Phosphorus Removal from Waste Waters Using Basic Oxygen Steel Slag

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Few studies have characterized reactive media for phosphorus (P) removal in passive treatment systems in terms of both batch and continuous flow experiments. This study uses basic oxygen steel slag (BOS) from a U.K. feedstock. Batch experiments demonstrated the effective removal of phosphorus with varying initial pH, initial P concentration, clast size, and ionic strength to represent environmental conditions. Continuous flow column experiments, operated for 406 days, with an influent P concentration of 1–50 mg/L (typical of domestic and dairy parlour waste) achieved removal of up to 62%; a second set of column experiments running for 306 days with an influent P concentration of 100–300 mg/L achieved a maximum effective removal of 8.39 mg/g. This figure is higher than that for other slags reviewed in this study (e.g., EAF Slag 3.93 mg/g and NZ melter slag 1.23 mg/g). XRD, E-SEM, and EDX data provide evidence for a sequential series of increasingly less soluble P mineral phases forming on the BOS surface (octa-calcium phosphate, brushite, and hydroxylapatite), which suggests that BOS may be a suitable substrate in passive treatment systems, providing a long-term P removal mechanism.

Introduction

Phosphorus, a common nutrient found in surface waters (*1*), is associated with both point and diffuse source pollution including effluent from sewage treatment works and surface runoff from agricultural practices such as fertilizer and manure application. Phosphorus pollution of watercourses leads to eutrophication; studies have shown that many rivers in Europe and worldwide are vulnerable to P pollution (*2*, *3*). Significantly, in Europe, since the introduction of the EU Water Framework Directive (WFD; 2000/60/EC), member states are responsible for ensuring that all surface and ground waters achieve "good" water quality status by 2013. Consequently, this statutory driver has generated much global

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interest in identifying potential low-cost solutions for P removal treatment systems (*4*, *5*). In addition, legislation on waste and resource efficiency (such as the Landfill Directive and the Waste Framework Directive in the United Kingdom and European Union) makes the use of sustainable materials (e.g., slag, fly ash, quarry fines, etc.) for P removal particularly attractive.

Numerous researchers have demonstrated the use of constructed wetland treatment systems for P removal from wastewater, primarily as tertiary effluent filters at sewage treatment works (*5–9*). Table 1 presents a review of the effectiveness of many of the substrates presented in the literature and the various types of experiments which have been performed to assess P removal capacities. A number of the substrates listed in Table 1 are industrial coproducts including several forms of slag (i.e., basic oxygen steel furnace slag, blast furnace slag, melter slag, converter slag, and electric arc furnace slag). BOS generated in the United Kingdom has not been used in any passive treatment systems for P removal. Importantly, there are physicochemical differences in the materials created during smelting, even when produced by the same manufacturing process, due to the different feedstock ores and fluxes used to manufacture specific grades of steel. These differences should be taken into account when comparing studies of industrial coproducts. This high degree of variability in their composition hinders true comparison of the coproducts as even similarly named substrates can be materially different. However, the obvious advantage of using industrial coproducts is that they are often classified as 'wastes' and are therefore inexpensive to source (*5*).

The BOS used in this study contains 4–6% free lime (CaO), which creates the potential for expansivity, rendering it unsuitable for use in construction applications as structural failure may have catastrophic consequences. The free lime leads to generation of high pH (*12*) leachates associated with leaching stockpiles of steel slag. If unmanaged the leachates can have serious effects on controlled waters (*10*, *11*). However, it is this high pH-generating potential and associated calcium release of BOS which has proved useful in several environmental engineering applications (*4*, *12–14*).

Materials and Methods

The BOS used in this work is from the Ex-Santon works in Scunthorpe, U.K. BOS is a coproduct from the steel industry which has elevated concentrations (~4–6%) of free lime bound in its matrix. XRD analysis of the BOS used in this study shows that the material is composed of mainly calcium- and iron-bearing mineral phases including di- and tricalcium silicates, wüstite, and ferrites (this study and Robinson (*15*)). Proportional (%) elemental compositional analysis (expressed as oxides) using XRF shows the chemical composition of the material to be CaO 42–44%, SiO_2 10–12%, Al_2O_3 1.2–5.6%, MgO 5–6%, Total S 0%, Total Fe (FeO/Fe_2O_3) 27–31%, MnO 3–6% P_2O_5 2–3%, and TiO_2 0.5% (*15*).

