

# Phosphorus Saturation Potential: A Parameter for Estimating the Longevity of Constructed Wetland Systems

ALEKSANDRA DRIZO,\* YVES COMEAU,  
CHRISTIANE FORGET, AND  
ROBERT P. CHAPUIS

*Department of Civil, Geological and Mining Engineering,  
Ecole Polytechnique of Montreal, P.O. Box 6079,  
Station Centre-ville, Montreal, Quebec, Canada H3C 3A7*

Phosphorus (P) adsorption capacities of materials derived from batch experiments can vary by several orders of magnitude depending on the method used, leading to potential misinterpretation of the P retention capacity on a long-term basis and unrealistic estimations of constructed wetland systems (CWS) longevity. The objective of this study was to determine if the P saturation of the material in a column could be used for this purpose with an improved accuracy. A 278-d column experiment with a synthetic P solution was conducted to investigate the long-term P retention capacity of electric arc furnace (EAF) steel slag up to its P saturation point. EAF slag showed a high affinity for P, reaching a saturation value of 1.35 g of P kg<sup>-1</sup>. Investigations of the regeneration of the P adsorbing capacity by this material showed that, after 4 weeks of water desaturated resting, EAF steel slag was able to increase its initial P adsorptive capacity to 2.35 g of P kg<sup>-1</sup>. A sequential P fractionation experiment was performed to quantify the proportion of P bound to mineral compounds in EAF. From the most loosely bound to the most strongly bound P fraction, P was associated with resin extractable (14%), Fe extractable (0.5 M Na<sub>2</sub>CO<sub>3</sub>, 47%), Al extractable (0.1 M NaOH, 1%), Ca extractable (1 M HCl, 12%), and Ca in a stable residual pool (concentrated hot HCl, 26.5%). X-ray fluorescence analyses of EAF steel slag chemical composition revealed that the continuous application of a P solution resulted in 75% and 59% increases in K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub>, respectively; Al<sub>2</sub>O<sub>3</sub> and FeO increased by 8%, while the portion of CaO remained unchanged. The investigated properties (P retention potential, regeneration of P adsorption, P fractionation) provide useful data about the suitability of slag material as a media for long-term P removal and should enable an improved prediction of the longevity of full-scale CWS.

## Introduction

The importance of substratum adsorption for phosphorus (P) removal by constructed wetland systems (CWS) has been recognized for more than 1 decade (1, 2). Adsorption and/or precipitation of P by a substrate in a CWS is a finite process; once the material becomes saturated, it will have to be either

washed or, more probably, replaced (3–7). Therefore, the P adsorption capacity of a material represents a central parameter for comparing and selecting candidate materials to be used as P removal media in CWS (3, 5, 8). However, while the knowledge of P adsorption capacity of the material can be used to estimate the maximum amount of P that can be taken and/or removed from a given wastewater, it cannot provide an accurate estimation of the longevity of a wastewater treatment system. The longevity of the material to be used as a medium in CWS is an important parameter for practical applications (5–8). It is restricted by the P saturation potential of the material as well as the feeding regime, hydraulic retention time (HRT), and influent P concentrations as the dominant factors (6).

**Previous Studies.** Many studies have been conducted to investigate the potential of various materials to remove P from wastewater. Gravel, fly ash, and blast furnace slag were studied in Australia (11); light expanded clay aggregates (LECA) were tested in Scandinavia (12–14) and Scotland (8); half-burnt dolomite and laterite were investigated in France and Ireland (15, 16); shale, bauxite, fly ash, burnt oil shale, limestone, and zeolite were also studied in Scotland (6, 8); and the potential of slag was further investigated in Japan (17), Australia (5, 18), Canada (19), and Europe (7, 20). More recently, the efficiency of wollastonite was studied in the United States (21) while several Danish sands, calcite, marble, vermiculite, and LECA were tested in Denmark (22). In Quebec, 57 materials were compared for their affinity to adsorb phosphorus, and it was found that electric arc furnace (EAF) steel slag had a high potential for P removal (10). The first criteria in selecting materials, tested in most of the above studies, were their chemical and physical properties such as Fe, Al, and Ca content; specific surface area; porosity; particle size distribution; and hydraulic conductivity because they all affect the rate of P adsorption and/or the P adsorption capacity (3, 5, 8, 14). The P adsorption capacity of candidate materials was then measured in the laboratory employing “pseudo-equilibrium” batch experiments, a technique established as a method of measuring P retention characteristics of soils and sediments for several decades (23–25). The P adsorption capacity of materials was estimated by fitting the Langmuir or Freundlich isotherm equations to experimental data (11, 14, 18, 8). However, it has been shown recently that using the Langmuir equation with such experimental data can lead to biased and unrealistic estimates of the adsorption parameters and should be used with caution for P adsorption studies for CWS applications (9, 10). A need for establishing a new procedure for P batch experiments that would provide a more realistic comparison of the materials was recognized, and several criteria for this purpose were suggested (9, 10). In addition, it was recommended that P batch experiments should be coupled with a longer-term investigation of materials performance in columns for the estimation of P removal efficiencies and retention capacities by different materials.

