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Removal of phosphorus, fluoride and metals from a gypsum mining leachate using steel slag filters

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ABSTRACT

The objective of this work was to evaluate the capacity of steel slag filters to treat a gypsum mining leachate containing 11-107 mg P/L ortho-phosphates, 9-37 mg/L fluoride, 0.24-0.83 mg/L manganese, 0.20-3.3 zinc and 1.7-8.2 mg/L aluminum. Column tests fed with reconstituted leachates were conducted for 145 to 222 days and sampled twice a week. Two types of electric arc furnace (EAF) slags and three filter sequences were tested. The voids hydraulic retention time (HRT_v) of columns ranged between 4.3 and 19.2 h. Precipitates of contaminants present in columns were sampled and analyzed with X-ray diffraction at the end of tests. The best removal efficiencies over a period of 179 days were obtained with sequential filters that were composed of Fort Smith EAF slag operated at a total HRT_v of 34 h which removed 99.9% of phosphorus, 85.3% of fluoride, 98.0% of manganese and 99.3% of zinc. Mean concentration at this system's effluent was 0.04 mg P/L ortho-phosphates, 4 mg/L fluoride, 0.02 mg/L manganese, 0.02 zinc and 0.5 mg/L aluminum. Thus, slag filters are promising passive and economical systems for the remediation of mining effluents. Phosphorus was removed by the formation of apatite (hydroxyapatite, $Ca_5(PO_4)_3OH$ or fluoroapatite, $Ca_5(PO_4)_3F$) as confirmed by visual and X-ray diffraction analyses. The growth rate of apatite was favored by a high phosphorus concentration. Calcite crystals were present in columns and appeared to be competing for calcium and volume needed for apatite formation. The calcite crystal growth rate was higher than that of apatite crystals. Fluoride was removed by precipitation of fluoroapatite and its removal was favored by a high ratio of phosphorus to fluoride in the wastewater.

KEYWORDS

Wastewater treatment, slag filters, mining remediation, hydroxyapatite growth

1 Introduction

Mining operations can have major impacts on the environment and indirectly affect human health. The site closure is a determinant step to limit long-term damage caused by mining leachate. Mining residual tailings are stocked in piles that can reach large dimensions. If rain and surface water are not well controlled, they may become contaminated while flowing through piles and discharged in the environment. While many modern mining companies take responsibility to restore the site after the mine life, old orphan mining sites still exist and create contamination from mining leachates. Gypsum mining leachates may favor eutrophication and be toxic as they contain high concentration of phosphorus, fluoride and metals. The objective of this research was to assess the capacity of steel slag filters for the passive treatment of multi-component gypsum mining leachates.

Slag is a waste material produced in iron and steel mills. When the original ore is melted, metallic and non metallic components are separated. The artificial lava floating over melted iron is recovered and cooled, resulting in slag. Different varieties of slag exist, depending of the metallurgical process it comes from. Two main types of slag are identified by the American National Slag Association: blast furnace slag and steel slag (National Slag Association, 2009). Blast furnace slag is produced from iron mills, where iron ore, flux stone (calcium rich stone) and coke react in a blast furnace. Its main components are silica oxides, alumina, lime and magnesia. Steel slag is produced from basic oxygen furnace (BOF slag) or electric arc furnace (EAF slag), where iron and scrap are processed with lime. Its main components are calcium silicates, aluminoferrites and oxides of calcium, iron, magnesium and manganese. Three types of slag shapes are produced (air cooled, expanded or granulated). Cooling processes determine the porosity and crystalline fraction of slag. Finally, crushing and/or sieving results in different slag grain size, from powder to coarse aggregates.

Using slag for phosphorus removal from wastewater effluents has been studied with short term batch tests, column tests and field scale tests (Yamada et al., 1986; Chazarenc et al., 2008; Vohla et al., 2011). Short-term batch tests remain the most documented approach (Chazarenc et al., 2008), but focus will be given to column and field-scale filters in the next paragraphs. Various types of wastewaters were treated

in recent field-scale studies: a contaminant plume from a septic tank (Smyth et al., 2002), effluent of constructed wetlands (Chazarenc et al., 2007), landfill leachates (Koiv et al., 2010), effluent of domestic wastewater treatment ponds (Pratt and Shilton, 2010) and fish farm sludge supernatant (Brient, 2012).

Some specific properties of slag filters were addressed in recent studies. Regeneration of slag filters after drying was shown to be possible by Drizo et al. (2002), who increased her column retention capacity from 1.35 to 2.35 mg P / g of slag with this process. The hydraulic retention time of slag filters has a direct impact on their removal performances (Liira et al., 2009; Shilton et al., 2005). Some authors highlighted important differences between short term tests and pilot tests performance results. Shilton et al. (2005) reported that full-scale tests gave higher removal performances than similar tests conducted in columns, possibly because of the influence of algae. Pratt and Shilton (2010) suggested that short-term batch tests are not suitable to characterize performances of slag filters even if phosphorus is treated by adsorption, because long-term slag alteration creates new adsorption sites. The major difficulties related with slag filters are clogging and decline of efficiency after 6 months (Chazarenc et al., 2008). Finally, the formation of hydroxyapatite was observed by many authors when the effluent pH of filters is high (Chazarenc et al., 2008; Vohla et al., 2011).