Both batch and continuous flow experiments were carried out in triplicate. The statistical package Minitab was used for all numerical analyses; the Anderson–Darling test was used to assess the normality of the distribution of a given data set. Where data was not normally distributed the data was transformed to obtain a normal distribution. The Pearsons' Perfect Product Moment correlation (parametric) test was then used to determine the relationship between two variables. One-Way Analysis of Variance (ANOVA) was used for comparison of group means to determine significant differences.

TABLE 1. Summary of Examples of Materials Tested and Results Obtained for Phosphorus Removal Experiments and Wetland Systems[a]

substrate	author	experiment type	P Removal (mg/g)	comments
iron ochre	Heal et al. (33)	B	1.00	initial [P] 50 mg/L
		C	30% capacity after 9 months	initial [P] 20 mg/L
blast furnace slag	Yamada et al. (34)	B	7.50	approximate value calculated from graph
	Mann (5)	B	0.40	
	Agyei et al. (35)	B	15.70	initial [P] 26 mg/L; removal related to percent CaO or Ca^{2+}
BOF Slag	Mann (5)	B	0.38	
	Drizo et al. (17)	B	0.58	
BOF-oxide	Baker et al. (4)	B and C	0.1 (100% removal)	25 μm size with surface area 4.5–4.7 m²/g; solution for B slightly acidic pH
electric arc furnace slag (dust and cake)	Drizo et al. (8)	B	3.93	particle size 2.5–10 mm
melter slag	Shilton et al. (36)	W	1.23	operational for over a decade; longest study for review
pulverized fly ash	Mann (5)	B	0.625	
	Drizo et al. (17)	B	0.86	
	Agyei et al. (35)	B	8.26	initial [P] 26 mg/L; removal reported to be related to percent CaO or Ca^{2+}

[a] B = Batch Experiment; C = Column Experiment; W = Wetland. P Removal data has been converted (mg/g) by the author to standardize the comparisons.

Synthetic ortho-phosphate solutions of varying concentrations were made up using tap water with KH_2PO_4 (Analar). Tap water was selected for the synthetic solutions for two reasons. First, other authors have demonstrated that it contains a range of ions which are present in natural waters and thus acted to simulate natural environmental conditions (8), except for residual chloride which may inhibit any potential biotic P removal. Second, due to the volumes of water (ca.1500 L) required over the course of the experiments the use of synthetic solutions using deionized water was found to be unmanageable given the limited laboratory availability of high-purity 14MΩ deionized water.

P concentration was determined using the ammonium–molybdate method BS EN1189:1997 (16). A Unicam 8625 UV-vis Spectrometer was used for all of the batch experiment analyses set at a wavelength of 880 nm for P. All of the experimental solutions and analytical reagents were made using 14MΩ deionized water. The limit of detection for the analysis was determined for each set of experiments from the analysis of blanks. In the continuous flow experiments analysis of P concentration was done by ion chromatography. Although this is not the standard method and is not as accurate as the colorimetric method, a comparative study with UV–vis data showed that the percentage error of the ion chromatography was approximately 10%.

For the batch experiments 20 mm BOS aggregate was ground to a fine powder in a Tema mill (tungsten carbide) and dry sieved (BS 1377-2) to obtain a range of particle sizes. BET analysis was used to ascertain specific surface areas associated with each size fraction. A 0.050 ±0.001 g (2%) amount of the <300 μm fraction was added to each tube and respective agents added. The initial pH in batch experiments was buffered to pH7 using 0.01 M HCl and 0.01 M KOH added by micropipette until pH 7 was attained, and ionic strength was kept at 0.01 M (conductivity of 1410 μS/cm which is comparable with secondary sewage treatment works effluent (5) unless otherwise stated). pH was measured using a Jenway 3310 pH meter (accurate to ±0.01pH unit and calibrated on each occasion). In all cases batch solutions were shaken for 24 h on an orbital shaker at 150 rpm to allow the reaction to reach equilibrium. This speed was selected as it was fast enough to ensure constant mixing but not so fast as to encourage disaggregation of particles which may undesirably affect the data by increasing surface area (17). Samples were centrifuged at 6000 rpm (8040G) for 15 min to separate the solid from the liquid phase. Aliquots of the supernatant were taken and refrigerated (4 °C) for no more than 24 h prior to analysis.

