

Increasing Soluble Phosphate Species by Treatment of Phosphate Rocks with Acidic Waste

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Abstract

The development of efficient fertilizers with a diminished environmental footprint will help meet the increasing demand for food and nutrients by a growing global population. Our objective was to evaluate whether an acidic mine waste (AMW) could be used beneficially by reacting it with sparingly soluble phosphate rocks (PRs) to produce more soluble P fertilizer materials. Three PRs from Brazil and Peru were reacted with different concentrations of AMW. Changes in mineralogy and P species were determined using a combination of X-ray diffraction and phosphorus K-edge XANES spectroscopy, in addition to extractable P concentrations. Increasing the AMW concentration typically increased extractable P. X-ray diffraction data showed transformation of apatite to other species when PRs were reacted with AMW at $\geq 50\%$ (v/v) in water, with gypsum or anhydrite forming at AMW concentrations as low as 12.5%. Linear combination fitting analysis of X-ray absorption near edge structure spectra also indicated a progressive transformation of apatite to noncrystalline Fe(III)-phosphate and more soluble Ca-phosphates with increasing AMW concentration. Because this AMW is costly to dispose of, reacting it with PR to produce a higher-grade phosphate fertilizer material could decrease the environmental impacts of the AMW and diminish the consumption of pure acids in conventional P fertilizer production.

Core Ideas

- Reusing fertilizer production waste can lower its environmental impact and enhance crop production.
- We evaluated products of acid mining waste reacted with phosphate rocks.
- Chemical speciation analyses indicated conversion of apatite to more soluble phosphates.
- New P products have agronomic potential.
- Plant growth tests are needed to measure these P products' performance as fertilizers.

A RELIABLE supply of phosphate fertilizers is essential for agriculture to continually meet increasing worldwide food demands. Commercial phosphate fertilizers are usually manufactured by the wet reaction of phosphate rocks (PRs) with pure acids (Chien et al., 2011). The quality of mined PRs used as a raw material for phosphorus fertilizer production is highly variable because the mineralogy, chemical composition, and reactivity of these materials depends on the geological conditions of formation (Chien and Menon, 1995; Chien et al., 2003). A projected scarcity of high-grade P sources has stimulated scientific and economic interest in more efficient and cost-effective P fertilizer production and P recovery technologies (Cordell et al., 2011). New processes for converting PRs into high-grade phosphate fertilizers are needed to help maintain a steady, cost-effective supply of this critical plant macronutrient.

There are about 350 known phosphate minerals (Nriagu and Moore, 1984). Within this group, apatites $[\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2]$ are the most important form of P in PRs used in fertilizer production. The manufacture of phosphate fertilizers involves acidification to induce proton attack on the apatite structure. The reactivity of the PRs depends on the component "X" in the structural formula of the apatite, which can be F^- , Cl^- , or OH^- , and on the degree of isomorphic substitution of CO_3^{2-} for PO_4^{3-} (Chien et al., 2011; Lehr, 1980, 1984; Young, 1974). The "X" ions in apatite crystals are more susceptible to proton attack because of their location in calcium (Ca) channels parallel to the c-axis, and acid dissolution begins with the detachment of these ions from apatite surfaces (Dorozhkin 1997, 1999, 2012; Young, 1974). Many factors, however, influence the kinetics of apatite dissolution, including rock composition, particle size, crystallinity, crystal

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Abbreviations: AMW, acidic mine waste; DCP, dicalcium phosphate; LCF, linear combination fitting; MCP, monocalcium phosphate; P_{CA} , phosphorus extractable in citric acid; P_{NAC} , phosphorus extractable in neutral ammonium citrate; PR, phosphate rock; P_{water} , phosphorus extractable in water; SSP, single superphosphate; XANES, X-ray absorption near edge structure; XRD, X-ray diffraction.

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defects, composition and strength of the reacting acid, temperature, and hydrodynamics (Chien et al., 2011; Dorozhkin, 2012).

Common acids used to solubilize apatite to produce soluble phosphate fertilizers include sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), and nitric acid (HNO_3). Acidification ideally forms monocalcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2$] (MCP), which is highly soluble in water (20 g L^{-1}) (Chien et al., 2011; Lehr, 1984). However, the complexity of PR matrices may result in intermediate compounds with unknown characteristics being produced during acidification (Dorozhkin, 2012), and the solubility of these intermediate phosphate compounds affects the quality of the phosphate fertilizers produced (Chien and Menon, 1995; Chien et al., 2011; Dorozhkin 2012; Lehr, 1984).

As an alternative to using pure acids to produce high-grade P-fertilizers, this research focuses on reacting a waste acid from a mining operation with PRs. Such beneficial use of an industrial waste stream could decrease the costs of both fertilizer production and waste disposal while diminishing negative environmental impacts of waste acid disposal. The management of industrial wastes to comply with legal standards is expensive, and efforts are on the rise to develop technologies that minimize waste generation and increase recycling and reuse (Capón-García et al., 2014; Mattiello et al., 2016; Puig et al., 2013). As a feedstock for industrial production of P-fertilizers, waste acids contain impurities such as Fe, Mn, K, Al, SO_4 , and trace elements (Ni, F, Pb, and Cd). Reaction of these components with PRs could produce unknown intermediate compounds that affect the quality of fertilizers produced. Consequently, research is needed to assess the solubility and speciation of fertilizers produced by reacting PRs with waste acids from mining operations.

Speciation of P in complex matrices can be achieved using synchrotron X-ray absorption near edge structure (XANES) spectroscopy (Beauchemin et al., 2003; Hesterberg et al., 1999; Lombi et al., 2006; Toor et al., 2006). Phosphorus K-edge XANES analysis can provide information about composition, transformation, and solubility of P species based on unique spectral signatures obtained when $\text{H}_x\text{PO}_4^{x-3}$ is bonded with different cations like Al^{3+} , Fe^{3+} and Ca^{2+} in minerals, amorphous solids, and adsorbed species (Beauchemin et al., 2003; Diaz et al., 2008; Hesterberg et al., 1999; Ingall et al., 2010; Kar et al., 2012; Kizewski et al., 2011; Lombi et al., 2006; Prietzel et al., 2013). Although P K-edge XANES has been applied to soils and animal wastes (Beauchemin et al., 2003; Hesterberg et al., 1999; Prietzel et al., 2013; Sato et al., 2005; Toor et al., 2006), its use in developing fertilizer technologies has been limited to only a few studies (Khatiwada et al., 2012; Lombi et al., 2006).