The availability of data on the long-term performance of different materials in columns is limited (5, 7, 8, 13, 19, 21). Moreover, the P saturation potential of the material (the point at which all of the available sites are saturated with P) was reported in only one study (8). This parameter is important because it enables us to estimate the duration of a full-scale system, if a specific material is going to be used in a field application (6, 8). When planning the design and construction of a wetland system to obtain efficient and cost-effective P removal, the longevity of the system is one of the major questions to address by the designer. Data from a long-term

\* Corresponding author e-mail: aleksandra.drizo@courriel.polymtl.ca.

**TABLE 1. Chemical Composition of Electric Arc Furnace (EAF) Steel Slag**

element	EAF (% g/g)	element	EAF (% g/g)
Fe	24.3	Mn	1.01
Ca	21.7	Cr	0.22
Mg	7.89	P	0.14
Si	6.43	Na	0.044
Al	2.47	K	0.014
Ti	2.47		

test, until it reaches P saturation, should provide a better estimate than batch tests of the long-term efficiency of the material.

In this paper, the short-term P adsorption capacity of EAF steel slag is first determined in batch experiments, according to a procedure suggested in a previous study (9, 10). Then, a long-term column study was conducted to investigate the long-term P retention capacity of EAF steel slag up to the P saturation potential of the material. The potential for regeneration of the P adsorptive sites with the same material was tested by using a water-desaturated resting period. The mineralogical composition of EAF slag samples before and after continuous P solution application was examined by X-ray fluorescence spectrometric analyses. Finally, P fractionation was conducted to quantify the amount of P bound to mineral compounds in EAF steel slag. The investigated properties provided useful data about the suitability of slag material as a media in CWS for long-term P removal and the prediction of the longevity of the full-scale design.

## Materials and Methods

**Materials.** The material used in this study was electric arc furnace (EAF) steel slag, a byproduct of steel production. During the steel-making process, a combination of iron ore and steel scrap are melted in an electric arc furnace along with fluxing agents (mainly lime) and the molten impurities from the selected scrap (26, 27). After the material has been cooled and solidified, the metallic component is removed and fed back to the steel mill, while the nonmetallic part is sized and crushed (26). The EAF steel slag used in this experiment was screened between 2.5 and 10 mm and was obtained from Ispat Sidbec, Tracy. This company produces approximately 1.5 million ton of steel annually, of which slag represents 17% of the total production in Quebec (Piché, personal communication). The elemental composition of the material is presented in Table 1.

**Chemical and Physical Properties (Elemental Composition, Hydraulic Conductivity, Porosity, and Particle Size Distribution) of EAF Slag.** Elemental composition analysis of EAF slag was carried out with atomic absorption spectrometry using a standard digestion method (28). Hydraulic conductivity was measured according to the ASTM D 2434-68 Method using a constant head parameter (0.40 m height). The hydraulic conductivity was calculated using Darcy's law (8).

The porosity was calculated from the specific gravity of material ( $G_s$ ) and volume of each layer of material packed in the column (29). Particle size distribution was determined by sieving the material through five different mesh sizes (ranging from 0.08 to 25 mm), drying at 105 °C, and subsequent weighing. A detailed particle size distribution of EAF steel slag was determined in a previous study by sieving of the material through eight (instead of five as in this study) different mesh sizes (ranging from 0.08 to 25 mm), drying at 105 °C, and subsequent weighing (39).

**Maximum P Adsorption Capacity.** The maximum phosphate adsorption capacity was determined using a slightly

modified batch equilibrium technique (8, 9) as described below. Nine P solutions, ranging from 1 to 320 mg of P L<sup>-1</sup> (1, 2.5, 5, 10, 20, 40, 80, 160, and 320 mg of P L<sup>-1</sup>, using KH<sub>2</sub>PO<sub>4</sub> as P source) were tested. This wide range of P concentrations was chosen to study the variability in P adsorption capacity values and its dependence on the initial P concentration. Each test used 35 g of EAF slag in 1-L glass Erlenmeyer flasks containing 700 mL of a P solution (KH<sub>2</sub>PO<sub>4</sub> in distilled water) giving a material:solution volume ratio of 1:20.