Continuous flow experiments were used to assess the maximum potential removal of P by BOS with influents of 1–300 mg/L P. The 20 mm BOS size fraction was used rather than the more reactive fines (<5 mm) in the continuous flow-through experiments as its larger hydraulic conductivity made it more suitable for use in flow-through reactors. Due to their pozzolanic nature the BOS fines (<5 mm) were not used as they are known to reduce hydraulic conductivity via cementation processes (18). Initial P concentrations reflected values which may be observed in real environments such as agricultural field drainage, sewage treatment works, and effluent from dairy parlour. Two sets of saturated continuous flow column experiments were operated, each with three replicates for statistical rigor. Set A of the columns (with hydraulic residence times varying between 4 and 22 h) were run for 406 days with low influent P concentrations (1, 5, 15, 25, 50 mg/L) and Set B for 306 days (hydraulic residence time of 8 h) with high influent P concentrations (100–300 mg/L).

BOS clasts were removed from near the effluent of the Set B reactors at time 0 (24 h), 1, 5, and 12 months. The mineral precipitates formed were analyzed using XRD and E-SEM (with EDX). Thin sections of the material were analyzed using E-SEM (with EDX).

Geochemical modeling of the P attenuation in the batch experiments was performed using the PHREEQC v.2.1 (19) modeling code to calculate the saturation indices (SI) for hydroxylapatite (HAP). In addition to the Ca and O leached from the BOS, K^+, H^+, and Cl^- concentrations were calculated from the initial solution concentrations added and K^+ was used in the modeling program to charge balance the simulations.

Results and Discussion

Batch Experiments. *Effect of pH.* Figure 1a shows that the highest P removal is observed at the highest (initial and) equilibrium pH (pH 2 [5.9 mg/g] to pH 12 [9.62 mg/g]). Since P adsorption to metal oxide surfaces decreases with increasing pH (20) then it is more likely that P removal by BOS at higher pH occurred via precipitation rather than adsorption. P removal in soils is affected by many factors, but at pH 4–7.5 adsorption to metal oxide surfaces (Al and Fe oxides) (1, 21)
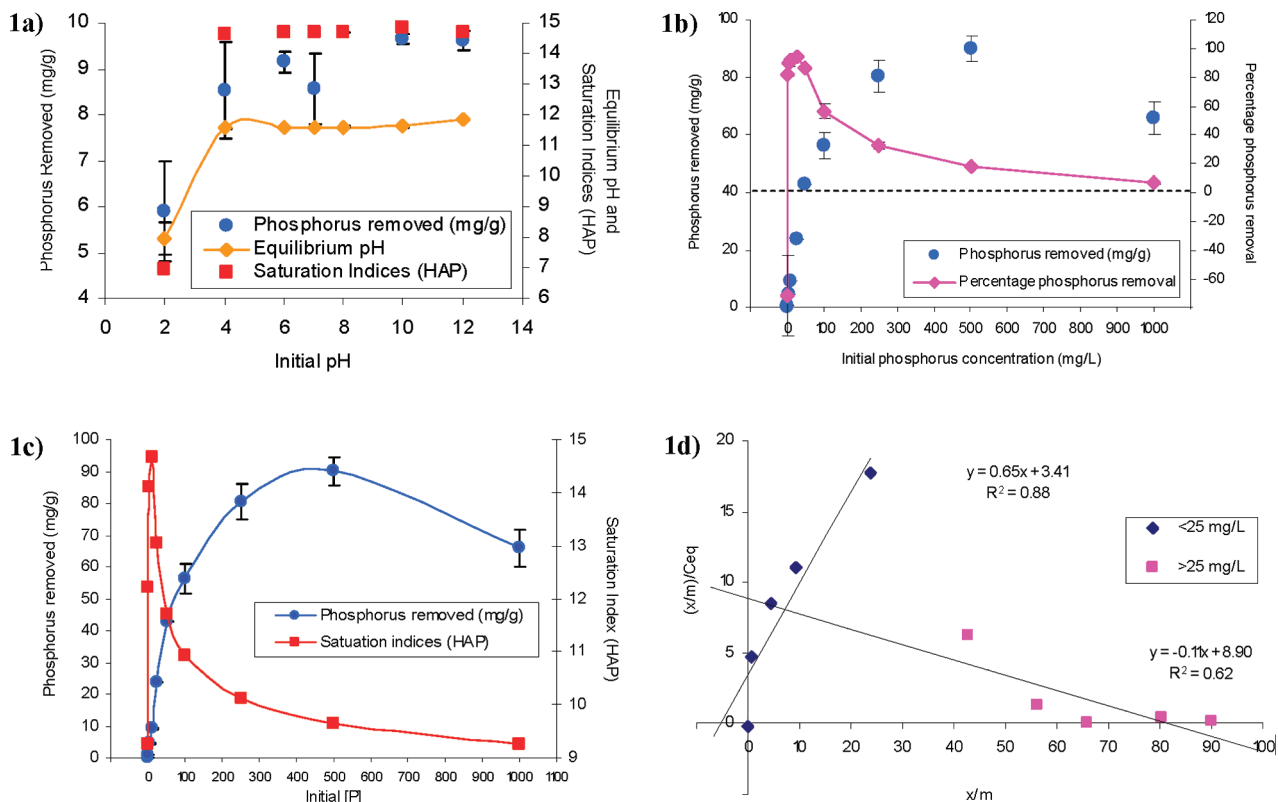
FIGURE 1. (a) Initial pH versus P removed (left ordinate) and equilibrium solution pH and calculated SIs for HAP (right ordinate). (b) Initial P concentration versus P removed (left ordinate) and percent P removal (right ordinate). (c) Initial P concentration and left ordinate P removed (left ordinate); saturation indices for HAP (right ordinate). (d) X/m (mg/L/mg/g) versus K_d (x/m/Ceq) (ordinate). The diamond points are for initial P concentration ≥ 25 mg/L and the square points for initial concentrations ≥ 50 mg/L P.