Our goal is to develop an alternative route of P fertilizer production using acidic mining waste (AMW). The specific objective of this research was to analyze transformation products and the extractability of P in materials produced by reacting AMW with PRs. Measurements of chemical composition, P extractability by reagents used to evaluate fertilizer quality, bulk mineralogy, and P speciation by XANES analysis were made on PRs that were reacted with varying concentrations of AMW diluted in water.

Materials and Methods

Phosphate Rocks

Two Brazilian PRs (Araxá and Patos) and one Peruvian PR (Bayóvar) were used in this study. Araxá and Patos PRs are deposits located in the state of Minas Gerais in Brazil, and the Bayóvar PR is from the Sechura Desert in Peru. Araxá PR is from an igneous deposit, and Patos PR is from a sedimentary deposit medium-grade metamorphism. The elements Fe, Al, Mn, Zn, Ni, Pb, Cu, Cr, and Cd were determined in PR samples digested for total elemental analysis (Alcarde, 2009) using inductively coupled plasma optical emission spectrometry (Optima TM 4300DV, PerkinElmer). The P in Araxá and Patos PRs had been concentrated before we received them from Bunge Fertilizantes S.A. and Ultrafértil S.A., respectively. Araxá and Patos PRs are normally not suitable for direct use as phosphate fertilizer due to the low P solubility but are used as raw materials to produce high-grade fertilizers by thermal or wet acidification processes (Beisiegel and de Souza, 1986; Lapidou-Loureiro and Melamed, 2006; Oba, 2004; Prochnow et al., 2004). Bayóvar PR is from a marine sedimentary deposit and is used as a raw material in fertilizer production without preconcentration. We received Bayóvar PR from Heringer Fertilizantes S.A. This PR has a high degree of isomorphic substitution of carbonate for phosphate and is more soluble than the Brazilian PRs. It is an adequate material for direct application to soils as a P fertilizer, but it is less effective than high-grade phosphate fertilizers for annual crops (Faria and Guardieiro, 2011).

Acidic Mine Waste

The AMW used in our experiments to solubilize PR is produced by London Scandinavian Metal Brasil S.A. (São João Del Rei, Minas Gerais State, Brazil). The AMW is a residue generated from the extraction of tantalum (Ta) and niobium (Nb) oxides from pegmatite ores using a mixture of H_2SO_4 , HF, and HCl. This process generates approximately $17,250 \text{ m}^3$ of AMW effluent and 12,700 t of mud annually, which must be neutralized before disposal into special landfills. These wastes currently constitute an important part of the company's environmental liability. As with PR digests, Fe, Mn, Al, K, Ca, Mg, Ni, Cu, Pb, Zn, Cr, and Cd were determined in AMW samples using inductively coupled plasma optical emission spectrometry. The anions Cl^- , F^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , and Br^- from AMW were quantified by ion chromatography (DX500, Dionex) with chemically suppressed detection of electric conductivity by using a mobile phase gradient consisting of ultra-pure water, methanol, and 0.1 mol L^{-1} NaOH, as proposed by Silva et al. (2001).

Experimentation

A 3×5 factorial design was used for P acidification experiments, including the three PRs (Araxá, Patos, and Bayóvar) and four AMW concentrations (12.5, 25, 50, and 75% v/v in H_2O) along with nontreated PR as a control (designated 0% AMW treatment). Nontreated PRs means that only distilled water was used on the control treatment. Treatments were blocked into three randomized complete blocks. All PRs were ground and passed through a $150\text{-}\mu\text{m}$ sieve (100 mesh). Five grams of each PR sample were reacted with 20 mL of each concentration of

AMW in 50-mL centrifuge tubes by shaking at 25°C for 60 min at 150 rpm on a horizontal reciprocating shaker. After shaking, uncapped tubes were heated to 80 ± 5°C for 4 h in a water bath to decrease the F concentration by volatilization. The materials were transferred to glass beakers and dried in an airflow oven at 105°C for 72 h. The cooled solids were again ground to pass through a 150-µm sieve to produce our alternative fertilizer materials.

Chemical Characterization

Total P concentrations (P_{total}) and fractions of water-soluble P (P_{water}), neutral ammonium citrate-soluble P (P_{NAC}), and citric acid-soluble P (P_{AC}) were measured in nontreated (0% AMW) and treated PR samples used for phosphate fertilizer characterization (Alcarde, 2009). Phosphorus concentrations in aqueous solutions were determined spectrophotometrically using the yellow phosphovanadomolybdate-complex method (Wright and Stuczynski, 1996).

X-ray Diffraction Analysis

Acidic mine waste-treated and nontreated PR samples were evaluated for mineralogical composition using an X'Pert Pro MPD diffractometer (Panalytical) and Co-K α radiation ($\lambda = 1.7889 \text{ \AA}$) produced at 40 kV and 30 mA. Powder mounts were prepared by packing ground samples ($\leq 150 \text{ \mu m}$) into aluminum holders. The scan range was from 4 to 80° 2 θ in 0.02° 2 θ steps at a rate of 1 step s $^{-1}$.

P K-edge XANES Analysis

Treated and nontreated samples of PR were ground to $\leq 75 \text{ \mu m}$ (200-mesh) for P K-edge XANES analysis. A thin layer of the powdered material was uniformly spread on double-sided (P-free) carbon conductive tape and mounted on a stainless steel sample holder. The XANES data were collected at the soft X-ray spectroscopy beamline at the Brazilian Synchrotron Light Laboratory in Campinas, Brazil. The electron storage ring was operated at 1.37 GeV with a current between 100 and 300 mA. The Si(111) double-crystal monochromator on the beamline was detuned by 20% to reject higher harmonics and calibrated to an energy (E0) of 2151.2 eV at the maximum in the first-derivative spectrum of a MCP standard. The XANES data were collected in fluorescence mode between 2110 and 2445 eV, with varying step sizes of 1.0 eV from 2110 to 2143 eV, 0.2 eV from 2143 to 2185 eV, 1.0 eV from 2185 to 2255 eV, and 5.0 eV from 2255 to 2445 eV. Standards and reacted PR samples were diluted to 50 mmol kg $^{-1}$ of P in boron nitride to avoid self-absorption (Kelly et al., 2008). Two to four scans were taken from each sample or standard and merged to reduce spectral noise.