The mixture was continuously shaken (175 rpm) on a 25-mm sway gyratory shaker for 24 h at room temperature (24 °C). The previous investigations showed that for a range of rotational speeds between 160 and 200 rpm, 175 rpm was the one that ensured sufficient mass transfer between the particles and the solution while ensuring minimal particle abrasion (39).

All experiments were conducted in triplicates. Orthophosphate-P was determined using the ascorbic acid method (30). P adsorption capacities were calculated from the difference between the initial P concentration added to the solution and the P concentration in the supernatant, using the nonlinear form of the Langmuir equation (8, 24):

$$P_a = abC/(1 + aC) \quad (1)$$

where  $C$  is the concentration of P in the solution at equilibrium (mg of P L<sup>-1</sup>),  $P_a$  is the amount of P adsorbed per unit mass of material (mg of P g<sup>-1</sup>),  $a$  is the constant related to the binding strength of P onto the material, and  $b$  is the maximum P adsorption capacity (mg P g<sup>-1</sup>).

**Phosphorus Saturation Potential for EAF Slag.** Perspex column (i.d.: 10.3 cm, height: 15 cm) was packed with 2.35 kg of air-dried EAF steel slag in six layers (1.8–2.5 cm height each), resulting in a porosity ( $n$ ) of 45% and a pore volume of 0.6 L. The column was closed on both sides with porous plates, and valves were attached to control the supply and discharge of the phosphorus solution. A synthetic solution containing 350–400 mg of P L<sup>-1</sup> (as KH<sub>2</sub>PO<sub>4</sub>) was prepared twice a week, and the column was gravity fed continuously at a flow rate of 1.73 L d<sup>-1</sup>, keeping the material saturated throughout the testing period. The average contact time (pore volume retention time, HRTp) between the solution and the material was 8.3 h (0.34 d). This relatively high feeding regime was chosen to investigate the capacity of EAF steel slag to retain P under high hydraulic loading conditions and to minimize precipitation processes, as it has been observed previously that deposition of Ca-P precipitates on the EAF slag surfaces did not occur to a significant extent at HRTp smaller than 12 h (39, 40). Samples of the influent and effluent were taken every third day and analyzed for P concentration, using the vanadomolybdophosphoric acid colorimetric method (30). pH and redox potential ( $E_h$ ) were also measured by standard techniques (28) using a conventional glass electrode, a calomel reference electrode, and a platinum electrode.

**Regeneration of Phosphorus Adsorption Sites.** After the P saturation point of EAF slag was reached, the solution was drained from the column, and the material was left to rest for a period of 4 weeks. This was done to test the possibility of regeneration of P adsorptive sites. Feeding of the column resumed employing the same feeding regime as described above (350–400 mg of P L<sup>-1</sup>; 0.34 d HRTp). Similar to the previous experiment, samples of the influent and effluent were taken every third day and analyzed for P concentration.

**X-ray Fluorescence and P Fractionation.** After reaching the regenerated P saturation level, the column was drained, and EAF slag was placed in the oven (105 °C) to dry overnight. Three samples of treated and untreated material were analyzed by X-ray fluorescence. Analyses were carried out in

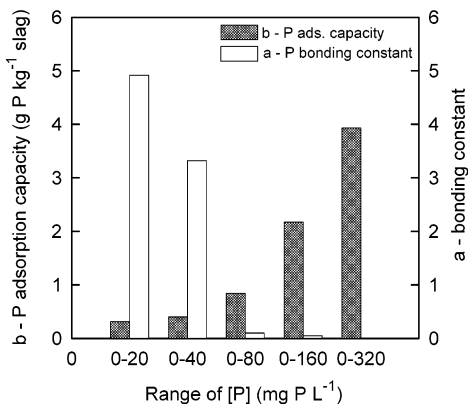


FIGURE 1. Effect of range of P concentration on maximum P adsorption capacity (b) and bonding capacity (a) of EAF steel slag.

the Dofasco Chemical analyses laboratory (Hamilton, Ontario) using a sequential X-ray spectrometer (Philips PW2400). Five samples of the material were taken for phosphorus fractionation analyses (31). A sequence of five extractions were conducted, each lasting 16 h: (i) an anion-exchange resin strip (SB-6407 Gelman Sciences, Inc.) in deionized water, (ii) 0.5 M NaHCO<sub>3</sub>, (iii) 0.1 M NaOH, (iv) 1 M HCl, and (v) concentrated HCl. Bicarbonate and hydroxide extractable phosphorus represented Fe- and Al-associated P fractions, 1 M HCl extract is defined as Ca-associated P, while the concentrated HCl extract represented the Ca-associated P in the stable residual pools (31).