Fluoride and metals removal was previously studied by adsorption on slag (Huang et al., 2011; Xu et al., 2011; Zhou and Haynes, 2010). Precipitation of CaF_2 using chemical additives (Yang et al., 2011) or fluidized bed (Aldaco et al., 2005) was also documented. Selective precipitation of phosphorus or fluoride from specific wastewaters containing both components was performed using staged chemical processes (Grzmil and Wronkowski, 2006; Warmadewanthi and Liu, 2009; Yang et al., 2001). The utilization of passive slag filters for single-metal removal was documented in several studies (Smyth et al., 2002; Renman et al., 2009), but further work is needed to assess the capacity of such systems to treat wastewaters containing phosphorus, fluoride and metals.

2 Materials and Methods

2.1 Reconstituted leachates and tested media

Two reconstituted wastewaters were prepared, representing low (L1) and high (L2) concentration leachates from an orphan gypsum mine, located in Joplin, Missouri. Laboratory-grade salts ($CaCl_2$, $NaNO_3$, KH_2PO_4, etc.) were individually dissolved and mixed together in tap water. pH was adjusted using 25 to 45 mL of H_2SO_4 6N. The resulting solution was settled for about 24 h and the supernatant was used for tests. Reconstituted wastewaters were sampled and analyzed at every new feeding barrel. The composition of reconstituted leachates is shown in Table 1.

Table 1: composition of reconstituted leachates

Component	Units	L1	L2
pH	-	6.92	5.67
Na	mg/L	154	311
Ca	mg/L	32	177
K	mg/L	17	132
Mg	mg/L	16	17
Al	mg/L	1.7	8.2
Mn	mg/L	0.24	0.83
Zn	mg/L	0.20	3.3
SO_4	mg S/L	201	317
Cl	mg/L	25	265
o-PO_4	mg P/L	11	107
F	mg/L	9	37

Two types of slags were used: EAF slag from Fort Smith, Arkansas (FS slag) and EAF slag from Blytheville, Arkansas (B slag). The chemical and mineralogical composition of the tested slags are given in Tables 2 and 3. Chemical analyses were performed by Acme Analytical Laboratories (Vancouver, Canada) using $LiBO_2/Li_2B_4O_7$ fusion and dilute nitric digestion followed by ICP-emission spectrometry. Mineralogical composition was determined by X-ray diffraction analysis in the Geology Department of Tartu University, Estonia.

2.2 Column tests

Column tests were conducted using transparent Plexiglas columns (17 cm long and 15 cm in diameter) fed continuously with a peristaltic pump from the bottom center (upflow) with the effluent coming out from the top center. Columns were filled with washed and 105°C-dried 5-10 mm slag. The column tests

setup is presented in Figure 1. Columns were continuously fed for the whole test duration (145 to 222

days, e. g. Figure 1) and no backwashing was needed. Feeding was stopped for very short periods to

clean tubings. The HRT_V for each column was computed following a weight procedure utilized in

permeability tests (Chapuis et al., 1989; ASTM, 2006). The effluent of each column was collected once or

twice a week for pH, P, F, Ca, Mn, Zn and Al determination. At the end of tests, columns were opened

and precipitates were sampled. White precipitates were considered inorganic as no biofilm formation

was observed in columns. Precipitates were picked up using a metal spatula and were partly dried using

absorbent paper. The resulting precipitate (having a paste aspect) was dried at room temperature. 22

powder samples were taken.

Table 2: Chemical composition of tested slags. B: Blytheville slag. FS: Fort Smith slag

Component	Units	Slag ID B	FS
CaO	%	31.7	28.8
Fe_2O_3	%	29.5	25.2
Al_2O_3	%	11.9	7.7
SiO_2	%	10.9	14.5
MgO	%	10.3	14.7
MnO	%	3.29	7.96
Cr_2O_3	%	0.68	1.09
TiO_2	%	0.50	0.37
P_2O_5	%	0.48	0.31
Na_2O	%	0.06	0.06
K_2O	%	0.03	<0.01
Ba	ppm	455	436
Sr	ppm	301	267
Zr	ppm	194	1011
Nb	ppm	182	180
Y	ppm	27	8
Ni	ppm	<20	103
Sc	ppm	6	2
Total	%	99.4	100.8

2.3 Analytical determinations

pH was determined on water samples in the half-hour following sampling, using a 4-point pH calibration

(pH = 4, 7, 10 and 12). Water samples were acidified with H_2SO_4 5N or HNO_3 6N prior to subsequent

analyses. Orthophosphates were determined using a Lachat QuikChem 8500 flow injection analyser,

using the ascorbic acid method (APHA et al., 2005). Analyses of metals were conducted with an AAnalyst

200 flame atomic absorption apparatus, using a standard mass spectrometry method (MDDEP, 2006).