Data analysis was performed using the IFEFFIT package in the Athena computer software (Ravel and Newville, 2005). Merged scans were normalized using a linear baseline function between -20 and -9 eV relative to E0 (~2151 eV) and a quadratic normalization function between 32 and 59 eV above E0, including use of the "flatten" feature in Athena. Linear-combination fitting (LCF) analysis was performed using the Athena software.

Two approaches to LCF analysis were used. In the first approach, spectra for samples from the 12.5 and 25% AMW treatments were fit with those of the 0 and 75% AMW treatments to determine whether there was a progression of P species transformation with increasing AMW treatment. In the second approach, LCF was conducted using 19 purchased or synthesized standards of Fe-, Al-, and Ca-bonded phosphates, most of which were previously published (Beauchemin et al., 2003; Hesterberg et al., 1999; Khare et al., 2005). The original (nontreated, 0% AMW) treatments were used as the hydroxyapatite standard, and an amorphous Ca-phosphate standard reported by Eveborn et al. (2009) was also included. The LCF analysis was conducted over a spectral range of -7 to +35 eV relative to E0, the first-derivative maximum of each sample or standard at ~2151 eV. For fitting with the full set of standards, we used both the standard elimination method described by Manceau and Nagy (2012) and fitting with all possible combinations of up to three standards (Kelly et al., 2008) to select the fits that were most consistent between methods. The energy scales of the standards were allowed to shift by a maximum of \pm one energy step ($\pm 0.2 \text{ eV}$).

Results

Chemical Composition of Phosphate Rocks and Acidic Mine Waste

All three PRs (0% AMW) used in this study contained 29 to 30% (w/w) P $_2$ O $_5$ but varied in concentrations of Fe, Al, Mn, and cationic trace elements (Table 1). The Araxá PR sample contained 1.2- and 4.8-fold more Fe than the Bayóvar and Patos PRs, respectively, but less Al (Table 1).

The AMW reacted with the PRs used in this study was very acidic and required 5.75 moles of NaOH to neutralize the pH from ~0 to 7 (Table 2). The AMW also contained elevated concentrations of Fe, Mn, Cr, Ni, Pb, and Cd (Table 2). The acidity and trace element concentrations make the AMW unsuitable for direct discharge into water bodies according to current waste-discharge standards adopted by the Brazilian legislation (Brasil, 2011).

Table 1. Chemical composition of Araxá, Patos, and Bayóvar phosphate rocks. Data were obtained from three replicates.

PRs	P $_2$ O $_5$ †	Fe $_2$ O $_3$	Al $_2$ O $_3$	MnO	Zn	Ni	Pb	Cu	Cr	Cd‡
	% w/w				mg kg $^{-1}$					
Araxá	30	6.3	0.83	0.22	264	69	52	50	37	1.1
Patos	30	1.3	1.45	0.014	63	5.5	29	22	16	0.1
Bayóvar	29	5.1	1.49	0.31	181	239	70	23	186	36

† Phosphorus concentrations were determined spectrophotometrically using the yellow phosphovanadomolybdate-complex method (Wright and Stuczynski, 1996).

‡ Concentrations of Fe, Al, Mn, Zn, Ni, Pb, Cu, Cr, and Cd were measured using inductively coupled plasma optical emission spectrometry.

Table 2. Chemical composition of acidic mining waste from London Scandinavian Metal Brasil S.A. and maximum permissible concentrations of elements according to waste discharge standards into bodies water (Brasil, 2011). Data were obtained from three replicates.

Density	pH	Acidity†	Fe‡	K	Mn	Al	Ni	Cr	Cu
kg m ⁻³		mol L ⁻¹				mg L ⁻¹			
1.6	0.0 (5–9)	5.75	13,595 (15.0)	3438 (uv§)	1199 (1.0)	897 (uv)	126 (2.0)	59 (1.0)	57 (1.0)
Pb	Ca	Zn	Cd	Mg	SO ₄ ²⁻	Cl ⁻	F ⁻	PO ₄ ³⁻	NO ₃ ⁻
		mg L ⁻¹					g L ⁻¹		
56 (0.5)	46 (uv)	44 (5.0)	11 (0.2)	4.7 (uv)	791 (uv)	128 (uv)	109 (10)	19 (uv)	18 (uv)

† Acid buffering measured by neutralization of acidic mining waste to pH 7 with 0.5 mol L⁻¹ of NaOH.

‡ Concentrations of Fe, K, Mn, Al, Ni, Cr, Cu, Pb, Ca, Zn, Cd and Mg were measured using inductively coupled plasma optical emission spectrometry. The anions Cl⁻, F⁻, SO₄²⁻, NO₃⁻, and PO₄³⁻ from acidic mining waste were quantified by ion chromatography. Maximum permissible concentration (MPC) data are shown in parentheses. For Fe, Mn, and Cu, the MPC values correspond to soluble forms. For others elements, MPC values are established to their total content in the waste.

§ uv, unrelated value.

Acidic Mine Waste–Induced Changes in Extractable P

The proportions of total P in the original (nontreated) and AMW-treated PRs that were dissolved in water, neutral ammonium citrate, or citric acid (P_{water}, P_{NAC}, or P extractable in citric acid [P_{CA}]) are shown in Fig. 1. These operational extractants provided a metric for changes in P solubility and potential plant

availability after treatment with AMW. For fully acidified P fertilizer, values of sequential extraction of P_{water} and P_{NAC} have been related to plant-available P (Chien et al., 2011). According to these authors, the water-insoluble but citrate-soluble compounds present in these P fertilizers do have some agronomic value when compared with compounds that are 100% water soluble, such as

