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# Model of phosphorus precipitation and crystal formation in Electric Arc Furnace steel slag filters

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ABSTRACT. The objective of this study was to develop a phosphorus retention mechanisms model based on precipitation and crystallization in electric arc furnace (EAF) slag filters. Three slag columns were fed during 30 to 630 days with a reconstituted mining effluent at different void hydraulic retention times. Precipitates formed in columns were characterized by X-ray diffraction and transmission electronic microscopy. The proposed model is expressed in the following steps: 1) the rate limiting dissolution of slag is represented by the dissolution of CaO, 2) a high pH in the slag filter results in phosphorus precipitation and crystal growth, 3) crystal retention takes place by filtration, settling and growth densification, 4) the decrease in available reaction volume is caused by crystal and other particulate matter accumulation (and decrease in available reaction time), and 5) the pH decreases in the filter over time if the reaction time is too low (which results in a reduced removal efficiency). Crystal organization in a slag filter determines its phosphorus retention capacity. Supersaturation and water

velocity affect crystal organization. A compact crystal organization enhances the phosphorus retention capacity of the filter. A new approach to define filter performance is proposed: saturation retention capacity is expressed in units of mg P/ mL voids.

KEYWORDS. phosphorus, apatite, wastewater treatment, slag, removal mechanisms

## INTRODUCTION

Phosphorus is generally the limiting nutrient in freshwater systems and its discharge from wastewaters favors eutrophication. Phosphorus is typically removed in wastewater treatment plants by chemical precipitation and by biological systems <sup>1</sup>. Stricter regulations for phosphorus discharges to smaller treatment plants creates a need for the development of new and extensive (requiring minimal operation) treatment technologies. Steel slag filters offer a promising treatment system for efficient and economical phosphorus removal used as post treatment units from constructed wetland systems and other small scale wastewater treatment systems <sup>2,3</sup>.

Steel slag is a by-product material from steel mills. The 2010 slag production in United States was estimated at 11 to 15 million metric tons <sup>4</sup>. The use of various types and sizes of slag in reactive filters has been studied in batch tests, column tests and field tests <sup>5-7</sup>. Fe-Ti rich slag filters were successfully used in a full-scale application<sup>8</sup>. Three potential limitations of slag filters were highlighted by Chazarenc et al <sup>5</sup>: a decrease in removal efficiency after 6 months was reported in a number of studies, filter clogging by physical and chemical solids accumulation, and diverging results in terms of a correlation between phosphorus removal efficiency and filter longevity between authors.

Calcium-rich slags are one type of slag of great interest. Calcium-rich slag filters result in high effluent pH, associated with efficient phosphorus removal <sup>5, 7</sup>. Two main mechanisms were studied in this type of filter: precipitation of phosphate phases and dissolution of slag.

Precipitation of phosphate phases occurs mainly as hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) formation in calcium-rich slag filters (e.g. <sup>5, 9</sup>). Nucleation and crystal growth of hydroxyapatite were proposed to be the limiting steps <sup>9</sup> for phosphorus removal. A succession of different phosphorus mineralogical phases on slag particles with time was also reported <sup>10</sup>. Some authors suggested that in a high pH environment

typical of calcium-rich slag, adsorption is inhibited and precipitation is the main removal mechanism <sup>9, 10</sup>.

Different aspects of slag dissolution were studied by some authors. pH rise was shown to be related to the dissolution of a succession of different complex mineralogical phases containing calcium oxides, such as bredigite ( $\text{Ca}_{14}\text{Mg}_2(\text{SiO}_4)_8$ ) and gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) <sup>11</sup>. The acid-neutralization capacity of slag was used to study the kinetics of pH rise. The effect of a longer hydraulic retention time on increased retention capacity was observed by some authors <sup>3, 12</sup>.

The lack of similarity between results obtained under different testing conditions (type of slag, type of wastewater, flow properties, filter geometry) and proposed explanations creates a need to develop a removal mechanism model to predict the performance of calcium-rich slag filters (P removal efficiency and longevity). The objective of this paper was to study phosphorus retention mechanisms in calcium-rich slag filters using column tests and to propose a phosphorus retention mechanism model.

## MATERIALS AND METHODS

### Reactive media and reconstituted effluent

The tested slag was 5-10 mm electric arc furnace (EAF) slag from Contrecoeur, Quebec, Canada. This slag was previously shown to be efficient for phosphorus removal <sup>12-14</sup>. The slag density is  $3.6 \text{ g/cm}^3$  and its  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{MgO}$  contents were 33%, 30%, 16% and 12%, respectively.