## Results

**Chemical and Physical Properties (Elemental Composition, Hydraulic Conductivity, and Particle Size Distribution) of EAF Slag.** The analyses showed that 46% (w/w) of the EAF slag consisted of Fe (24.3%) and Ca (21.7%). Of other elements, Mg and Si represented 7.9 and 6.4% (w/w), respectively (Table 1). The saturated hydraulic conductivity ( $k$ ) was  $5 \times 10^{-3}$  m s<sup>-1</sup>, which is in the range of granular materials recommended for use in CWS (8). Particle size analyses showed that the largest fraction (78%) of EAF slag particles was between 5 and 10 mm. Particle sizes larger than 10 mm represented only 3%, between 2.5 and 5 mm represented 17%, and smaller than 2.5 mm represented 2%. This was in agreement with results reported in the previous study (39).

**Maximum P Adsorption Capacity.** P adsorption data were plotted according to the nonlinear Langmuir equation, and P adsorption maxima  $b$  and bonding capacities  $a$  were determined for each set of initial P concentrations. Depending on the range of concentrations applied, the P adsorption maximum of EAF steel slag increased 13 times (from 0.31 to 3.93 mg of P g<sup>-1</sup>) while the bonding capacity decreased 830 times (from 4.96 to 0.01) in magnitude, respectively. These results demonstrated variabilities that could occur if CWS longevity is estimated from the P adsorption maxima values derived from batch experiments. The greatest mean P adsorption in EAF steel slag (3.93 mg of P g<sup>-1</sup>) was obtained when the highest ( $C_i = 1-320$  mg of P L<sup>-1</sup>) initial P concentration was considered (Figure 1).

**Phosphorus Saturation Potential for EAF Slag.** In the long-term column test, a P saturation level of the material was reached after 124 d of continuous P solution application (Figure 2a). During this time, 360 pore volumes were passed through the EAF slag column, resulting in a total of 75.2 g of P added. The total output from the column was 72.0 g of P, giving a saturation value of 1.35 g of P kg<sup>-1</sup> (Figure 2a). The pH of the initial solution varied between 8.5 and 9.0, while the pH of the effluent was higher, ranging from 9.9 to 10.5.

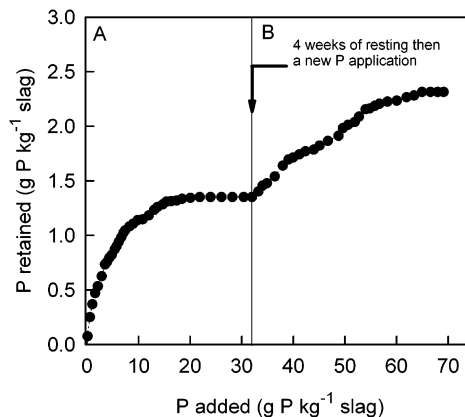


FIGURE 2. Saturation (A) and regeneration (B) of EAF steel slag. Phosphorus concentration =  $375 \pm 25$  mg of P L<sup>-1</sup>; pore volumetric hydraulic retention time (HRT<sub>p</sub>) = 0.34 d.

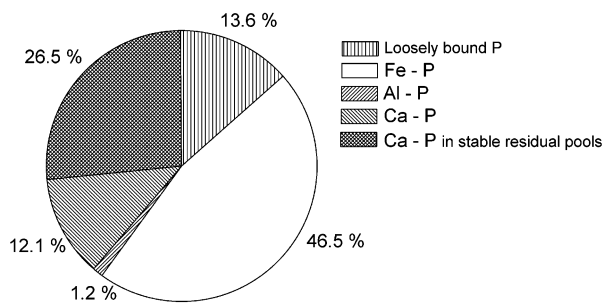


FIGURE 3. P fractionation experiment showing the proportions of loosely bound P and P bound to Fe, Al, and Ca compounds in EAF steel slag after 278 d of P solution application.

$E_h$  of the initial solution ranged from 150 to 220 mV, while  $E_h$  of the effluent was slightly higher and ranged from 180 to 240 mV.