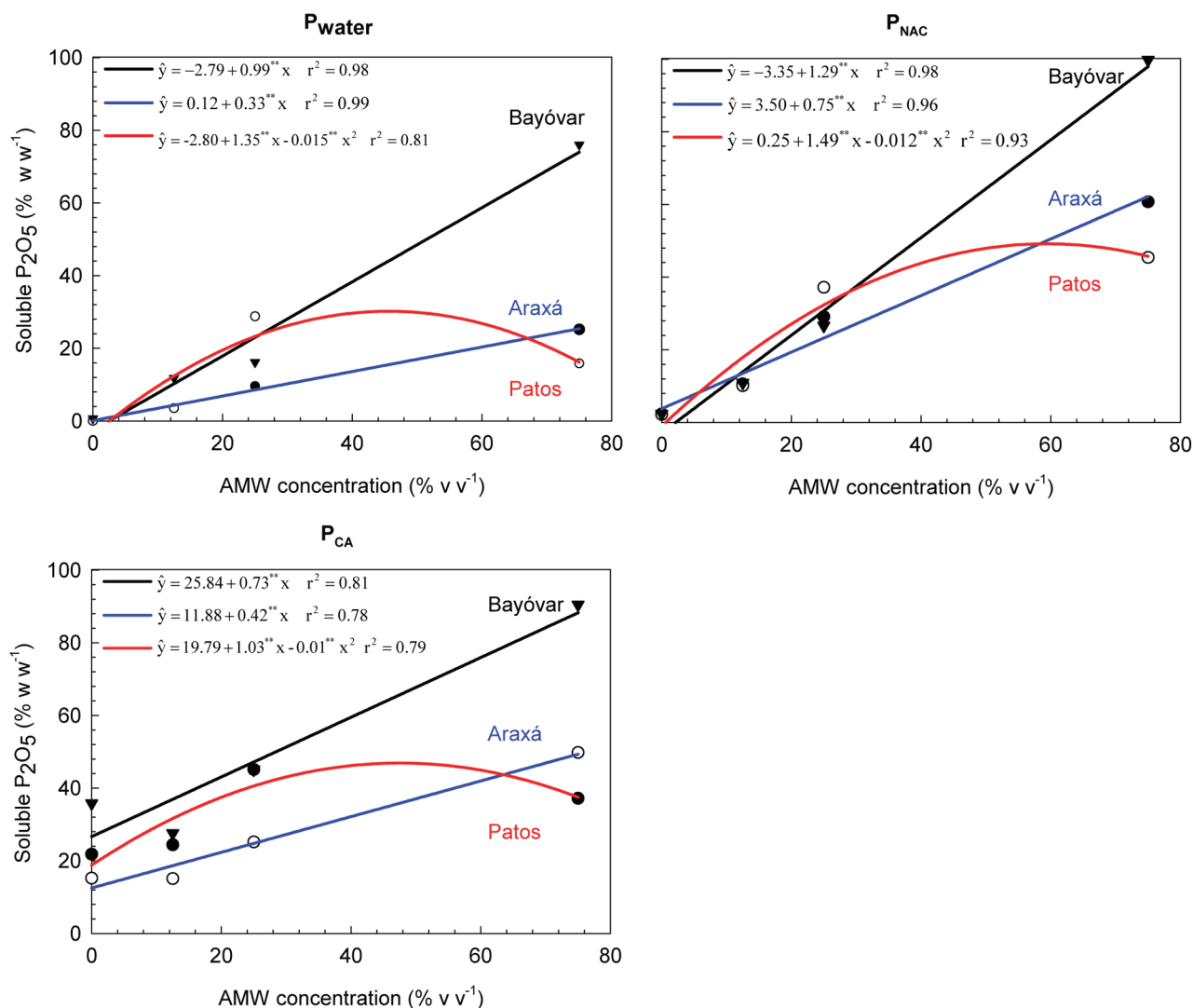


Fig. 1. Percentages of water-soluble (P_{water}), neutral ammonium citrate-soluble (P_{NAC}), and citric acid-soluble (P_{CA}) P₂O₅ in phosphate rocks reacted with acidic mining waste (AMW) generally increased with increasing AMW concentration. Linear or quadratic regression relationships between soluble P₂O₅ and AMW concentration were significant at the 99% (p = 0.01) level.**

MCP. In terms of P available to plants, agronomic performance is different for various fertilizers with low contents of P_{water} .

For most samples, extractable P increased in the order $P_{\text{water}} < P_{\text{NAC}} < P_{\text{CA}}$, especially for AMW treatments of <50% (v/v). Both P_{water} and P_{NAC} for the nonreacted PRs were considered to be low (≤ 0.7 and $\leq 2.4\%$ w/w) but increased by up to 526-fold (P_{water}) and up to 42-fold (P_{NAC}) when treated with AMW, respectively. Citric acid–extractable P increased only by up to threefold but already constituted 15 to 36% (w/w) of total P in the nontreated PRs (Fig. 1). In general, extractable P increased linearly with increasing concentration of AMW, except for the Patos PR, where the best fit was quadratic (Fig. 1). Based on the linear models, treatment with our maximum evaluated concentration of a 75% (v/v) solution of AMW yielded the greatest proportion of all three extractable P concentrations for Araxá and Bayóvar PRs. Based on derivatives of the quadratic models for Patos PR, AMW concentrations of 45, 62, and 47% (mean, 51

$\pm 9\%$) produced the maximum P_{water} , P_{NAC} , and P_{CA} for this PR (Fig. 1). These results indicate that PR acidification by AMW can increase the fertilizer value of PR by increasing plant-available P. Although higher solubility of phosphate fertilizers can improve agronomic efficiency, factors such as soil properties, management practices, and species selection also affect plant availability (Bolan et al., 1990; Chien and Menon, 1995; Chien et al., 2011). For example, some studies have indicated that even soluble P fertilizers have low agronomic efficiency in soils with high P-fixing capacity (McLean and Logan, 1970; Moreira et al., 2002).