A reconstituted gypsum mining effluent was used for column tests. Chemical salts were dissolved in distilled water to form three 2-liter concentrated solutions. Solution 1 contained  $\text{KH}_2\text{PO}_4$ ,  $\text{NaF}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaNO}_3$ ; solution 2 contained  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and solution 3 contained  $\text{CaCl}_2 \cdot 3\text{H}_2\text{O}$ . These solutions were mixed together in a 200-liter barrel half-filled with distilled water. Then, distilled water was added up to 200 liters. Concentrated  $\text{NaOH}$  was added for pH adjustment. Floccs formed during pH adjustment were settled and the clear water was analyzed and used from the barrel for testing. The main characteristics of the settled reconstituted water were  $\text{pH} = 6.52$ ,  $[\text{Ca}] = 151 \text{ mg/L}$ ,  $[\text{Na}] = 146 \text{ mg/L}$ ,  $[\text{K}] = 52 \text{ mg/L}$ ,  $[\text{Mg}] = 8 \text{ mg/L}$ ,  $[\text{Mn}] = 0.72 \text{ mg/L}$ ,  $[\text{Zn}] = 0.53 \text{ mg/L}$ ,  $[\text{Cl}] = 197 \text{ mg/L}$ ,  $[\text{SO}_4] = 134 \text{ mg S/L}$ ,  $[\text{o-PO}_4] = 26 \text{ mg}$

P/L and [F] = 6.9 mg/L. Sampling and analyses of the reconstituted effluent were performed for each new 200-liter feed barrel.

#### Column tests

Three vertical transparent columns of 15 cm in diameter by 17 cm in length were continuously fed by a peristaltic pump with the reconstituted effluent. Void volume hydraulic retention times ( $HRT_V$ ) of 16.3 h, 3.8 h and 1.5 h were maintained for a duration of 630, 152 and 30 days, respectively. The void volume was defined as that occupied by liquid and air at the beginning of the test. The void volume was determined with a weight method proposed by Chapuis<sup>15</sup>, using the volume of the empty column and the mass and density of the slag in the column. These initial  $HRT_V$  corresponded to water velocities of 14, 49 and 152 mm/h, respectively.

The effluent from each column was sampled every two weeks for o- $PO_4$  and calcium concentration, and for pH. pH determinations were conducted within a half-hour of sampling to minimize interference with atmospheric carbon dioxide.

The precipitate formed in the columns was sampled at the inlet of the columns at the end of the operation of a column, and air-dried. An extra precipitate sample was taken in the column with an  $HRT_V$  of 16.3 h during operation after 438 days.

#### Analytical determinations

Analysis for slag composition was performed by Acme Labs (Vancouver, B.C., Canada) with ICP-emission spectrometry preceded by a  $LiBO_2/Li_2B_4O_7$  fusion and dilute nitric digestion. Analyses of o- $PO_4$  were conducted with a Lachat QuikChem 8500 flow injection analyser, using the ascorbic acid method<sup>16</sup>. Analyses of Ca were conducted with a AAnalyst 200 flame atomic absorption apparatus, using a standard mass spectrometry method<sup>17</sup>. Powdered precipitate samples were used for X-ray diffraction (XRD) and transmission electronic microscope (TEM) analyses. XRD analyses were performed with a Philipps X'Pert diffractometer operated at 50 kV and 40 mA, using the Bragg-Brentano geometry and a  $CuK_\alpha$  radiation. The mean size of crystal was determined from XRD diffractograms with the Scherrer equation<sup>18</sup>. TEM analyses were performed with a Jeol JEM-2100f field

emission gun microscope operated at 200 kV, using bright field imaging technique. Samples were prepared on a typical copper grid covered with Formvar lightly coated with amorphous carbon.

## RESULTS

All columns had an effluent pH between 11.0 and 11.5 at the beginning of the test. A pH decrease in the effluent was observed after 20 and 1 day for columns having initial  $HRT_v$  of 3.8 and 1.5 hours, respectively. No pH drop was observed in the column having an initial  $HRT_v$  of 16.3 h after 630 days. Calcium concentration at the columns effluent was approximately 200 mg/L when the effluent pH was over 11. The relationship between effluent pH and effluent  $o\text{-PO}_4$  concentration is presented in Figure 1. The increase in phosphorus concentration at the effluent of these columns was associated with a decrease in effluent pH.