Analyses of sulfates were conducted with the turbidimetric method (APHA et al., 2005). Fluoride

concentration was determined using a Cole-Parmer epoxy combined probe filled with KCl 3M.

Table 3: Mineralogical composition of tested slags

|			Slag ID	
Mineral phase	Chemical formula	Units	B	FS
Merwinite	$Ca_3Mg(SiO_4)_2$	%	9.2	3.9
Wuesitite	FeO	%	31	42
C2S, beta	Ca_2SiO_4	%	26	29
C4AF	$Ca_2Fe_{0.28}Al_{1.72}O_5$	%	3.5	3.5
Mayenite	$Ca_{12}Al_{14}O_{33}$	%	4.7	2.7
Gehlenite	$Ca_2Al(Si,Al)_2O_7$	%	2.1	0.9
Periclase	MgO	%	3.2	3.3
Akermanite	$Ca_2MgSi_2O_7$	%	2.0	1.7
Magnesioferrite	$MgFe_2O_4$	%	15	5.1
Bredigite	$Ca_{14}Mg_2(SiO_4)_8$	%	3.0	7.3
Spinel, submagnesian	$MgAl_2O_4$	%	0.5	0
Quartz	SiO_2	%	0	0.4
Total		%	99.9	100.0
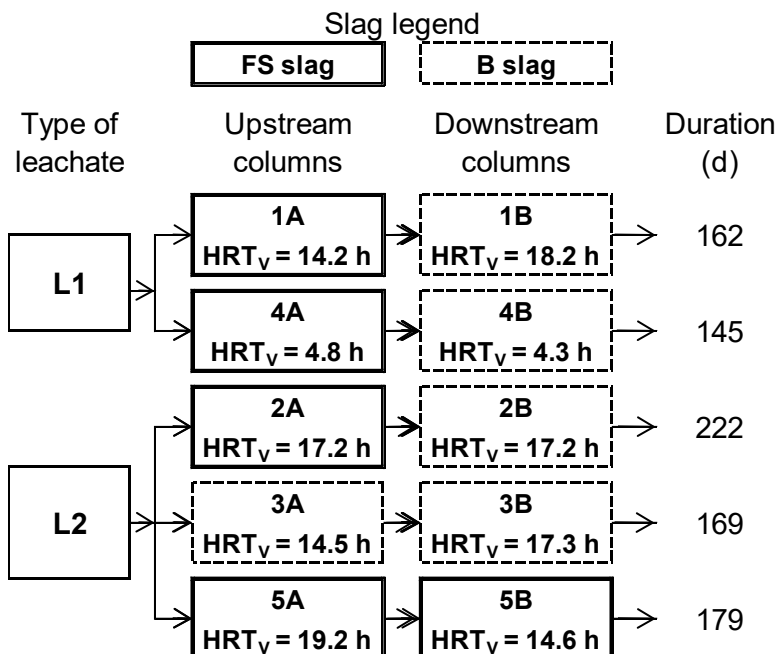
Figure 1: Schematic of the column tests experimental setup and operational conditions.

Crystal powder samples were analyzed using the X-ray diffraction powder method. A Philipps X'Pert

diffractometer operated at 50 kV and 40 mA and a Bragg-Brentano geometry with Cuk$_\alpha$ radiation were

used. The Scherrer equation (Cullity, 2001) was used for the determination of the mean crystal size from

diffractograms (peak at θ= 25.9° for apatite and θ = 29.5° for calcite). A new parameter was created to

qualitatively compare the proportions of apatite and calcite ($CaCO_3$) within samples: the HAP/$CaCO_3$

ratio. It was defined as the ratio between the intensity of the apatite peak at position 2θ = 25.9° and that

of the calcite peak at position 2θ = 29.5°.

2.4 Toxicity tests

Toxicity tests were performed to assess the environmental innocuity of slag. A 35 g slag sample was

placed in a 1000 mL Erlenmeyer flask filled with 700 mL of extraction fluid. Two extraction fluids were

tested: distilled water and acetic acid (Toxicity Characteristic Leaching Procedure (TCLP) extraction

solution #2 (USEPA, 1992)). The Erlenmeyer was mixed for 24 h, after which metal concentrations were

determined. Samples were tested in duplicates and mean concentrations were reported.