Acidic Mine Waste–Induced Changes in P Speciation

X-ray diffraction (XRD) and XANES analyses provided complementary, direct evidence for mineral alterations induced by AMW treatments of PRs. X-ray diffraction analysis showed a dominance of apatite in the original samples (0% AMW treatment) for all three PRs (Fig. 2). The diffraction peaks for the

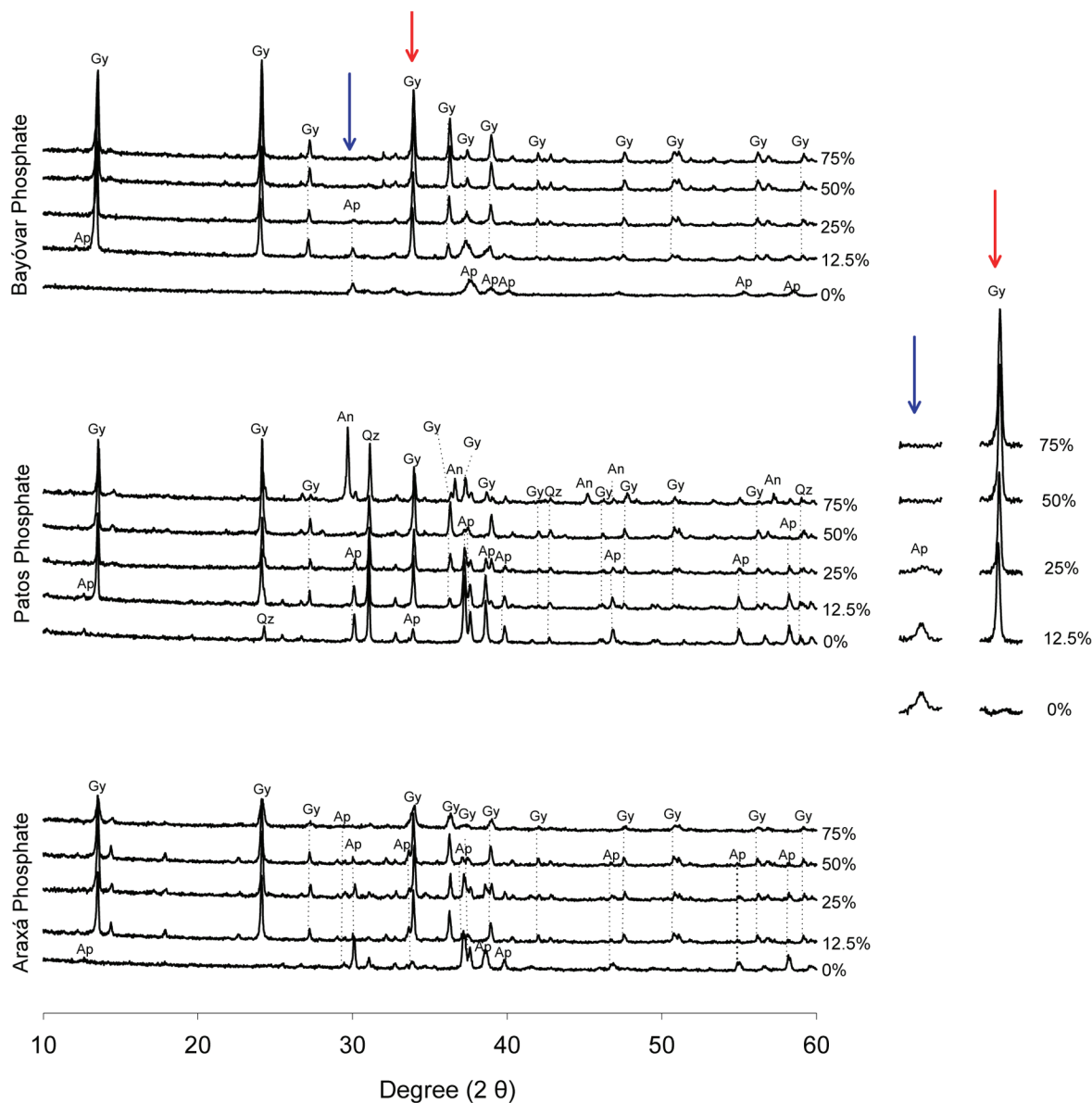


Fig. 2. X-ray diffraction patterns from phosphate rocks (Araxá, Patos and Bayóvar) after treatment with different concentrations of acidic mining waste (AMW): 0, 12.5, 25, 50, or 75% (v/v). An, anhydrite; Ap, apatite; Gy, gypsum; Qz, quartz. X-ray diffraction shows the disappearance of apatite and the appearance of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrite (CaSO_4) with increasing AMW concentration. Quartz is present in all the AMW treatments using Patos PR. Data were collected using $\text{Co K}_{\alpha 1}$ radiation (1.789 Å).

Bayóvar PR sample were broader than those for the Araxá and Patos PRs, indicating that Bayóvar PR contained more poorly crystalline apatite. Consistent with XRD results, P K-edge XANES spectra for the original PR showed a post-edge shoulder near 2154 eV (Fig. 3, arrow) and a broad peak near 2162 eV. These peaks are indicative of hydroxyapatite (Hesterberg et al., 1999).

The intensity of XRD peaks for hydroxyapatite (e.g., at 30, 37–40, 55, and 58° 2 θ) progressively diminished with increasing AMW concentration (Fig. 3). The broader peaks for Bayóvar PR essentially disappeared in the 25% AMW treatment, whereas the sharper peaks for Araxá and Patos PRs were detected up to at least the 50% treatment. After the breakdown of hydroxyapatite structure, gypsum (CaSO₄·2H₂O) was formed from all PRs. The Patos PR treated with 75% AMW also contained anhydrite (CaSO₄), probably due to gypsum dehydration during drying (Fig. 3). X-ray diffraction patterns also showed that minor amounts of quartz persisted in the Patos PR after all AMW treatments.

Qualitative changes in P K-edge XANES spectra showed a progressive transformation of apatite in PRs into new P species. A loss of apatite with increasing AMW treatment concentration is apparent from the decreasing prominence of both the post-white line shoulder near 2154 eV (Fig. 3, arrow) and the broad peak near 2162 eV, consistent with XRD data. Although the shape of the shoulder at 2154 eV varies between different Ca-phosphate minerals, hydroxyapatite shows the most prominent shoulder (Beauchemin et al., 2003; Hesterberg et al., 1999; Ingall et al., 2010; Lombi et al., 2006; Toor et al., 2006). Concurrent with a loss of hydroxyapatite, the progressive formation of a weak pre-white line peak between ~2146 and 2149 eV (Fig. 3, arrow and inset) with increasing AMW concentration indicated that the AMW treatments induced the formation of Fe(III)-bonded phosphate (Franke and Hormes, 1995; Hesterberg et al., 1999; Khare et al., 2005; Okude et al., 1999). Khare et al. (2007) reported that this pre-white line

peak is formed due to a P 1s electron transition into Fe(4p)-O(2s) antibonding molecular orbitals and indicated that the peak intensity is related to the number of PO₄-Fe(III) bonds in the species (Khare et al., 2007). Consequently, the intensity of the pre-edge peak is greater for strengite than for less crystalline Fe(III)-phosphates. Iron phosphate was not detectable by XRD, suggesting that it was either amorphous or at a concentration below detection.