can play a major role. The potential for adsorption to metal oxide surfaces present in the BOS may therefore account for some of the P removal for solutions with pH < 7.5. The combination of elevated (initial and) equilibrium pH and increased calcium concentration in solution may encourage the precipitation of calcium phosphate minerals (5, 22, 23) onto the BOS surface. Khelifi et al. (24) and Søvik and Klove (25) state that chemical precipitation of calcium phosphate minerals will spontaneously occur and is the dominant P removal process at pH ≥ 8. It is therefore proposed that calcium phosphate precipitation is the dominant removal mechanism in the experiments presented at pH ≥ 8.

Effect of Initial Phosphorus Concentration. Figure 1b shows that initial P concentration and P removed (mg/g) are strongly positively correlated ($r = 0.93$, $p < 0.001$). The opposite relationship holds for initial P concentration and the percentage P removal ($r = -0.85$, $p < 0.004$); this correlation excludes the result from the 0.1 mg/L initial P concentration where it is likely that desorption of P (known to be present at 2−3% (P_2O_5) from XRF data) from the surface of the BOS was greater than the rate of adsorption from solution. For low initial P concentrations (1−25 mg/L) the percentage P removal rate is high (81.8−94.6%). These concentrations represent levels most likely to be encountered in the majority of real future applications.

At the highest initial P concentrations (50−1000 mg/L) the highest P removal (mg/g) was observed (89.97 mg/g) and the SI for hydroxylapatite (HAP) were strongly positive (>10.5) (Figure 1c). It is likely that P removal is primarily occurring as calcium phosphate precipitation (at pH > 7), though adsorption to any Al, Fe, or Mg oxides present in the BOS cannot be discounted at pH < 7.5 (21). The Langmuir-type isotherm provides a good fit for the data set ($r = 0.91$; $p < 0.001$), but the sorption curve rises very steeply close to the ordinate. This is representative of a H-type isotherm (Figure

1d), which suggests that inner-sphere complexes are forming (i.e., chemisorption or precipitation) (20), suggesting that chemisorptive processes, i.e., precipitation, are the predominant attenuation mechanism. Søvik and Klove (25) noted that a two-phase sorption isotherm in calcareous shell sand filter systems was a result of adsorption of phosphorus at low P concentrations and precipitation of calcium phosphate minerals at higher initial P concentrations with the adsorbed P acting as nuclei for crystal growth.

Effect of Ionic Strength. An ionic strength 0.001−1 M did not affect removal of P by BOS in the batch experiments by any significant amount (8.71−9.30 mg/g). There is no statistically significant correlation between ionic strength and phosphorus removal ($r = 0.44$; $p < 0.07$).