3 Results

Results of column tests are presented in Figure 2. Exhaustive data tables are presented as online

supplementary data. In general, a better removal of contaminants was correlated to high pH and calcium

concentrations. Several upstream columns displayed a pH drop during the experiment (Figure 2A). The

pH drop of the B slag was observed sooner than that of the FS slag. Downstream columns all had an

effluent pH over 11, except column 3B which had a pH drop after 70 days of operation (results not

shown). Phosphorus concentration was between 0.01 and 1 mg P/L when the effluent pH was over 10

independently of the slag type (Figure 2C). In general, downstream filters polished the upstream filters'

effluent to concentrations between 0.01 and 0.1 mg P/L (Figure 2D). Phosphorus removal efficiency was

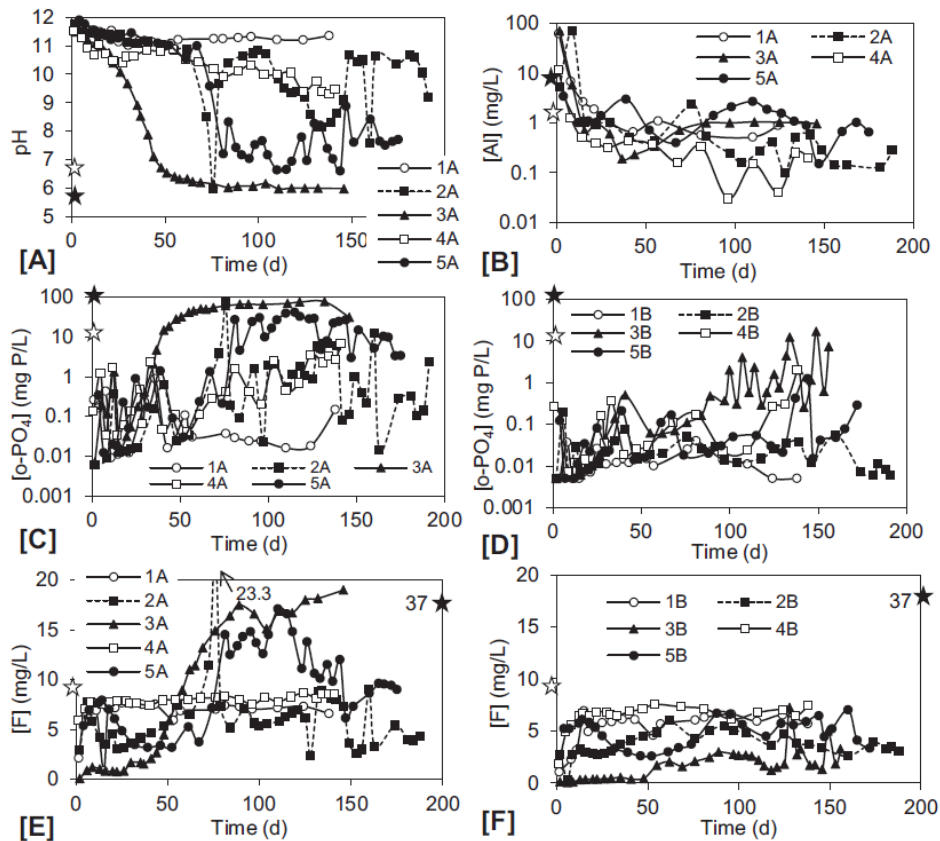greatly affected by a reduction in pH in columns 3A, 3B and 5A.

Figure 2: Selected column tests results: pH (A), Al (B), o-PO$_4$ (C and D) and F (E and F). The letter A or B besides the column refers to the upstream (A) or downstream (B) position of the series of columns. The average influent concentration is shown on the vertical axis for the L1 (empty star) and L2 (full star) leachates.

Fluoride removal (Figure 2E and F) performance was low from L1 (initial concentration of 10 mg/L, treated concentration of 7 mg/L) and high from L2 (initial concentration of 40 mg/L, treated concentration of 4 mg/L). B slag provided significant fluoride removal from L2 (<1 mg/L, column 3A) compared to FS slag (4 mg/L, column 2A). Fluoride removal was reduced when the pH became less than about 7 in column 3A and 9 in column 5A. Downstream filters removed approximately another 1 mg/L of fluoride from the upstream filter effluent.

Metals removal resulted in a manganese concentration below 0.1 mg/L and a zinc concentration below 0.5 mg/L when the pH was above 10 (results not shown). Manganese and zinc removal was affected by a reduction in pH in columns 3A and 5A. This relationship was not observed for aluminum (Figure 2B), whose concentration was in general below 1 mg/L. Leaching of aluminum, however, was observed for all columns at the beginning of operation.

X-ray diffraction analysis confirmed the presence of apatite (hydroxyapatite or fluoroapatite) in all crystal samples. Calcite was present in 9 samples (columns 1A, 2A, 2B, 4A, 4B, 5B). Apatite mean crystal sizes of samples were between 16 and 65 nm while calcite mean crystal sizes were between 31 and 316 nm. The HAP/CaCO$_3$ ratio was between 0.18 and 0.64 for columns 1A, 1B, 4A and 4B and between 0,59 and 2.56 for columns 2A, 2B, 3A, 3B, 5A and 5B.

Toxicity test results are presented in Table 4. The TCLP criterion (Environmental Health and Safety Online, 2008) for Ag, Cd and Pb were met in both the distilled water and the acetic acid extraction fluid.