**Regeneration of Phosphorus Retention Sites.** This column test experiment demonstrated that a resting period of 4 weeks resulted in the regeneration of the P retention sites within EAF steel slag material. Over the following 124 d, 74% of the initial P retention capacity of EAF slag was regained, increasing the P saturation potential of the material 1.75-fold, from 1.35 to 2.35 g of P kg<sup>-1</sup> (Figure 2b). During this period of investigation, 360 pore volumes of liquid were passed through the EAF slag column, adding 77.4 g of P (33 g of P (kg of slag)<sup>-1</sup>). Since the beginning of the experiment, a total of 152.6 g of P was added to the EAF slag column (64.9 g of P kg<sup>-1</sup>) before reaching the regenerated saturation of 2.35 g of P kg<sup>-1</sup> (Figure 2b). The pH of the initial solution varied between 8.7 and 9.0, while the pH of the effluent was a little lower than in the first part of the experiment, ranging from 9.6 to 10.0.  $E_h$  of the initial solution ranged from 175 to 220 mV, while  $E_h$  of the effluent was slightly lower and ranged from 160 to 210 mV.

**X-ray Fluorescence and P Fractionation.** The results revealed that the largest amount of extracted P was bound to Fe (46.5%), followed by Ca-associated P (1 M HCl extract and hot concentrated HCl extract) representing 12.3 and 26.5%, respectively (Figure 3). The composition of EAF steel slag before and after the testing, measured by XRF fluorescence analyses, is presented in Table 2. The continuous application of a synthetic P solution (as KH<sub>2</sub>PO<sub>4</sub>) over a period of 248 d along with a 30 d resting period resulted in 75% and 59% increases in K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub> content, respectively. Al<sub>2</sub>O<sub>3</sub> increased by 8.2% and FeO increased by 7.6%, while CaO value remained the same as before the testing. Contrary to all other oxides, the amount of MnO decreased by 56%.

**TABLE 2. X-ray Fluorescence Analyses of EAF Steel Slag ( $n = 3$ )**

composition	before treatment (%)	after treatment (278 d) (%)
CaO	33.2 ( $\pm$ 2.2)	33.1 ( $\pm$ 0.7)
FeO	30.2 ( $\pm$ 1.2)	32.5 ( $\pm$ 1.2)
SiO <sub>2</sub>	15.8 ( $\pm$ 0.4)	15.2 ( $\pm$ 0.4)
MgO	10.4 ( $\pm$ 1.0)	10.4 ( $\pm$ 1.3)
Al <sub>2</sub> O <sub>3</sub>	4.5 ( $\pm$ 0.4)	4.9 ( $\pm$ 0.1)
MnO	3.2 ( $\pm$ 0.5)	1.4 ( $\pm$ 0.1)
TiO <sub>2</sub>	0.8 ( $\pm$ 0.04)	0.9 ( $\pm$ 0.02)
P <sub>2</sub> O <sub>5</sub>	0.3 ( $\pm$ 0.03)	0.8 ( $\pm$ 0.04)
S	0.04 ( $\pm$ 0.003)	0.04 ( $\pm$ 0.004)
K <sub>2</sub> O	0.02 ( $\pm$ 0.001)	0.08 ( $\pm$ 0.005)

## Discussion

**Phosphate Adsorption Capacity and Saturation Potential for EAF Steel Slag.** Factors affecting the “maximum” P adsorption capacities of materials in batch studies that were studied earlier are the nature of the material used, the period and temperature of contact between material and solution; the solution:material ratio (24, 9), the type and concentration of the supporting electrolyte, the moisture content of the material prior to shaking, and the range of the initial P concentrations used (24, 9). Apart from these factors, the geometry of mixing (volume of material suspension to headspace volume in the equilibration vessel), type, and extent of solid/solution separation after equilibration (25) and the rotational speed of the shaker were also tested (9). Among these factors, the range of the initial P concentrations applied causes one of the greatest variability.

Although it has been reported that the maximum P adsorption capacity of the filter media may be underestimated when using sorption isotherms (45) when calculated from observations at low concentrations, the maximum P adsorption capacity is often exceeded when higher P solution concentrations are used (24). Our batch experiment confirmed the latter pattern as the highest initial P concentration employed (0–320 mg of P L<sup>-1</sup>) resulted in a 13 times increase in maximum P adsorption capacity of EAF steel slag (from 0.31 to 3.93 mg of P g<sup>-1</sup>) (Figure 1). Estimating the potential longevity of slag-based CWS from batch experiments data would suggest a 13 times overestimation of the potential longevity when considering 0–320 mg of P L<sup>-1</sup> experiment. Another example of the risk of overestimation was shown in an Australian study (18) in which phosphate adsorption characteristics of soils, slags, and zeolites were investigated using the initial P solution concentration ranging from 0 to 10 000 mg of P L<sup>-1</sup> to conclude that blast furnace (BF) slag had the highest P adsorption capacity (44 g of P kg<sup>-1</sup>). Despite the extremely high initial P solution concentrations employed in their experiment, the phosphorus saturation time of several materials was estimated. It was concluded that, for secondary treated domestic sewage effluent, BF slag-based wetlands would have a lifetime of 60 yr. If P concentrations more typical for municipal wastewater (20 mg of P L<sup>-1</sup>) been used, the P adsorption capacity would have been smaller and would have predicted longevity for the same wetland of only a few years.