Effect of Clast Size. P removal decreased with increasing clast size. An anomalous result was found for the largest class size tested (2−6 mm), which had the smallest surface area ($0.7 m^2/g$) but removed a larger amount of P than all but the finest <63 μm size fraction. It is proposed that during the grinding process the most easily powdered minerals in the BOS disaggregate first, forming the finest fraction (<63 μm) with the harder minerals making up the larger size fractions (up to 2 mm). Thus, as the more reactive mineral phases (such as CaO) are also likely to be the most easily disaggregated minerals they make up the finest size fraction and therefore potential reactivity is increased, increasing P removal accordingly. However, if at the 2−6 mm size the softer minerals have not been fully separated from the harder silicate minerals (as suggested by E-SEM imaging) then this size fraction may be chemically quite reactive due to smaller sized particles being attached on clast surfaces. This suggests that sieving of unsorted fines (0−6 mm) would not be necessary to increase reactivity and efficacy if these were to be utilized in full-scale P removal treatment systems, potentially reducing the cost of implementation.
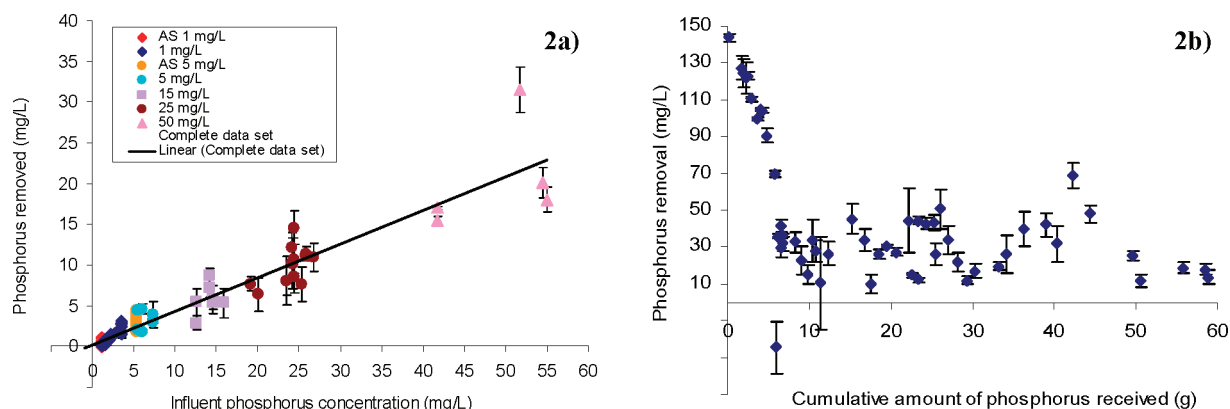
FIGURE 2. (a) Influent phosphorus concentration (mg/L) versus phosphorus removed (mg/L). (b) Mean cumulative amount of phosphorus received (g) versus mean phosphorus removal (mg/L) for Set B column reactors. Error bars are for one standard error ($n = 3$); where error bars cannot be seen the bars are smaller than the plotting symbol.

Continuous Flow Experiments. P removal by BOS in the column experiments showed a significant linear relationship with the influent P concentration ($r = 0.96$, $p < 0.001$; Figure 2a). The relationship between cumulative P received (g) versus cumulative P removed (g) is linear ($r = 0.99$, $p < 0.001$) for Set A columns (1−50 mg/L influent P); percentage P removal is 35−62% across the range of initial P concentrations for Set A continuous columns for hydraulic residence times of 8−22 h. Percentage P removal decreases with increasing initial P concentration to the columns. At the outset of the experiments for the lowest influent concentration, 1 mg/L, removal increases after 15 days, almost doubling from 32% to 62%; this may be evidence of initial adsorbed P forming nucleation sites from which precipitation and apparently more efficient P removal (as precipitation) can occur.

The relationship between the cumulative amount of P received (g) versus cumulative amount of P removed (g) for Set B columns (100−300 mg/L influent P, HRT 8 h) shows that P removal is initially very high (max 74%; mean 52%), then reducing and gradually reaching a more stable level of P removal (24%) (Figure 2b). It is proposed that the initial high P removal may be attributed to chemisorptive processes as the initial flush of easily liberated calcium is leached from the BOS. Once this initial calcium becomes unavailable due to armoring of the BOS surface by precipitates only the calcium present in the influent solution is available for reaction with P. At this stage calcium would be rate limiting, explaining the gradual decrease in P removal to stable levels. Significantly, therefore, once the BOS has facilitated the initial nucleation of P precipitation, provided there is a continuing source of calcium in the influent solution, P precipitation will continue to proceed. This was demonstrated in both sets of columns; however, the effects were clearer in the Set B columns where phosphorus was in excess due to the higher influent loading.