Table 4 : Toxicity tests results using acetic acid (TCLP) and distilled water as extraction fluid

Contaminant (mg/L)	B slag		FS slag		TCLP criteria
	Distilled water	Acetic acid	Distilled water	Acetic acid	
Fe	0.05	101	0.03	99	
Mn	<0.01	14.8	<0.01	49	
Zn	0.024	6.6	0.014	2.9	
Cu	0.02	0.38	0.01	0.13	
Cd	<0.01	<0.01	<0.01	<0.01	1
Pb	<0.01	0.23	<0.01	0.36	5
Ni	<0.01	0.13	<0.01	0.26	
Ag	0.015	0.027	0.012	0.039	
Ca	159	903	116	1429	
Al	66.9	107	16.6	33	

Note : detection limit = 0.01 mg/L

4 Discussion

4.1 Efficiency and longevity of filters

Results of column tests showed that efficient treatment by reactive filters of a multi-component mining leachate is possible. The treatment performance of upstream columns is shown in Table 5. The best global removal efficiency in L2, which corresponded to a concentrated leachate, was obtained by the sequence B-B. This sequence achieved global removals of 98.8 %, 94.8 %, 94.4 % and 98.6 % for P, F, Mn and Zn, respectively, after 169 days of operation. However, a decrease in pH and removal efficiency was observed in the upstream column after 30 days, limiting its use as a long-term treatment system. The sequence FS-FS resulted in lower fluoride removal efficiency, but in a greater longevity as the pH decrease in the upstream column was observed after 70 days of operation. The global removal of

sequence FS-FS after 179 days of operation was 99.9 %, 85.3 %, 98.0 % and 99.3 % for P, F, Mn and Zn, respectively. The highest retention capacity value obtained for phosphorus was 8.3 mg P/g media with FS slag. This value is higher than typical retention capacities obtained in column or field tests for EAF slag, which are between 1 and 2.5 mg P/g media (Chazarenc et al., 2008; Vohla et al., 2011).

Table 5: Contaminants retention for column tests

Column ID	Type of wastewater	Type of slag	HRT_V (h)	Retention capacity reached (mg contaminant/g media)				
				P	F	Mn	Zn	Al
1A	L1	FS	14.2	0.737	0.16	0.010	0.011	0.050
2A	L2	FS	17.2	8.26	2.30	0.053	0.241	0.369
3A	L2	B	14.5	4.54	2.46	0.026	0.183	0.387
4A	L1	FS	4.8	2.62	0.30	0.035	0.048	0.227
5A	L2	FS	19.2	8.11	2.21	0.054	0.244	0.516

The different longevity of B and FS slags can be explained by their mineralogical composition. FS slag contained 7% of bredigite ($Ca_{14}Mg_2(SiO_4)_8$) while B slag contained only 3% of bredigite (Table 3). It was previously shown that bredigite is the first calcium oxide that dissolves, causing the pH to rise (Kostura et al., 2005). Slag B started to exhaust its dissolution capacity before slag FS presumably because it did not contain enough readily soluble oxides.

Treatment results of the best tested sequence (two successive FS slag filters operated at total HRT_V of 34 h) are presented in boxplots and compared with effluent concentrations of the actual lime treatment plant of the Joplin mine in Figure 3. The tested slag filters were more efficient than the lime treatment plant for most of the contaminants studied (phosphorus, manganese, zinc, aluminum). However, slag filters were less efficient than the lime treatment plant for fluoride. However, as slag filters are passive and efficient for removal of phosphorus and metals, they could replace the precipitation treatment plant which involves sludge disposal, constant chemical addition and maintenance. The proposed slag filter design for the Joplin mine leachate is presented in Figure 4. The system is composed of "*n*" successive FS slag filters operated at an HRT_V of at least 19 h. The utilization of successive filters would increase the

efficiency and longevity of the system because upstream filters offer partial removal that extends the removal capacity of downstream filters.
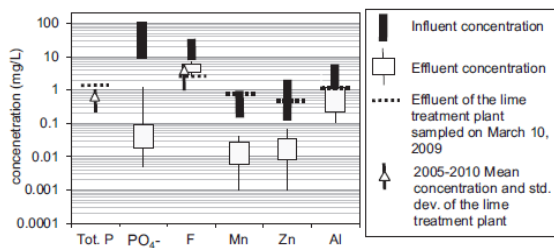

Figure 3: Effluent concentrations of an efficient slag filter (two successive FS slag filters operated at a total HRT_V of 24 h) compared with the influent and actual effluent concentrations of the lime treatment plant
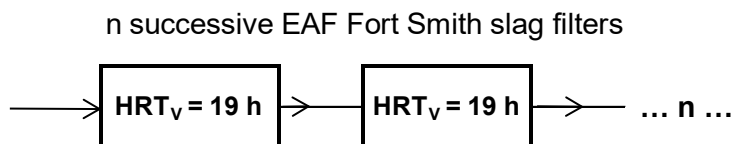
n successive EAF Fort Smith slag filters