Quantitative assessments of P speciation changes are shown by linear combination fitting results (Table 3). The two fitting approaches that we used were intended to evaluate the consistency of our fitting models: fitting the 12.5 and 25% AMW-treatment samples with endmembers of 0 and 75% AMW treatments (“fit with endmembers”) or fitting with combinations of up to four standards (“fit with standards”). Although better fits were obtained with standards as indicated by the typically lower residual (R-factor) for a given sample (Table 3) and the excellent agreement between sample data and fits (Fig. 3), the fits with endmembers indicated that there was a progressive decrease in the starting materials (PRs) and a progressive increase in the ending materials (75% treatment samples) with increasing AMW concentration (Table 3). Results of fitting with standards (Supplemental Fig. S1) were generally consistent with this progressive trend. The proportion of the original PR in the fits progressively decreased with increasing AMW concentration, and the proportion of Fe(III)-bonded phosphate increased. The Fe(III)-bonded phosphate was best fit with a standard of “FePO₄·2H₂O” from Sigma-Aldrich (CAS 13463-10-0), which was verified by XRD analysis to be noncrystalline rather than with the poorly crystalline or well crystalline strengite standards published by Hesterberg et al. (1999). The progressive formation of up to 78, 38, and 70% of P as amorphous Fe(III)-phosphate in the AMW-treated samples of Araxá, Patos, and Bayóvar PR samples, respectively, was consistent with the lack of detectable peaks for Fe(III)-phosphate minerals in our XRD patterns (Table 3; Fig. 2). Based on the

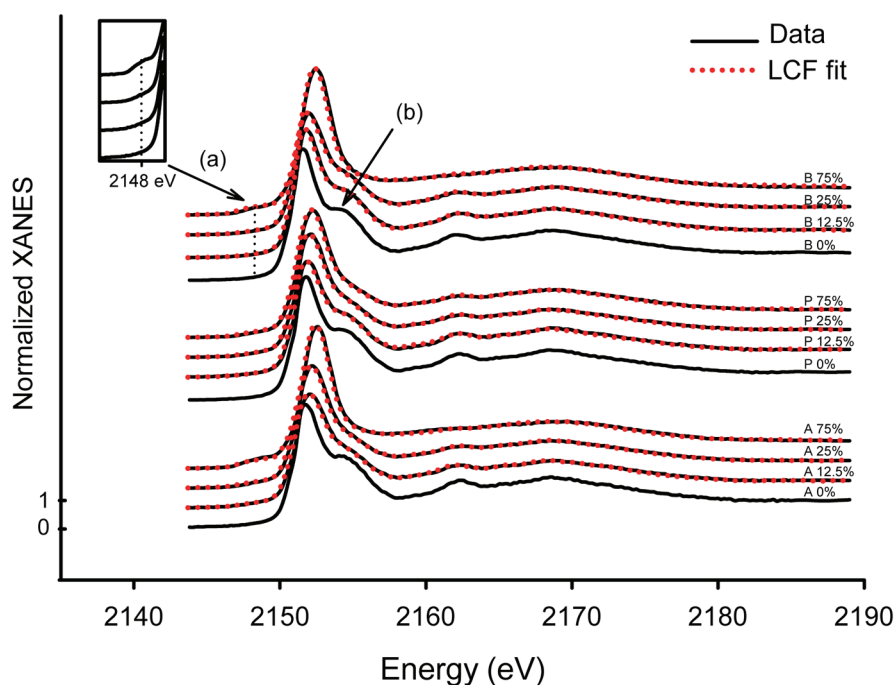


Fig. 3. X-ray absorption near edge structure spectra show changes in P speciation with increasing concentration of reacted acidic mining waste, including a disappearance of apatite as indicated by the weakening of a shoulder near 2154 eV (arrow b) across treatments and the appearance of Fe(III)-bonded phosphate as indicated by a growth in a pre-white line feature near 2148 eV (arrow a and inset). LCF, linear combination fitting

Table 3. Best-fit proportions of standards (\pm uncertainties) from two approaches to linear combination fitting of P K-edge XANES spectra of phosphate rocks (PRs) for the different AMW treatments: fitting of the 12.5 and 25% AMW samples using the original PR (0%) and 75% AMW samples as "endmember" treatment standards and fitting with the original PR and standards of amorphous iron(III) phosphate (Am-FePO₄), amorphous calcium phosphate (Am-Ca-P), monocalcium phosphate (MCP), dicalcium phosphate (DCP), and amorphous aluminum phosphate (Am-AlPO₄).†

PR	AMW concentration %	Fit with endmembers		Fit with standards						R factor ($\times 10^4$)‡
		Original PR	75% AMW	Original PR	Am-FePO ₄	Am-Ca-P	MCP	DCP	Am-AlPO ₄	
		-% of total P -								
Araxá	12.5	70 \pm 1	30 \pm 1	59 \pm 1	19 \pm 0		22 \pm 1			14, 4
	25	48 \pm 1	52 \pm 1	33 \pm 2	37 \pm 0	17 \pm 2	13 \pm 1			8, 4
	75				78 \pm 1	22 \pm 1				14
Patos	12.5	73 \pm 2	27 \pm 2	74 \pm 2			12 \pm 2	7 \pm 2	7 \pm 2	20, 13
	25	27 \pm 1	73 \pm 1	43 \pm 2	25 \pm 1	13 \pm 2		19 \pm 2		3, 3
	75			27 \pm 2	38 \pm 1	14 \pm 2		22 \pm 2		4
Bayóvar	12.5	89 \pm 0	11 \pm 0	85 \pm 1	8 \pm 0	3 \pm 2	4 \pm 1			3, 2
	25	71 \pm 1	29 \pm 1	62 \pm 1	19 \pm 0		19 \pm 1			19, 3
	75				70 \pm 1			30 \pm 1		16

† Fitted proportions of standards all summed to between 96 and 104% and were renormalized to a sum of 100%. Uncertainties calculated by Athena were rounded to the nearest whole number. Percentages of standards <5% of total P are considered to be at "trace" levels relative to the sensitivity of XANES analysis.