The phosphorus removal within each column is presented with respect to the influent P loading expressed in mg P added / g slag (Figure 2A) and mg P added / mL voids (Figure 2B). The expression of P removal in mg P / mL voids is proposed to account for P accumulation in the filter voids, as explained in a subsequent section. The saturation retention capacity was defined as the maximum amount of phosphorus removed by a filter and was determined for two of the three columns. Saturation retention capacities were 2.0 and 14.5 mg P/ void mL for columns with  $HRT_v$  of 1.5 and 3.8 h, respectively. Saturation was not reached for the column with HRT of 16.3 h but was greater than 23 mg P/ mL void.

Results from crystal analyses and observations are presented in Figures 3 and 4. White precipitate accumulation was visible in all columns. A slowly moving precipitation bed was observed in the column with an  $HRT_v$  of 16.3 h and its position is shown in Figure 3. Settling of crystals was visible within this column. In the other columns, white precipitates were uniformly distributed within the column and no settling was observed.

Precipitates in columns were sampled and analyzed. It was determined by X-ray diffraction that precipitates were crystalline and that they corresponded to the theoretical hydroxyapatite diffractogram by more than 95%. Mean crystal sizes determined by X-ray diffraction were from 20 to 86 nm in different columns. Apatite crystal shapes seen in transmission electronic microscope (TEM) imagery

were either acicular or fibrous crystals. Crystals were organized in agglomerates of one mean crystal size (Figure 4). The mean crystal width in one agglomerate was between 5 and 40 nm. Fibrous crystals were smaller than acicular crystals. Crystal formation around filter cavities was visible to the naked eye, as shown in Figure 4A. Determination of the crystal size was done using the diffractogram peak at position  $2\theta = 26^\circ$ .

## DISCUSSION

### Slag dissolution and role of pH

Phosphorus treatment in calcium-rich slag filters depends largely on the dissolution of slag in the water to be treated. Dissolution of slag involves complex kinetic reactions of various mineralogical phases such as bredigite ( $\text{Ca}_{14}\text{Mg}_2(\text{SiO}_4)_8$ ) and gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ )<sup>11</sup>. However, dissolution of slag can be approximated by the dissolution of CaO, which results in an increase of calcium and hydroxide (pH) concentration.

A high pH is the major factor that ensures an efficient phosphorus removal. Under basic conditions, phosphorus is precipitated in a variety of metastable calcium phosphates<sup>19</sup> that are transformed into hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ), a final stable mineralogical phase. A strong link between  $\text{o-PO}_4$  concentration and pH in the effluent was observed (Figure 1). The hydroxyapatite composition of the precipitate was confirmed by XRD. Particles were efficiently retained in the filter by filtration. Should water velocity in the filter have been too high, precipitates could have leached out of the columns. This phenomenon was observed for columns with  $\text{HRT}_{\text{VS}}$  of 1.5 and 3.8 h. When the water velocity was low enough, particles settled in the column as observed in that with an  $\text{HRT}_{\text{V}}$  of 16.3 h.

### Water velocity and crystal behavior in the filter

Columns with longer hydraulic retention times reached greater retention capacities. As column size and geometry were identical, testing different hydraulic retention times meant testing different water velocities. A non linear relationship between P retention capacity and water velocity was observed in this study (Figure 5).

XRD analyses indicated that apatite crystals were of different mean sizes for different conditions (different HRT<sub>v</sub> and sampling time). The rate of crystal growth appeared to be constant for the conditions tested, independently of water velocity (Figure 6). TEM analyses showed that apatite crystals formed acicular agglomerates. Different mean crystal sizes of different agglomerates in the same column were observed. It is suggested that each crystal agglomerate offers a growing hydroxyapatite (HAP) seed. During operation, pre-existing seeds continue to grow while new seeds are formed, resulting in different seed crystal sizes. These results indicate that crystal growth represents a major part of the P removal mechanism in calcium-rich slag filters and that the rate of crystal growth is independent of water velocity. Thus, crystals have a maximum rate of growth that cannot be increased by higher loading rates. If the growing capacity of existing seeds is exceeded by input phosphorus, new seeds will be formed and they will contribute to the phosphorus removal.

While the rate of crystal growth is independent of hydraulic conditions, it is influenced by the chemical composition of the water in contact with HAP crystals. pH has a major impact on the rate of crystal growth, as phosphorus removal is not significantly achieved at pH values under 7 (Figure 1). In this study, since the influent composition was constant and completely soluble; it was not possible to assess the influence of phosphorus or other ions concentration on crystal growth rate. However, some authors have shown the influence of hydroxide, phosphorus, calcium and other metallic ions on crystal growth behavior of apatite <sup>19, 20</sup>. Metals as Zn and Cd were found to be nucleation promoters by precipitation of insoluble compatible metal phases in the apatite seeds and metals as Pb were found to be growth inhibitor of apatite because of adsorption onto crystals <sup>19</sup>. Hydroxides were shown to act as growth catalysts of apatite while Ca acted as a nucleation catalyst <sup>20</sup>.