Figure 4: Schematic of the proposed slag filter design for the Joplin mining leachate

Phosphorus removal

The environmental safety of tested slags was assessed from toxicity tests. Toxicity tests performed in distilled water resulted in low or below detection limit metal concentrations. This result may be representative of the leaching behavior of a full-scale filter at its maximum efficiency (high effluent pH). On the other side, toxicity tests performed in acetic acid resulted in higher concentrations in the extraction fluid for several metals. This result illustrates the potential leaching problem of an acidic influent on a slag filter. When the filter's neutralizing capacity starts to extinguish, it will not be able any more to raise the pH of the acidic influent and leaching of metals may take place. Filters should be replaced before their treatment capacity is reached to minimize metal leaching. pH monitoring could be a reliable indicator of the filter performance.

A strong link between a high pH and a low effluent phosphorus concentration was observed (Figure 5). Different logarithmic regressions were obtained for the pH-o-PO_4 relation between pH 6 and pH 9. These variations may be caused by different initial water compositions. Initial leachates have different chemical equilibrium caused by different contaminant concentrations and the absence or presence of the carbonate system. Moreover, different precipitation behaviours could explain the different relationships

between columns 3A and 5A that were fed with the same influent solution. Fluoride removal was more efficient in column 3A than in column 5A. The formation of fluoroapatite (and competition with the formation of hydroxyapatite) had an effect on pH and o-PO_4 concentration.
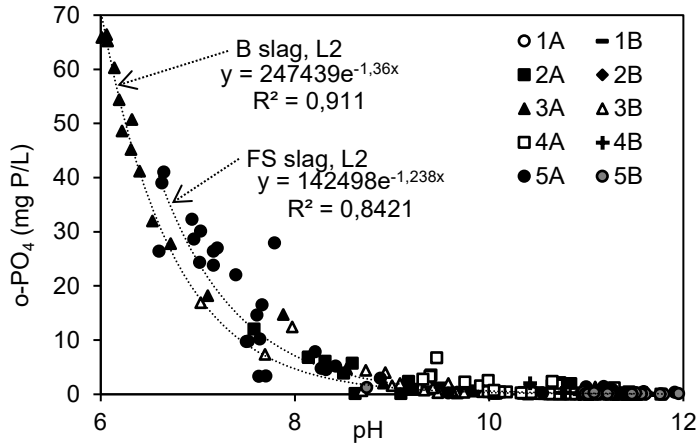

Figure 5: Relationship between effluent o-PO_4 and pH

4.2 Fluoride and metals removal

Effluent fluoride concentration was related to effluent pH (Figure 6). A high pH always resulted in a lower fluoride concentration. The composition of the leachate also influenced the efficiency of fluoride removal as with the FS slag, the fluoride removal was 10% with L1 and 85% with L2 (the more concentrated leachate). The fluoride removal efficiency was increased when the fluoride/phosphorus ratio of the wastewater was low, favouring the precipitation of fluoroapatite. Fluoroapatite has the same molecular structure as hydroxyapatite, but precipitation of hydroxyapatite is probably favoured by the constant dissolution of hydroxide ions from slag. The fluoride/phosphorus mass ratio was 0.88 in L1 and 0.33 in L2. In comparison, the stoichiometric fluoride/phosphorus mass ratio of fluoroapatite is 0.20. The requirement of phosphorus for fluoride precipitation in fluoroapatite may explain the poor fluoride removal capacity of downstream filters that were exposed to a low concentration of phosphorus, compared to upstream filters.
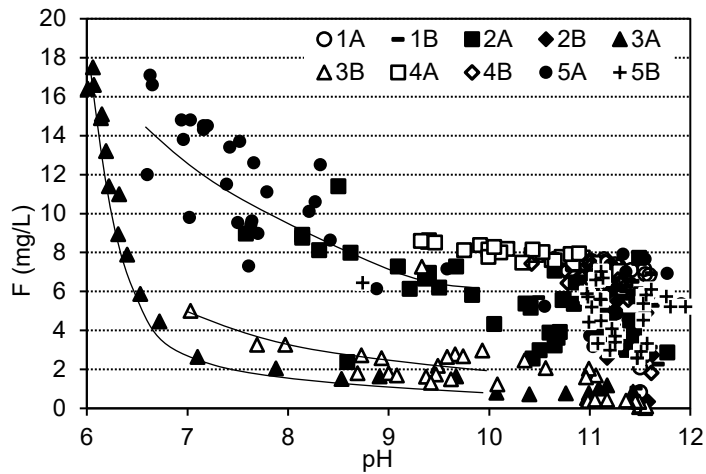
Figure 6: Relationship between fluoride and pH in column effluent