‡ R-factor = $\Sigma(\text{data-fit})^2/\Sigma(\text{data})^2$ is a measure of the residual in the fit. The first of two numbers for 12.5 and 25% treatments is for fits with the endmember.

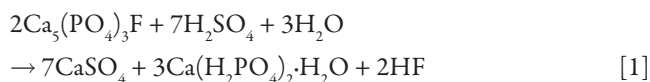
Fe and P concentrations in Tables 1 and 2 and a mass balance analysis given our reaction conditions, molar ratios of Fe/P in the reacted PR and AMW samples indicate that the maximum proportions of amorphous FePO₄ that could form in the 75% AMW treatments are 32, 19, and 29% of total P for the Araxá, Patos, and Bayóvar PR samples, respectively. These results indicate that our XANES fitting analysis overestimated the proportion of P present as FePO₄. However, it is probable that the methodology described by Alcarde (2009) to extract total P concentration from PRs underestimates Fe concentration.

In addition to the loss of apatite and the apparent formation of amorphous Fe(III)-phosphate, linear combination fitting results indicated the formation of other Ca-phosphate species after AMW treatments. These species were fit with an amorphous Ca-phosphate standard (published by Eveborn et al. [2009]), a MCP standard [Ca(H₂PO₄)₂ purchased from Vetec Química Fina Ltda], or a dicalcium phosphate (DCP) standard (CaHPO₄ purchased from Vetec Química Fina Ltda) (Table 3 and Supplemental Fig. S1). The tendency was for a species fit with MCP to be formed in the 12.5 and 25% AMW samples, with species fit with amorphous Ca-phosphate and DCP standards becoming progressively greater with increasing AMW concentrations. Although the fits included up to 30% of total P as MCP or DCP, the overall concentration of these minerals (for PRs containing 30% P₂O₅) would be $\leq 10\%$ (w/w), and therefore these minerals were not detected by XRD analysis.

In the Patos sample treated with 12.5% AMW, the best fit included 7% of total P represented by an amorphous Al-phosphate standard (Table 3). Perhaps at this lowest acid treatment, Al³⁺ was preferentially dissolved over Fe³⁺ in this sample of greatest Al/Fe ratio (Table 1) and amorphous Al-phosphate formed in preference to amorphous Fe-phosphate. Because fits with species at concentrations of <10% of total P are considered minor species near the limit of sensitivity of P K-edge XANES analysis, conclusions about their mechanisms of formation and their overall contribution to the reactivity of the AMW-treated PR samples are tentative.

Discussion

Treatment of Araxá, Patos, and Bayóvar PRs with AMW increased the fertilizer value of the material as indicated by the increasing extractable amounts of P (P_{water}, P_{NAC}, and P_{CA}). The AMW-induced changes were somewhat consistent with those induced by reaction of PRs with pure acids such as sulfuric acid in the production of single superphosphate (SSP) fertilizer (Leikam and Achorn, 2005), for example:



Results of XRD and XANES showed a loss of apatite with increasing AMW concentration between 12.5 and 75% (v/v), and XRD showed formation of gypsum and anhydrite (Fig. 2 and 3; Table 3). Moreover, XANES spectral fitting indicated a progressive formation of amorphous Fe-phosphate (Table 3), apparently induced by high concentrations of Fe in the AMW (13,595 mg L⁻¹ or 0.24 mol L⁻¹ (Table 2) and the PRs (9100–44,000 mg kg⁻¹) (Table 1). Although our XRD patterns showed no evidence for formation of SSP [Ca(H₂PO₄)₂ · H₂O] according to Reaction 1, XANES fitting results suggested that apatite was converted to more soluble Ca-phosphate species that were fit as amorphous Ca-phosphate, MCP, and DCP. Linear increases in P_{water}, P_{NAC}, and P_{CA} with increasing AMW concentration for the Araxá and Bayóvar PRs (Fig. 1) indicate that the greatest fertilizer value can be achieved with maximum AMW treatment for these PRs. Thus, we recommend an AMW treatment of 75% for these PRs in any commercialization process to maximize P solubility and the consumption of AMW that would otherwise contribute to the waste stream of the Ta and Nb oxides production process. For the Patos PR, derivatives of quadratic relationships between P_{water} and P_{CA} with respect to AMW concentration (Fig. 1) showed maxima at 45 and 62%, respectively. We recommend an AMW treatment of 50% in any commercialized processing of Patos PR.

The effect of the AMW treatment in terms of solubilization of PRs can be better understood by considering changes in P speciation. For instance, XANES spectra analysis showed a negative relationship between soluble fractions of P (P_{NAC} , P_{CA} , and P_{water}) and the proportion of total P fit as hydroxyapatite, whereas a positive relationship was observed between such soluble fractions with the proportions of amorphous Ca-phosphate, DCP, and amorphous Fe-phosphate. These relationships imply that conversion of apatite to other P forms after AMW treatment is key to increasing the solubility of P in the PR samples. The greater positive slopes for the Ca-phosphates compared with the amorphous Fe-phosphate suggest that the species fit as amorphous Ca-phosphate and DCP were more soluble, and both species showed identical linear relationships when regressions were forced to the origin. Although the proportion of the species fit as MCP showed no significant relationship with P_{NAC} , we expect this Ca-phosphate species to be more soluble than hydroxyapatite. Moreover, P_{CA} and P_{water} showed similar trends as P_{NAC} with XANES species but generally had higher p values (Fig. 4).

In summary, the AMW treatment causes speciation changes that should enhance the fertilizer quality of PRs based on common extractions used to evaluate plant-available P concentrations. However, because commercial fertilizers produced using pure acids apparently contain phosphate only in soluble Ca-phosphate species (e.g., SSP), evaluations of the AMW-treated PRs in soils are needed to determine, for example, the plant availability of the amorphous Fe-phosphate species in a soil matrix in which pH and interactions with Fe-oxides and organic matter should affect Fe-phosphate dissolution.