A high P retention capacity was favored by two factors, a low water velocity and a large mean crystal size. These two factors also resulted in a more compact organization of crystals. A low water velocity favored settling and the accumulation of crystals at the bottom of a vertical upflow filter. Large crystal sizes meant that phosphorus was removed by crystal growth on preexisting seeds instead of precipitating in new seeds, resulting in a denser crystal structure and a greater P removal capacity.



## Proposed conceptual model

A model for phosphorus removal mechanisms in calcium-rich slag filters is presented on the basis of two main hypotheses:

a) Phosphorus removal is achieved by the formation of hydroxyapatite at a high pH <sup>9</sup> which is the result of the rate limiting dissolution of CaO from slag <sup>11</sup>. Thus, the HRT<sub>v</sub> should be long enough to allow the dissolution of CaO from the specific slag used into the effluent to be treated.

b) The hydroxyapatite crystal state (size, organization) in the filter determines the P retention capacity of the slag filter.

The model is expressed in four steps:

A minimum hydraulic retention time is necessary to kinetically raise the pH up to a value that allows phosphorus precipitation and crystallisation as hydroxyapatite (pH > 10.5 according to this study). This time is dependent on the type of slag and the influent water composition (pH, buffer capacity, concentration of phosphorus, concentration of competitive compounds such as inorganic carbon, organic soluble and particulate matter, inorganic particulate matter, etc). A preliminary treatment (e.g. aeration, settling, filtration) can reduce the concentration of competitive compounds.

Phosphorus precipitates accumulate in the filter by three means: 1- precipitation of new crystals and filtration, 2- settling and 3- crystal growth on preexisting seeds.

The P removal efficiency gradually decreases as explained by two phenomena. First, HRT<sub>v</sub> decreases with time because crystal accumulation creates confined cavity volumes and short-circuiting in the filter. If the hydraulic retention time decreases under a critical value, the pH rise and precipitation become kinetically limiting, resulting in a decrease in treatment efficiency. Second, a decrease in P removal efficiency is caused by a decrease in the rate of dissolution of slag. The dissolution rate will decrease because of the complexity of the slag composition. Some calcium oxides present at the slag surface are readily dissolved. These oxides determine the dissolution rate at the beginning of the filter life. When they become largely dissolved, the dissolution rate will be determined by the slower dissolution of more complex oxides from surfaces still exposed to the flowing liquid.

The volume fraction of confined cavities (degree of short-circuiting) is affected by the accumulation of crystals. A compact accumulation of crystals in voids favours an efficient utilization of the available space and limits short-circuiting. A loose accumulation of crystal in voids, however, creates more confined void spaces that are not any more available for water circulation and favours short-circuiting.

The impact of crystal organization and the effect of water velocity are illustrated in Figure 7, where two slag filters with different water velocities are represented. These two filters have the same initial geometry and mass of slag. They also have the same mass of formed crystals, but with different crystal organization. The loose crystal organization creates a large proportion of confined spaces, where flowing water has limited access. When this filter reaches a critical effective volume (i.e. volume available for water circulation and reaction) after which the dissolution of slag becomes kinetically limited, the amount of crystals accumulating in the filter (instead of being washed out) becomes low, resulting in a poor retention capacity. Therefore, the crystal organization behavior in a slag filter is a key concept to describe its retention capacity. Factors that influence crystal accumulation and organization are discussed in the next section.

#### Parameters that influence crystal accumulation and organization

Two main feeding conditions influence crystal accumulation and organization. The first parameter is the composition of the influent solution. First, organic and inorganic particles directly accumulate in the filter. If particles are removed in an upstream treatment, only the dissolved components contribute to accumulation by precipitation. Dissolved components include mainly organic matter, inorganic carbon, phosphorus and cations. This parameter was not directly evaluated in this study, as only one influent was used, containing no organic matter and low soluble inorganic carbon. However, it was shown that the degree of supersaturation influences the crystallization behavior <sup>21, 22</sup>. A high supersaturation index of crystals favours the formation of new crystal seeds against crystal growth on pre-existing seeds for fluoride precipitates <sup>21</sup>. Different crystal shapes under different phosphorus concentrations for various calcium phosphate precipitates were observed <sup>22</sup>. Other authors have shown that the presence or deficiency in different ions influenced crystal shape, crystal nucleation and crystal growth <sup>19, 20, 23</sup>.