While P batch experiments can be useful to select and compare available materials for their suitability as substrates in CWS, the longevity of a full-scale system should more reliably be evaluated from a P saturation value derived from a long-term column study (6–8) for which the P concentration to be used should be properly chosen. P removal by various blast furnace slag, crystalline slag, and slag/sand mixtures was investigated in a column study over a period of 13 months (7). However, even though the P concentration in the feeding solution was representative of a medium strength domestic wastewater (10 mg of P L<sup>-1</sup>), the duration was not sufficient

for the material saturation to occur, and the longevity of the full-scale system could not be estimated. Similarly, another column study was conducted to investigate P removal by various sands (22). However, because of time constraints, the experiment was terminated after only 12 weeks, before any of the materials had sufficient time to reach P saturation. Again, the longevity of a full-scale system could not be reliably estimated (22). The duration of the experiment was also a constraint in a third column experiment that investigated the P saturation potential of shale and bauxite (8). Therefore, after 6 weeks of exposure of the materials to the solution containing 35–42 mg of P L<sup>-1</sup>, the P loading rate was increased 4-fold (by increasing the initial concentration and flow rate), which resulted in P saturation of the investigated materials being reached within the following 6 weeks. Given the P sorption values reported in the literature for slag as high as 2 kg of P (m of slag)<sup>-3</sup> (5, 7) and considering results from previous experiments (10), the P saturation value of EAF steel slag was expected to be between 1.0 and 1.5 g of P (kg of slag)<sup>-1</sup>. Because of the high affinity of slag for P, we decided to employ a high feeding regime in our experiment (375  $\pm$  25 mg of P L<sup>-1</sup>; HRT = 0.34 d) to reduce the duration of the column experiments. This resulted in the P saturation potential being reached after 17 weeks, during which time 1.35 g of P kg<sup>-1</sup> was retained by EAF steel slag. Had we employed a lower feeding regime, the experiment would have taken much longer to complete. When the objective is to determine the P saturation value of material to estimate longevity of the full-scale system, a high feeding regime can hardly be avoided despite not being representative of a real field situation.

The P saturation potential of the material obtained from column studies is more realistic than the maximum P adsorption capacities determined from batch experiments using high P concentrations (0–320 or 0–10000 mg of P L<sup>-1</sup>; 14, 18). An excessive rotational speed of the shaker employed in the P batch experiments can break particles increasing the specific surface area and lead to an overestimation of the amount of P adsorbed by the material (9). In a column study, the material remains intact inside the column, providing a more even distribution and sufficient contact with the feeding solution, with the sites available for P retention becoming saturated more gradually. However, once the material reaches its P saturation value, it will no longer be able to retain any P from the feeding solution for given operating conditions (Figure 2). Because of the time constraints for such experiments and based on previous investigations (8), we suggest feeding concentrations from 40 to 400 mg of P L<sup>-1</sup>, depending on the material's affinity to retain P. If this range of concentrations is employed, the P saturation point of a material could be determined within 3–5 months.

**Regeneration of Phosphorus Retention Sites.** More than 2 decades ago, it was observed that soils which had been successively treated with a P solution regained their capacity to adsorb P after drying and wetting cycles (32). Since then, only a few authors mentioned P regeneration as one of the mechanisms contributing to P removal via wetland substrates (33, 34). In a recent review of the development of CWS in Europe, it was stated that general design guidelines for P removal have not yet been developed (35). Multistage systems, consisting of several cells laid out in parallel or in series, have been suggested by several authors, mainly to prevent or solve problems with hydraulic design and short-circuiting experienced previously (6, 34, 36). For P removal, two or more parallel cells could, in theory, prolong the longevity of the system. Our experiment demonstrated that a resting period of 4 weeks was sufficient for EAF steel slag to regain 74% of its P retention capacity. Currently, there is no clear explanation about the mechanisms involved in P retention regeneration although the rejuvenation of P