One potential concern with using AMW to improve the fertilizer quality of PRs is the addition of potentially toxic trace elements to the resulting fertilizer product. Mass balance calculations on the additions of trace elements relative to the native concentrations for the various PR sources and AMW treatments showed that the fertilizer products would be enriched in trace elements by up to 126-fold for the 75% AMW treatment. Trace-element enrichment in all three fertilizers generally followed the order $\text{Cd} > \text{Ni} > \text{Mn} > \text{Cu} > \text{Cr} > \text{Pb} > \text{Zn}$. The greatest enrichment occurred for the Patos PR, mainly because it contained the lowest native concentrations of trace elements. However, for all PR sources and AMW treatments, the concentrations of Cd, Pb, and Cr in the AMW-treated byproducts never exceeded the maximum allowable concentrations of 4, 20, and 40 mg kg^{-1} , respectively, per percentage (1% w/w) of P_2O_5 content, according to standards adopted in Brazil for phosphate fertilizers (Brasil, 2011). The maximum computed concentrations of trace elements (assuming 100% incorporation of these elements added with AMW 75% and a mass yield of AMW of 0.54 g mL^{-1}) in the end products were 2279, 235, 151, 138, 91, 84, and 26 mg kg^{-1} for Mn, Ni, Zn, Cr, Pb, Cu, and Cd, respectively.

We know that the Cd content in PR depends of the degree of isomorphic substitution of Ca by Cd in the apatite structure. In general, isomorphic substitutions in Brazilian apatites for either anionic or cationic sites are considered low, which explains the low content of Cd. Campos et al. (2005) reported Cd contents in Brazilian phosphates up to 8.7 mg kg^{-1} . Gabe and Rodella

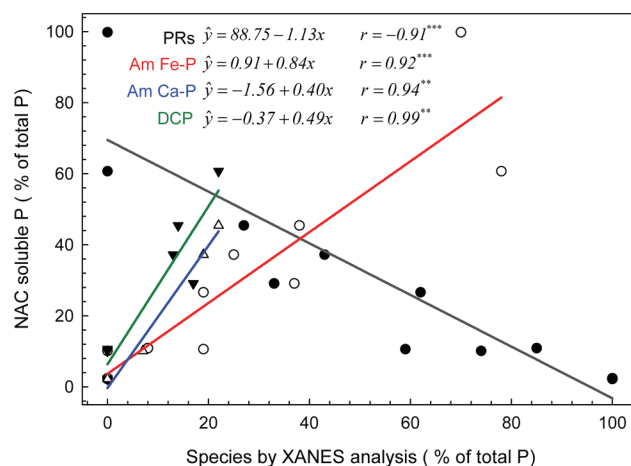


Fig. 4. Linear relationships between P extractable in neutral ammonium citrate (P_{NAC}) and proportions of selected P species fit to P K-edge XANES spectra (Supplemental Table S1) for all three phosphate rocks (PRs) treated with all concentrations of acidic mine waste (AMW). Fits with amorphous Fe(III)-phosphate (Amorph Fe-P), amorphous calcium phosphate (Amorph Ca-P), and dicalcium phosphate (DCP) were extrapolated to the origin (0, 0) to compare slopes, and levels of statistical significance were always less than $p = 0.01$. Fits for water-soluble P (P_{water}) and citric-acid-soluble P (PCA) (not shown) gave similar trends.

(1999) reported that Cd concentration in Brazilian phosphates varied from 4 to 7 mg kg^{-1} .

We did not measure As or Hg in our samples. However, previous work from our research group has detected very low concentrations of these elements in PRs or in the AMW (Mattiello et al., 2016).

Except for the Bayóvar PR, our AMW treatments produced lower concentrations of P_{water} and P_{NAC} than are found for commercial phosphate fertilizers such as SSP and triple superphosphate- $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. However, some poor-quality SSP sources may contain as little as 50 to 60% water-soluble P (Chien et al., 2011). Although high concentrations of water-soluble P can be a quality index for phosphate fertilizer, several papers show that partially acidulated PRs can be more effective for slower release of P (Chien and Hammond, 1988; McLay et al., 2000; Prochnow et al., 2002, 2006) than more water-soluble superphosphate fertilizers. Because Bayóvar is a sedimentary phosphate rock and is considered the highest quality of the three PRs that we evaluated, the produced P fertilizer has comparable solubility to commercial phosphate fertilizers. Nevertheless, by consuming 100% of the $17,250 \text{ m}^3$ of AIW produced by the mining industry each year and considering the best AMW concentrations that we found to solubilize Araxá or Bayóvar PRs (75%) or Patos PR (50%), it is possible to produce 15,000 or 22,600 t of P fertilizer from these PRs, respectively. We note, however, that if our proposed use of AMW becomes commercially viable, then approaches to remove and capture F and other trace elements should be considered.

Our research represents a first step toward evaluating the feasibility of the beneficial reuse of acid mine waste, which would be a positive environmental outcome in terms of waste disposal and in terms of the energy burden and production cost of producing P fertilizers using pure acids. Our ongoing research is evaluating the efficiency of the AMW-treated rock

phosphates as a plant nutrient source. Such low-cost fertilizers might be beneficial for application to nonfood crops, such as in the extensive areas of intensely managed eucalyptus forests in Brazil.

Conclusions

Reacting PRs with AMW appears to be a viable alternative to using pure acids to produce higher-grade (more soluble) phosphate fertilizers. Production with AMW eliminates the cost of the pure acids and has an added environmental benefit of consuming a hazardous acid waste from a mining industry, but it should be recognized that trace elements in the waste could be incorporated into the fertilizer. Our AMW treatments increased P_{water} , P_{NAC} , and P_{AC} by approximately 300-, 30-, and 3-fold, respectively. Complementary XRD and P K-edge XANES analyses indicated that the increased solubility of P was due to conversion of apatite to more soluble phosphates, including amorphous iron(III) phosphate and possibly amorphous Ca-phosphate, DCP, or MCP. Our speciation analysis would also be valuable for understanding the fate of fertilizer products from AMW treatment when applied to soils.

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