Further work is needed to assess the contribution to crystal accumulation and organization of organic matter and inorganic carbon.

The composition of the slag also influences crystal accumulation. If the slag leaches metallic ions, they may act as catalysts or inhibitors. Adsorption phenomena onto slag surface may influence the nucleation step of apatite formation. Adsorption bonds between phosphorus and iron present in slag have been reported <sup>13</sup>.

Water velocity in the filter is the second main parameter that influences crystal accumulation and organization. A low water velocity allows phosphorus to completely precipitate in a shorter distance than a high water velocity, as illustrated in Figure 7. When precipitation and crystallization occur over a short distance, crystals are more likely to be organized in a dense network by growth on existing crystal seeds. When precipitation and crystallization occur over a longer distance, crystals form in a dispersed space and more confined voids are created. Therefore, the hydraulic properties of the filter should be designed to avoid local high velocities at the entrance and to uniformly distribute the influent. Moreover, a low water velocity allows newly formed seeds to settle, favouring a compact crystal organization. Further work is needed to compare the crystal organization of filters in continuous and intermittent inflow conditions.

The proposed model is expressed in a conceptual mathematical expression for the pH at the effluent of the filter (equation 1).  $k$  is the kinetic constant of dissolution of slag and it is dependent on the slag type, the influent composition and time.  $HRT_v$  is the theoretical initial void volume and it has a constant value.  $F_c$  is the crystal accumulation factor, introduced in the mathematical expression to consider the volume occupied by crystal and confined voids. Its value is between 0 (volume completely filled with crystals or confined voids) and 1 (all the volume is available).  $F_c$  depends on influent composition, filter geometry, water velocity and time.

$$pH_{\text{effluent}}(t) = f(k, HRT_v, F_c) \quad [1]$$

Knowing the expressions for  $f$ ,  $k$  and  $F_c$  would allow to determine the duration when the effluent pH will be above a critical value such as 10.5 and to estimate the longevity of the filter. Further work is needed to evaluate these expressions and to validate the conceptual equation 1.

#### A new approach for the expression of phosphorus retention capacity

P retention capacities are usually reported in mg P/g slag<sup>5-7, 10, 13</sup>. An expression of this type refers to P retention capacity related to the slag itself. In this study, it was shown that the P retention capacity was related to HAP crystal accumulation in the filter voids. Therefore, retention capacities are reported in mg P/ mL voids. These units can be easily converted into g hydroxyapatite / mL voids using the stoichiometric ratio 16.19 g HAP/g P. These last units allow to compare observed P retention capacities with some reference or theoretical P retention values. As an example, the theoretical maximum P retention capacity is between 2.6 and 3.0 g hydroxyapatite / mL voids, which is the range for the density of many natural HAP crystals. This value represents an ultimate upper limit that is impossible to reach, as it would mean that the filter would be completely filled with rock apatite. Another interesting retention capacity value is 1.8 g hydroxyapatite / mL voids, which corresponds to a natural spherical sand density. This value corresponds to an extremely high removal efficiency, as no confined spaces would be created except for the spaces between compacted spheres. Again, this value is not possible to reach because crystals organize in acicular aggregates, which are less compact than sand. The higher retention capacity obtained in this study was 0.35 g hydroxyapatite / mL voids, which is 4 times lower than a natural sand density. This value is higher than obtained (0.15 g hydroxyapatite / mL voids) in previous experiments conducted with the same media<sup>13</sup>.

Crystals were determined to be composed of >95% hydroxyapatite. Retention capacities were converted from mg P / mL voids to mg hydroxyapatite / mL voids using the stoichiometric composition of hydroxyapatite. With real effluents containing organic inorganic matter in both soluble and particulate forms, including inorganic carbon, other compounds would accumulate or form (e.g. calcite precipitates). Therefore, retention capacities would be converted from mg P / mL voids to mg crystal /

mL voids using the mean stoichiometric composition of the crystal. The advantage of this approach is to consider the effect of competitive compounds on treatment capacities of slag.