Fluoride removal performance and mechanisms observed in this study were quite different from what was tested with other kinds of wastewaters containing both phosphorus and fluoride. Fluoride removal from electronics wastewater by CaF_2 precipitation was reported (Yang et al., 2001). These authors noted that phosphorus competes with fluoride for precipitation and that the addition of CaF_2 seeds increases the selective precipitation of fluoride, which is optimized at a pH below 9. Grzmil and Wronkowski (2006) performed selective precipitation of phosphorus and fluoride by CaF_2 addition from a phosphoric acid production wastewater, using a sequence of different pH and chemical additives. These authors reached final concentrations of 5-10 mg P/L and 8-18 mg F/L from initial concentrations of 200 mg F/L and 200-400 mg P/L. Selective precipitation of phosphorus from semiconductor wastewater containing fluoride was performed using magnesium salts (Warmadewanthi and Liu, 2009). The initial wastewater contained 936 mg F/L, 118 mg P/L and other compounds. It seems that in the presence of a high fluoride concentration, the precipitation of CaF_2 is favoured. Yehia and Ezzat (2009) observed the precipitation of fluoroapatite and CaF_2 at low and high concentrations on apatite media. Processes based on the selective precipitation of phosphorus or fluoride could allow the recovery of relatively pure phases, even if they involve the use of chemical additives and mechanical maintenance. Combined removal of phosphorus and fluoride by slag filters, however, offers the advantage of reaching a low fluoride concentration and of being relatively simple and economical.

The slag composition influenced the efficiency of fluoride removal. The mean fluoride removal at maximum efficiency was >90% with the B slag and 75% with the FS slag when columns were fed with the high concentration leachate L2. Hydroxyapatite and fluoroapatite have essentially the same molecular structure as they only differ by the OH or F ion that is located within the hexagonal pattern. It is possible that a solid solution of hydroxyapatite and fluoroapatite was precipitated and that the B slag had some specific characteristics that catalyzed the formation of fluoroapatite. The leaching of some trace metallic compounds, for example, or the presence of a specific mineralogical phase, may have affected the presence of fluoride in nucleation and growth processes.

Metals removal efficiency was linked with pH as was phosphorus removal (Figures A.1 and A.2). The mean removal efficiency at maximum efficiency of B slag and FS slag was 75% for Mn and >90% for Zn. Mn was not removed if the pH was lower than 6. The B and FS slags showed an initial Al leaching (concentration at effluent up to 70 mg/L), but Al removal was >90% after that initial period.

4.3 Crystal growth

Crystal growth in filters was investigated using crystal size determination. A qualitative interpretation of apatite growth in upstream filters is presented in Figure 7. Crystal-size-time curves had fan shapes, suggesting that new crystal seeds are constantly formed while older seeds continue to grow. It resulted in a distribution of crystal sizes, older seeds being larger and younger seeds being smaller. Crystal growth rates were dependent on the leachate composition. For the same slag media (FS slag), the crystal sizes was smaller in L1 than in L2, suggesting that a higher phosphorus concentration results in a higher apatite growth rate. As efficient crystal growth increases the retention capacity of slag filters (Claveau-Mallet et al., 2012), the high initial phosphorus concentration of L2 may explain the high retention capacities obtained in the present study compared with typical low phosphorus concentration experiments. However, it was previously shown that highly concentrated wastewater favours nucleation instead of crystal growth (Seckler et al., 1991), resulting in an inefficient crystal organization.

Crystal size (nm)
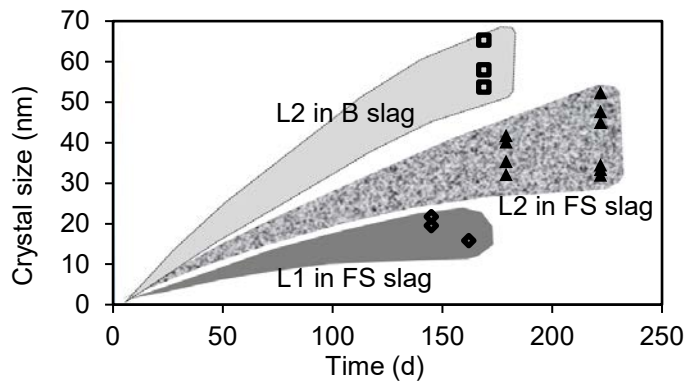
L2 in B slag

L2 in FS slag

L1 in FS slag

Time (d)

Figure 7: Apatite growth in upstream filters

Apatite crystal growth was also dependent on pH. With respect to saturation, hydroxyapatite has three stability zones related to phosphorus concentration and pH (Kim et al., 2006). The first one (low pH and low phosphorus concentration) corresponds to soluble hydroxyapatite. The second one (high pH and high phosphorus concentration) involves direct precipitation and crystal growth of hydroxyapatite. The last zone is an intermediary meta-stable zone (high phosphorus concentration and neutral pH) where hydroxyapatite may remain supersaturated. In that meta-stable zone, specific conditions such as hydroxyapatite crystal seeds are necessary for hydroxyapatite precipitation and crystallization, otherwise ions remain in solution. This phenomenon may have happened in column 3A, where crystal seeds were formed in the first 30 days of operation at a pH over 9. During the following period (pH near 6 between t = 50 and 150 d), crystal growth occurred. At these neutral-pH conditions apatite growth resulted in the biggest crystals observed (squares in Figure 7).

