred to the total amounts of arsenate present in the aluminum–arsenate coprecipitates aged for 30 d at 50 °C ranged from 20% (7R0.1) to 2% (4R0.1) (Figure 4). After aging for 210 d the percentage of arsenate removed by phosphate from the samples formed at pH 7.0 (23%) or 10.0 (30%) increased, whereas that from the sample formed at pH 4.0 remained practically unchanged (2%) (data not shown).

The quantities of arsenate desorbed from the sample obtained at pH 4.0 were particularly low, about 35% and 25% of the quantities released from the samples formed at pH 7.0 or 10.0, respectively. Probably, in this sample arsenate was particularly protected being occluded into the precipitate whose particles were also very strongly aggregated (Table 1). Previous studies (30, 31) also demonstrated that competition of arsenate with phosphate was stronger in acidic systems, whereas phosphate desorbed greater amounts of arsenate from Al oxide at pH 7.8 than at pH 4.5 (33). It is particularly important to consider that arsenate both coprecipitated with metals or added to preformed oxides (Al, Fe) may form different surfaces complexes as well as precipitates, whose nature and amounts are affected by arsenate concentration, nature of the sorbent, pH, and aging (8, 9, 33, 38). The mobility of arsenate is influenced by the nature of different species. It is possible to hypothesize that at pH 4.0 more than in neutral or alkaline systems, there are conditions which promote the formation of aluminum–arsenate precipitates (33) (Figures S2 and S3) or surface complexes particularly strong, with a consequent decrease of desorbable arsenate anions. A recent work of Jia et al. (39) strengthens our findings. These authors evidenced that surface precipitation of ferric arsenate occurred at acidic pH (3.0–5.0) and was promoted with increasing equilibration time, whereas at pH 8.0 arsenate was sorbed predominantly via surface adsorption. Certainly, a combination of spectroscopic techniques and sorption/desorption studies should be of great importance in understanding the mechanisms of arsenate sorption and the factors which promote the formation of precipitates (33) and its subsequent mobility from coprecipitates.

The results of this study show that arsenate coprecipitated with aluminum at different pH values and As/Al molar ratios affect the mineralogy, chemical composition, surface properties, and reactivity of the precipitates. Spectroscopic studies may give important information on the mechanisms of retention of arsenate (and arsenite) in these materials.

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Supporting Information Available

Table showing the positions of the ν (As–O) bands in the IR spectra of coprecipitates formed at different pH values, $R = 0.1$ and aged 30 or 210 d at 50 °C (Table S1); Infrared spectra

(FTIR) of selected samples formed at pH 7.0 or 10.0 after 30 or 210 d of aging at 50 °C (Figure S1); Infrared spectra of an aluminum arsenate precipitate formed at pH 4.0 and aged 3 d at 50 °C and of the samples 4R0.1 and 7R0.1 aged 210 d at 50 °C (Figure S2); X-ray powder diffractogram of a randomly oriented aluminum arsenate precipitate formed at pH 4.0 and aged 3 d at 50 °C (Figure S3) This material is available free of charge via the Internet at <http://pubs.acs.org>.

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