#### Practical recommendations

In full scale applications, the phosphorus removal performance of a calcium-rich slag filter can be increased by providing an efficient upstream treatment. Components of wastewaters that compete with phosphorus precipitation should be removed prior to slag filtration. A biological treatment (e.g. constructed wetland) reduces the organic matter loading to the slag filter, limiting biofilm formation and solids accumulation that would favor filter clogging. Chemical clogging by carbonate precipitates may happen, particularly at a high HRT <sup>24</sup>. The formation of carbonate precipitates was not observed in this study because of the composition of the synthetic wastewater that did not contain inorganic carbon. In full-scale applications, the HRT should be high enough to favor compact crystallization and low enough to minimize the precipitation of carbonates. The formation of calcium carbonate in the slag filter can be limited by trapping bicarbonate in an easily cleaned preliminary coarse slag filter and by minimizing exposure to air (instead of CO<sub>2</sub> trapping in a high pH solution). Major cations such as Ca or Mg, if present at high concentration, may limit the dissolution rate of slag and should be removed if possible. Secondary metallic ions may also inhibit or promote the formation of hydroxyapatite. The slag filter effluent should be neutralized prior to discharge by dilution or neutralization by peat <sup>25</sup> or gaseous CO<sub>2</sub> neutralisation <sup>26</sup>.

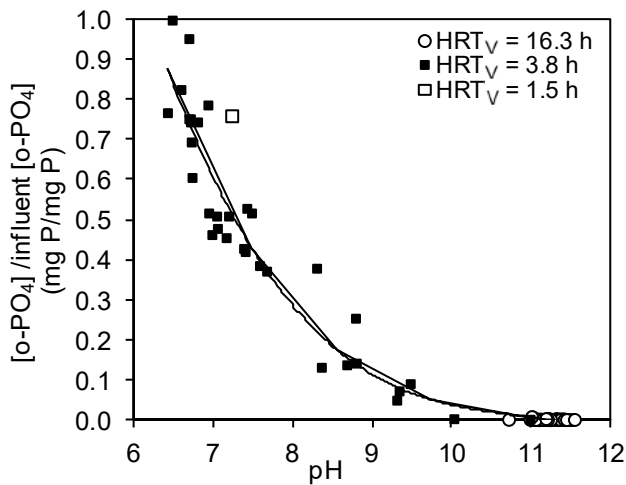
The type of slag for the filter should be selected on the basis of several properties. The slag used in the filter should be a non hazardous material as determined by standard leaching testing such that its effluent should be non toxic to meet discharge criteria and to facilitate final disposal or valorization. It should have a strong mechanical stability to avoid disaggregation and the formation of fines during preparation, which would favor clogging. Its calcium oxide dissolution rate in the effluent to be treated should be sufficient and steady enough to increase the pH even with wastewaters having a high buffering capacity for long-term operation. Factors influencing the dissolution rate should be studied in

greater detail, but it should be related, notably, to slag size, precipitates accumulation and CaO and FeO content.

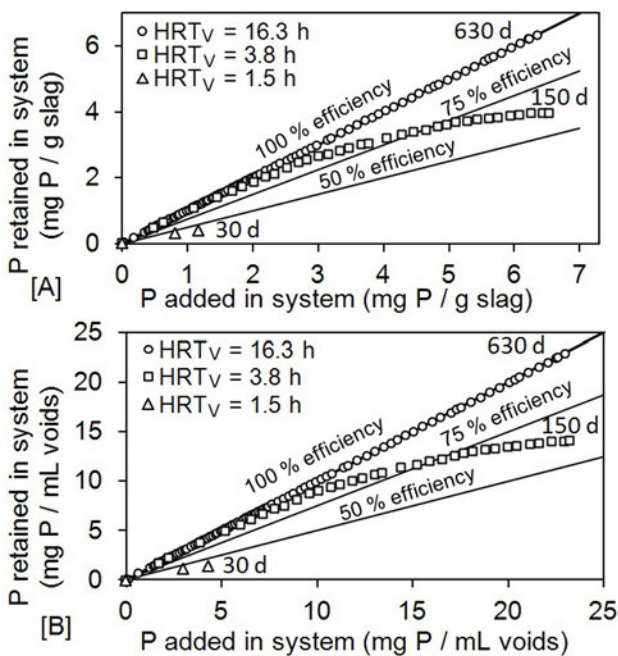
Crystal growth rather than the formation of new crystal seeds should be favored. To promote crystal growth, the water velocity should be kept low enough (high  $HRT_v$ ) and the configuration of the filter should provide uniform influent distribution (using vertical flow, inlet diffuser, uniform slag size) to avoid high local water velocities and short-circuiting. The minimum  $HRT_v$  required to favor crystal growth and long-term operation is related to the hydroxyapatite crystal growth rate, which is related to the composition of the water.