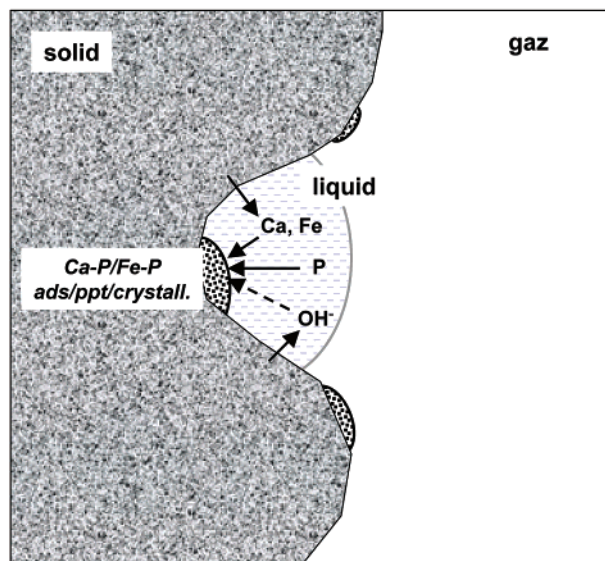


FIGURE 4. Proposed mechanism to explain regeneration of P saturation potential by adsorption/precipitation/crystallization in calcium, iron, and hydroxyl ions supersaturated pools.

exchange sites was mentioned by two other authors (33, 34). It is suggested that draining of material results in elevated pH bringing Ca, Fe and other mineral surfaces and ions (via diffusion) in supersaturation with the EAF slag solution occupying the pores creating new sites for P adsorption/precipitation/crystallization (Figure 4). The redox potential ( $E_h$ ) of the effluent varied between 180 and 240 mV during the first 124 d of the experimentation and then decreased to 160 mV after the resting period of 30 d, varying between 165 and 210 mV over the following 124 d of investigation. A decrease in redox potential might have caused an increase in P adsorption capacity because of transformation of crystalline Fe and Al minerals to amorphous forms, which have a greater surface area and more sorption sites due to their larger number of singly coordinated surface hydroxyl ions (8). However, the exact principles of P retention regeneration phenomenon remain uncertain and should be investigated in future studies.

**Life Expectancy of an EAF Slag-Based System.** Results from this study provide data for the theoretical estimation of the life expectancy of an EAF steel slag system on the basis of P removal capacity. The longevity of any system will depend on the type of wastewater to be treated. Assuming that the P removal potential at low feeding rate is going to be similar to that obtained at a high feeding regime, we can estimate the longevity of the systems as follows: for municipal wastewaters, a total of 2.3 g of P per population equivalent (PE) (40% excreted from humans and 60% from cleaning compounds) is discharged per person per day (37). The life expectancy of a shale (P saturation reached at 0.73 g of P  $\text{kg}^{-1}$ ) based system was estimated to be 7–20 yr, depending on the CWS design guidances (5  $\text{m}^2$  PE, depth 0.6, or 10  $\text{m}^2$  PE, depth 0.9 m) (8). In the current experiment, P saturation of EAF steel slag was 1.85-fold higher (1.35 g of P  $\text{kg}^{-1}$ ) than for shale, suggesting that the life expectancy of a full-scale system would increase to 13–37 yr.

Phosphorus retention, under the conditions studied, took place much more by adsorption than by precipitation. Even though we cannot exclude the possibility of the occurrence of concurrent adsorption and precipitation, evidence from previous experiments carried out in our laboratory (38–41) and literature data (42–44) suggest that the value of 1.35 g of P  $\text{kg}^{-1}$  should mainly represent P retention via adsorption processes. It has been reported (42–44) that generally, in

solutions containing Ca and P, a number of Ca-P phases may form depending on the solution composition (pH,  $\text{PO}_4$  concentration, supersaturation index). At pH values between 7 and 9, amorphous calcium phosphates (ACPs) are thought to be converted to an octacalcium phosphate (OCP) precursor phase to thermodynamically more stable hydroxyapatite (HAP). Under more alkaline conditions (pH > 9.3), the rapid hydrolysis of OCP to HAP makes it difficult to detect the OCP precursor phase, and the conversion from ACPs to HAP appears to take place directly without intermediates (43, 44).