After 306 days of operational time Set B reactors had not reached absolute capacity for P removal: the columns in Set B had sequestered 8.39 g/kg of P. The fact that BOS does not reach breakthrough with regard to P is indicative that P attenuation is occurring as precipitation with calcium in solution (either initially, Ca leached from the BOS or ultimately, Ca contained in the influent solution).

With regard to pH evolution in the columns the mean pH of the influent solution to the column reactors was 7.20 ($n = 31$); this was raised by approximately one-half a pH unit to 7.62 ($n = 412$) at the effluent of the columns. The mean effluent pH during the first 48 h of operation was 7.90. The fact that significantly elevated pH from the BOS was not encountered is indicative that the material was reacting rapidly with the influent P solution. Indeed, Khelifi et al. (*24*)

suggest that at pH ≈ 8 precipitation of HAP will occur if there is sufficient calcium and phosphorus in solution.

Mineralogy. White precipitates were clearly identifiable on the surface of the BOS clasts after approximately 60 days. Samples of BOS taken from Set B reactors were analyzed using E-SEM (with EDX) and XRD. Figure 3 shows the time series of data for these samples. Phases present at 0 months (24 h) are calcite, aragonite, and portlandite, all associated with the hydrolysis and atmospheric carbonization of BOS (*26*). Subsequent formation of a series of different calcium phosphate minerals has been recognized by a number of authors, typically occurring after 3−6 months (*27, 28*), but importantly none (to the authors' knowledge) have recognized this succession on coproducts such as BOS. Both the E-SEM images and the XRD information presented show that there is a succession of calcium phosphate minerals forming on the BOS surface in the continuous flow columns. The sequence of calcium phosphate mineral precipitation progresses from the most soluble, brushite, to the least soluble, final end-member phase, HAP. Calcite is identified in all of the samples, which is significant as calcite has been recognized to provide sorption sites for P leading to nucleation and precipitation of calcium phosphates (*4, 29, 30*). If calcite is coprecipitating with calcium phosphate minerals on the BOS surface this may be significant for the continued successful operation of the treatment system (i.e., system longevity). If the nucleation sites for calcium phosphate precipitation are being continually replenished then removal of P from solution will continue as long as there is available calcium and P in solution. The limiting factor to calcium phosphate removal will therefore be whether there is sufficient permeability and interclastic porosity in the system for precipitates to form without the hydraulic conductivity of the system decreasing.