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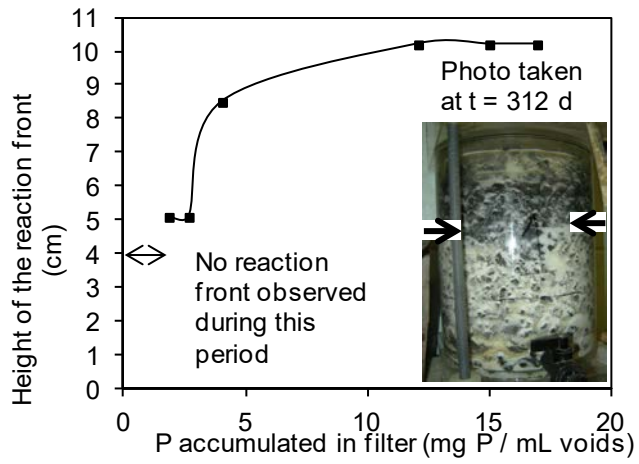
FIGURE CAPTIONS



**Figure 1.** Relationship between effluent pH and normalized effluent o-PO<sub>4</sub> (influent [o-PO<sub>4</sub>] = 26 ± 2 mg P/L).

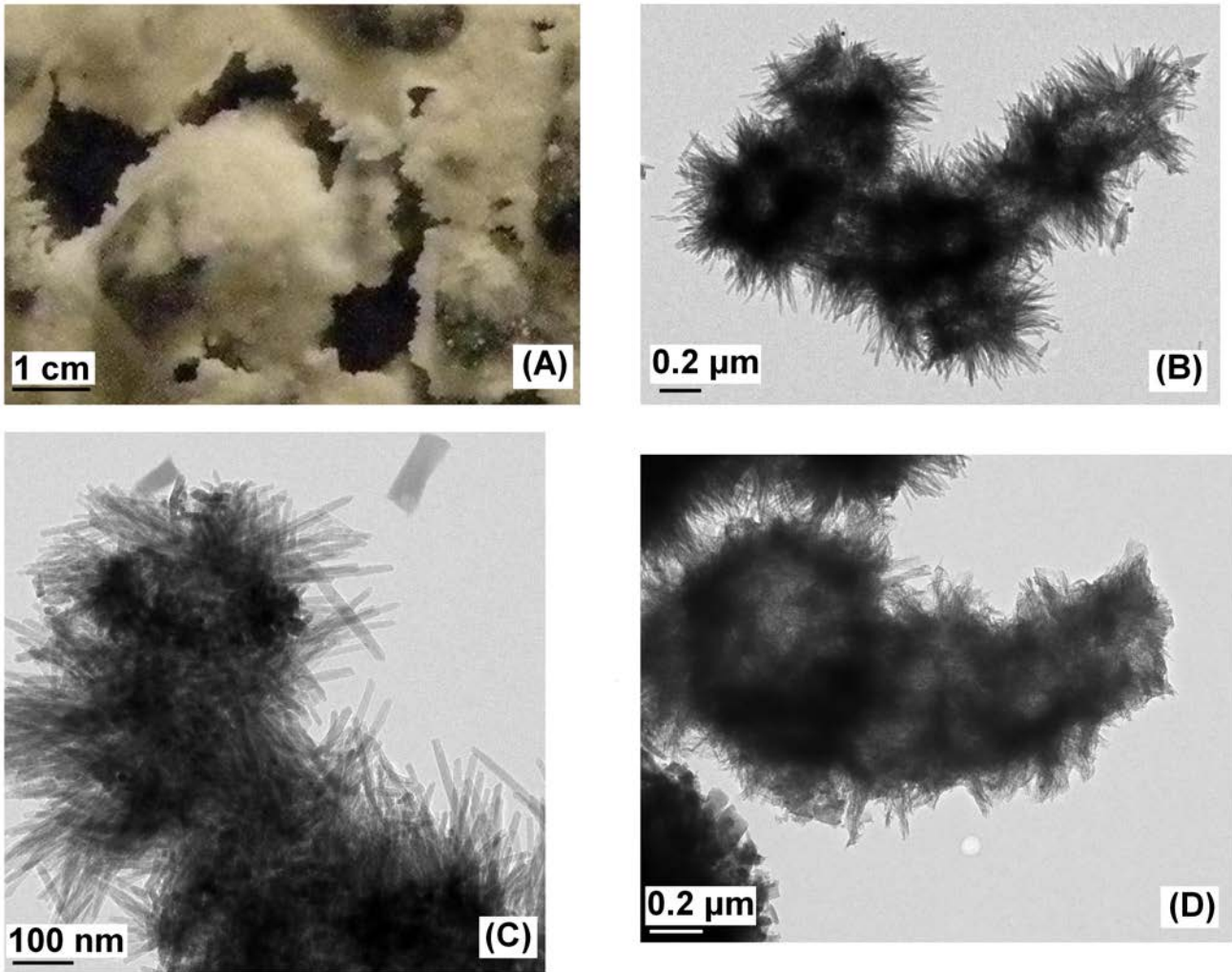


**Figure 2.** Phosphorus removal efficiency at different HRT<sub>v</sub> expressed in traditional mg P / g slag (A) and newly proposed mg P / mL voids (B). The duration of the experiment is indicated besides the last data point presented.