In our experimental setup, both the feeding solution reservoir and the column were sealed, minimizing the interference with the atmospheric  $\text{CO}_2$  that could lead to  $\text{CaCO}_3$  formation. The pH of the effluent ranged from 9.5 to 10.5 (from 9.9 to 10.5 for the first 124 d, decreasing to 9.5 after the period of resting of 30 d, and reaching 10.3 at the end of experimental period for another 124 d), which is in the range of the pH values suggesting direct formation of HAP (39, 42–44). If HAP formation had occurred, it would be visible as a white deposit on the slag surfaces and detectable by XRF analyses, as demonstrated in previous studies conducted on the same material at higher HRT (0.5 and 1 d) and both lower (20 and 80 mg of P  $\text{L}^{-1}$ ) and higher (400 mg of P  $\text{L}^{-1}$ ) P concentrations (38, 39). At the low hydraulic retention time (HRT<sub>p</sub> of 0.34 d) used, chances of forming Ca-P deposits on the EAF steel slag surfaces would be even smaller, further minimizing precipitation processes. This was confirmed both by X-ray fluorescence and by P fractionation analyses. Unlike in the studies conducted at higher retention times (HRT<sub>p</sub> > 0.5 d), no macroscopic deposition was visually observed on the EAF steel slag surfaces, nor was there a change in CaO composition (Table 2). The P fractionation experiment showed that the highest proportion (46.5%) of retained P was bound to Fe with Ca-P representing only 13.6%. The remaining 26.5% of Ca bound fraction was present in a stable residual pool (Ca-SRP). P fractionation analyses carried out in a separate experiment conducted at higher HRT<sub>p</sub> (1 d) and fed with a lower initial P concentration (85 ± 5 mg of P  $\text{L}^{-1}$ ) for 5 months and then at a higher P concentration (375 ± 25 mg of P  $\text{L}^{-1}$ ) for 1 month showed that Ca-P deposition represented the highest proportion (49.8%) of retained P. Ca-SRP was also high (31.8%) while Fe-P bound fraction represented only 8.4% (38).

In addition, the P batch experiments carried out at different contact times, ranging from 0 to 100 h, and different P concentrations showed that P isotherms at both lower (0–20 mg of P  $\text{L}^{-1}$ ) and higher (0–80 mg of P  $\text{L}^{-1}$ ) concentrations had a similar shape, with P concentrations decreasing rapidly (suggesting adsorption processes) between 0 and 30 h and then leveling up, reaching a sorption equilibrium between 50 and 100 h (39, 41). Therefore, on the basis of evidence from the literature, on the investigations on EAF steel slag carried out in our laboratory (38–41), and on the results of this study, we suggest that amount of 1.35 g of P  $\text{kg}^{-1}$  was mainly retained through adsorption processes.

A separate experiment was conducted, allowing sufficient contact time for precipitation to take place (by increasing the contact time between the solution and the material, HRT<sub>p</sub> of 1 d) that achieved P saturation of EAF steel slag as high as 3.65 g of P  $\text{kg}^{-1}$  (38). This is the highest value for a long-term P retention in a column study reported in the CWS literature to date. Assuming that an extrapolation can be made, it would indicate that the theoretical life expectancy of a slag-based system could be as high as 35–100 yr. Considering that the efficiency (% P removed) of the system was low when the system was approaching saturation, replacing the medium before saturation would reduce the duration of the calculated longevity but would favor precipitation in addition to adsorption.

To facilitate the understanding of P retention mechanisms within the EAF steel slag material, we used a synthetic P solution (KH<sub>2</sub>PO<sub>4</sub>) that prevented clogging by organic matter. Given the problems experienced with the hydraulic design of the full-scale systems as frequently reported in the literature, any attempt to estimate the longevity of a slag-based system should take into account the effects of organic matter, suspended solids, and other effluent components on the system's performance. Most CWS use a septic tank or another kind of a settling basin/anaerobic digester that removes about 5–10% of the P load in the accumulated sludge (37).

Taking these factors in consideration, even if the estimated life expectancy of a slag-based system is decreased by 50%, the P saturation value of this material indicates that a longevity of 17–50 yr may be possible. Multistage systems, where separate units are laid out in series or in parallel are preferred ways for CWS design today (8, 35, 38). Given that observed pH effluent values from slag material are rather high (pH 10.5–11.5), plant growth and development in this material could be impeded (J. Higgins, personal communication). In that respect, we recommend establishing several separate units in series where the first one would be filled with material more suitable for the plant growth (2, 4, 36) followed by an unplanted slag unit for P removal, and possibly a third planted cell for final effluent polishing and lowering of pH. As indicated in our regeneration experiment, the lifetime can be enhanced even further, by altering operating and resting periods in different units, integrating drying and wetting cycles.

P adsorption capacities of materials derived from P batch experiments and Langmuir equation do not provide realistic values and should only be used with caution for estimating the longevity of full-scale systems. The determination of the P saturation potential of a material in a longer-term column study appears to provide a better indicator of its capacity to retain P and could serve as a parameter for estimating the lifetime of full-scale systems. EAF steel slag has a high potential for P removal from wastewater, with P saturation value as high as 1.35 g of P kg<sup>-1</sup>. We also showed that when slag was drained and left to rest for 4 weeks, it was able to increase its P retention capacity by 74%, reaching a regenerated P saturation value of 2.35 g of P kg<sup>-1</sup>. This result demonstrated that the lifetime of a slag-based system could be enhanced even further, giving a new insight for the design and optimization of full-scale systems.

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