BOS clasts were observed to expansively crack at various points in the operation of the systems. Expansion of free lime in the BOS and thus the 'time release' of calcium at various points may be significant for removal of P from solution as calcium phosphates. This is an advantage for phosphorus removal using BOS against materials which have no free lime component. A cross-section through a BOS clast which had cracked and released free lime clearly shows a ∼250 μm thick surface crust of mineral precipitate (containing Ca and P); the minerals octa-calcium phosphate (OCP) and HAP were identified by XRD and EDX (Figure 3). Thin sections were made in order to ascertain whether any phosphorus had diffused toward the center of the BOS clast. The data suggested that the crust of calcium phosphate is forming only on the surface of the BOS. Figure 4 shows points where EDX data was obtained from the crust. Points 1 represent Ca
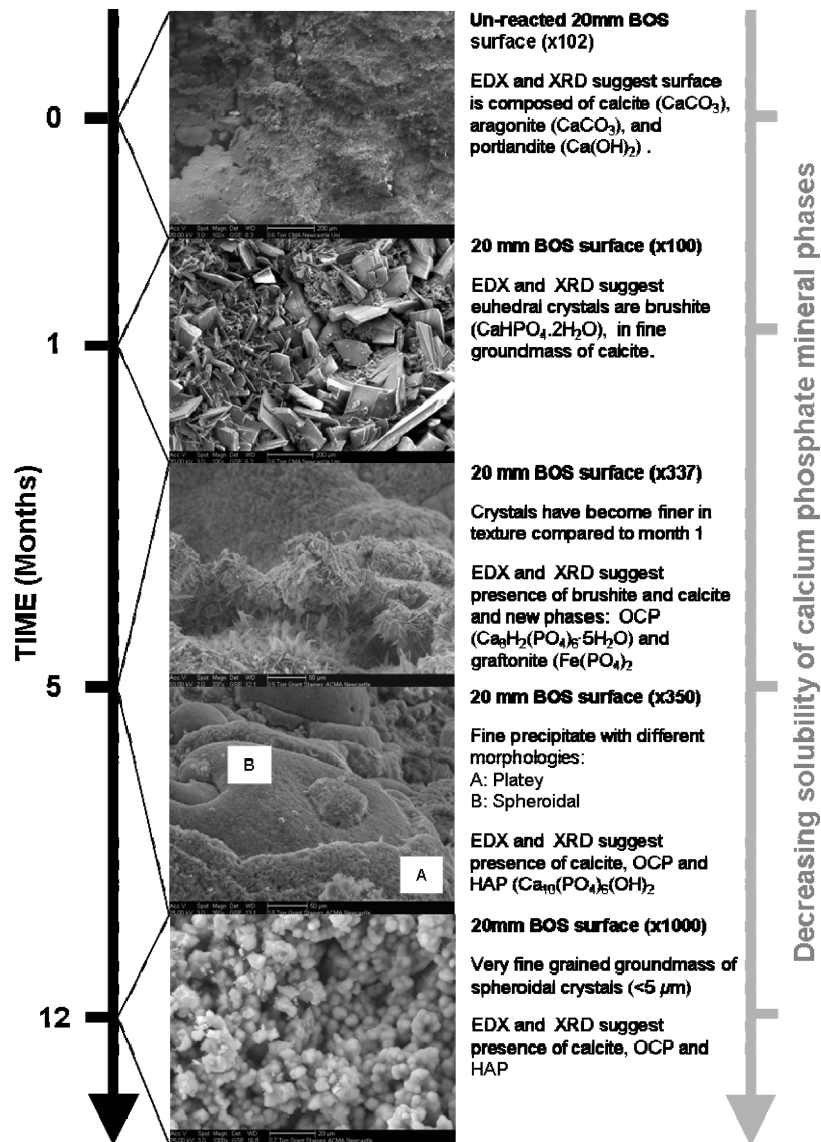
FIGURE 3. Time series of E-SEM images showing mineral phases present at a number of time intervals from Set B columns. XRD data for mineral phases is also presented. Note different magnifications of images.
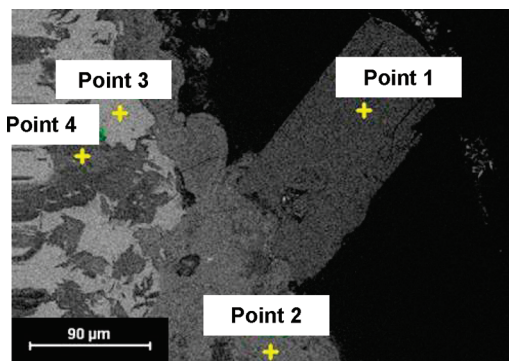

FIGURE 4. Back-scatter electron E-SEM image of a thin section of BOS reacted for 12 months. EDX showed elemental composition of the euhedral crystal to be calcium and phosphorus. The dark area is the glass slide.

and P, and Points 3 and 4 represent Ca and Si with no P. Point 2 comprises Ca and no P or Si, which suggests calcite. Notably, the five-month sample (Figure 3) showed the presence of graftonite ($Fe(PO_4)_2$) on the BOS surface, which is significant as this mineral precipitates under more acidic conditions (pH < 7) (*31*), which are less favorable for calcium phosphate precipitation (*24*). Iron bound in the BOS may precipitate with P or act as an adsorption surface (*31*). Therefore, graftonite precipitation cannot be dismissed as a removal mechanism.

Environmental Implications. The continuous flow column reactors were subjected to both tap water desorption tests and SPLP (pH 4.20) and TCLP (pH 2.88) leaching tests. The tap water leach resulted in <0.1 mg/L P in the effluent. SPLP and TCLP led to higher P concentrations, 86 and 564 mg/L, respectively. However, in both the SPLP and TCLP leachates no potentially toxic elements specified by the leaching test protocols are released. This differs from work carried out by Hedström and Rastas (*32*), where they comment that the risk of sulfuric compounds leaching from their (blast furnace) slag beds is considerable. However, there is no sulfur present in the BOS used in this work. The conclusive evidence for the sequential series of increasingly stable P mineral phases forming on the BOS surface (octa-calcium phosphate, brushite, and HAP) suggests that BOS may be successfully used as a long-term removal mechanism for P.

Acknowledgments

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