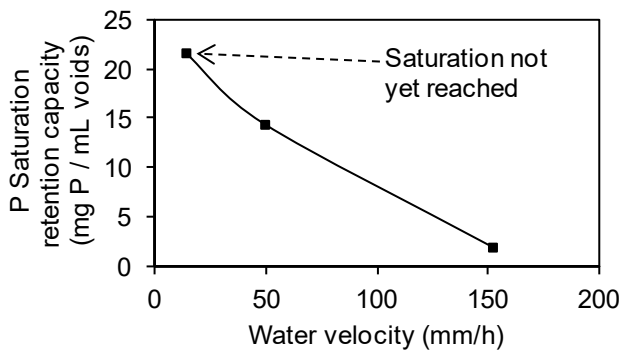


**Figure 3.** Progression of the precipitate bed within the  $HRT_V = 16.3$  h column. The position of the reaction front was determined visually.

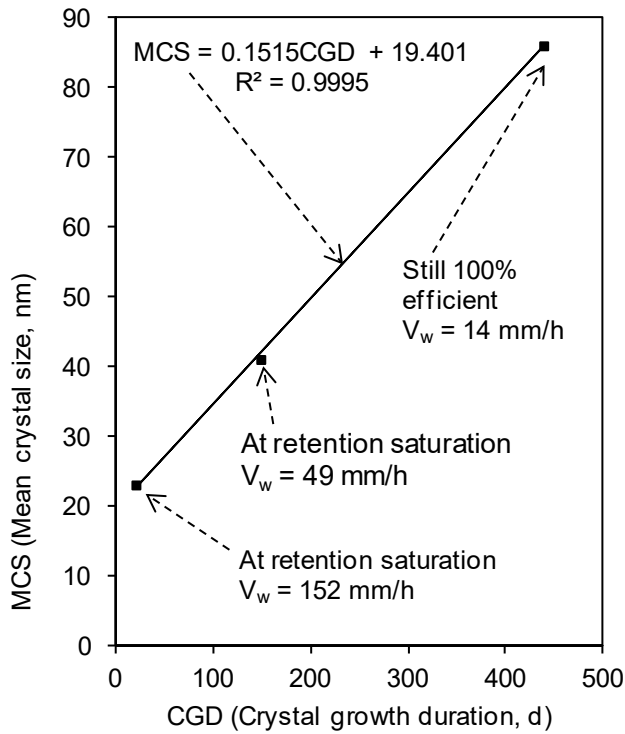




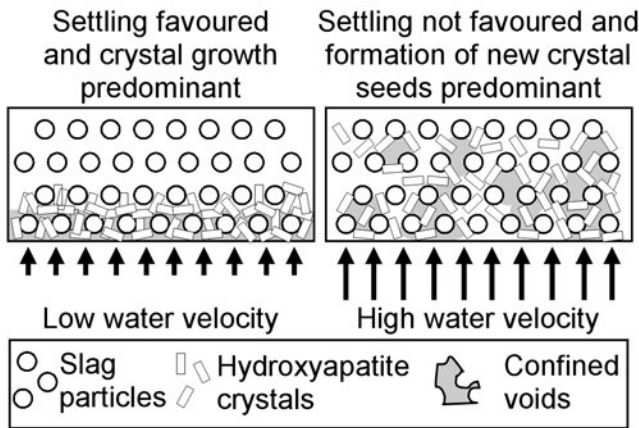
**Figure 4.** Photo of white crystals (>95% apatite confirmed by X-ray diffraction) formed on cavity wall (A); TEM photo of apatite crystal aggregate (B); TEM photo of acicular apatite crystals (C); TEM photo of a crystal seed with fibrous aspect (D).



**Figure 5.** Effect of water velocity on phosphorus retention capacity.



**Figure 6.** Crystal growth observed in filters (three data points for three different filters). Mean crystal size was determined by XRD and  $V_w$  stands for water velocity.



**Figure 7.** Conceptual representation of a compact (left) and a loose (right) crystal organization in a slag filter. The mass of apatite crystals in the filter is considered identical in both filters.

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