Results of this study highlight the importance of calcite formation in slag filters as a competitive reaction to apatite formation. For the same influent (L1), crystals in column with HRT_V of 14 h had a mean HAP/CaCO$_3$ ratio of 0.64 while crystals in column with HRT_V of 4.8 h had a mean HAP/CaCO$_3$ ratio of 0.33. Thus, calcite formation was favoured by a higher HRT_V, meaning that calcite grows faster than apatite. These observations, also reported by Liira et al. (2009), highlight the importance of the hydraulic retention time. A high hydraulic retention time favors compact precipitation and increases the crystal retention capacity, but considering that calcite grows faster than apatite, this should result in a larger proportion of calcite. As calcite crystals occupy void spaces that are no longer available for apatite

formation and growth, an efficient filter should be operated to minimize calcite formation. In summary, choosing the hydraulic retention time of a slag filter is a compromise between a high retention time for efficient crystal accumulation and a low retention time to limit calcite formation. Calcite formation may also be diminished by removing inorganic carbon from the wastewater in a preceding process and limiting contact between the atmosphere and the filter.

5 Conclusion

The objective of this work was to evaluate the capacity of steel slag filters to treat a gypsum mining leachate containing phosphorus, fluoride and metals. The proposed slag filter process was composed of two successive Fort Smith EAF slag operated at total hydraulic retention time of voids of 34 h. This system was still removing 99.9% of phosphorus, 85.3% of fluoride, 98.0% of manganese and 99.3% of zinc after 179 days of operation. Mean concentration at this system's effluent was 0.04 mg P/L phosphorus, 4 mg/L fluoride, 0.02 mg/L manganese, 0.02 zinc and 0.5 mg/L aluminum. Thus, slag filters are promising passive and economical systems for mining remediation. Technical aspects (filter geometry, contact of the filter with atmosphere, pH stabilization of the effluent) and economical considerations (transport cost, frequency of replacement) need to be considered for future full-scale applications.

Apatite growth was observed in filters. The apatite growth rate was favored by high phosphorus concentration in the influent. Calcite crystals were present in filters and were identified as competing with phosphorus removal. The growth rate of calcite crystals was higher than that of apatite crystals. Fluoride was removed by precipitation of fluoroapatite and its removal was favored by a high phosphorus/fluoride ratio in the influent. Fluoride removal was poor when no phosphorus was present in the influent.

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Québec Nature et technologies.

7 Appendix A

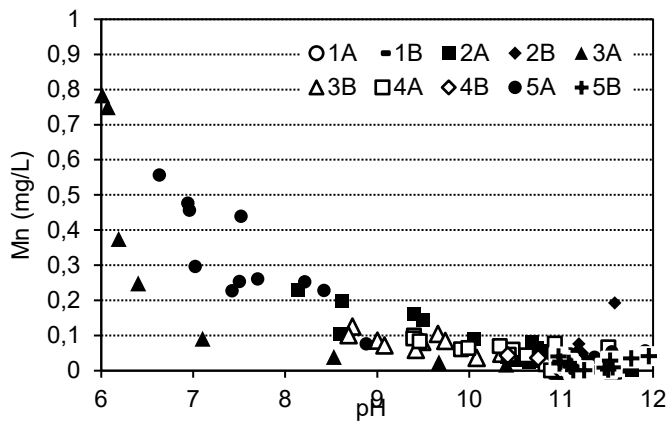The relationship between Mn, Zn and pH is shown in Figures A.1 and A.2.

Figure A.1: Relationship between manganese and pH in column effluent
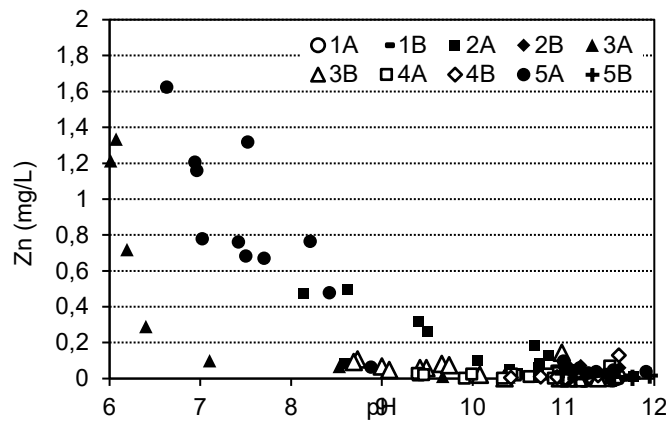

Figure A.2: Relationship between zinc and pH in column effluent

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