# Cover layer design based on bauxite residue for ecological restoration: A Northern climatic zone study case—geochemical phase

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#### Abstract

The restoration of bauxite residue disposal areas (BRDA) is one of the most important environmental challenges that the aluminium industry faces. It must take into consideration several factors including country regulations and standards, social acceptability, and the climatic zones in which the industry operates. Rio Tinto operates the only alumina refinery in Canada, the Vaudreuil refinery, located in the province of Quebec. The BRDA is nearly at full capacity and will have to be reclaimed in the coming years. The overall objective of this research project is to develop a cover layer favourable to plant growth conditions for the BRDA ecological restoration. This cover should be composed of a mixture of bauxite residue (BR), inorganic and organic residual materials from local industries and woody plants native to the province. Before creating composite soils from bauxite residue, it is essential to understand the hostile environment conferred by these residues, so as to create an ecosystem in which plants and microorganisms can grow. Since each bauxite residue has its own characteristic properties, the aim of this paper is to describe the results of the first phase of the research project (acidification) for Vaudreuil BR, i.e. the behaviour of residue chemical species under different pH conditions (target pH of 5-9) using hydrochloric acid (HCl). Preliminary results of bauxite residue acidification with HCl indicate that fluoride (F) and trace metal elements are present mostly in the solution at basic pH, and that the ideal pH for compliance with the agri-environmental standards is neutral-basic. Following these results, the challenge will then be to create fertile soil while maximizing the proportion of bauxite residue to enhance plant growth while satisfying environmental and geotechnical criteria.

Keywords: bauxite residue, restoration, acidification, fluorine, metal element

#### 1 Introduction

Rio Tinto's Aluminium division operates the only alumina refinery in Canada, the Vaudreuil plant (Jonquière, Quebec) since 1936. Using the Bayer process, this plant produces roughly 1.5 million tonnes of alumina per year, for its aluminium smelters in Quebec. Presently, approximately 1 million tonnes of bauxite residue (BR) per year are buried at the bauxite residue disposal area (BRDA). This site is located less than 500 meters from

the plant. It began operating in the 1940s and now contains more than 40 million tonnes of BR. The disposal method has evolved over the years from a mud-farming management method which, over a period of 3 to 4 years, achieved a water content in the BR of less than 30%, to a filter press dehydration method which achieves the same water content in less than 20 minutes. The BR leaving the filter press is highly alkaline (pH  $\sim$  12.5) due to the presence of residual caustic soda. In 2019, the commissioning of the filtration plant reduced the volume of sludge going to the BRDA, thereby extending the life of the site and refinery operations. Despite that, the current BRDA is near full capacity and will have to be restored in the next few years. Although there are a few R&D initiatives under study around the world for the recovery of BR, none are sufficiently advanced or economically viable to recover the BR produced by Vaudreuil plant. It is therefore interesting to work on restoring the BRDA and developing a fertile cover layer.

The overall objective of the research project is to develop a cover layer which conditions are favorable to plant growth for the BRDA ecological restoration. The governmental regulations require the site to be closed by applying a vegetated cover layer. Typically, industries use herbaceous vegetation for this purpose. In a best practice in industrial ecology perspective, the developed cover would include of a mixture of BR, inorganic and organic residual materials from local industries and planted woody species native to the province. Before creating composite soils from BR, it is essential to understand the hostile environment conferred by these residues, so as to create an ecosystem in which plants and microorganisms can grow. Since Vaudreuil BR has its own characteristic properties, the aim of this paper is to describe the results of the first phase of the research project (acidification) for Vaudreuil BR, i.e. the behaviour of residue chemical species under different pH conditions at different incremental acid concentrations.

For some years now, the scientific literature has shown a growing interest in the restoration of BR sites (Gräfe & Klauber 2011; Evans 2016; Courtney et al. 2009; Santini et al. 2019). However, the success of restoration is highly dependent on local materials and climatic conditions. The majority of BR storage sites are found in tropical environments; it is therefore necessary to adapt the best practices and develop new restoration techniques adapted to northern climatic conditions. Two main approaches for managing the closure of tailings sites are predominant in the industry: i) cap and store (Taki et al. 2023), which consists of partitioning the BR using an initial insulating layer on which a layer of vegetated cover is deposited; and ii) in situ restoration (Jones et al. 2011), which consists of depositing a layer of vegetated cover directly on the BR. Using the cap and store approach, the team of Taki et al. (2023) has developed a technique called 'Blended by-product capping'. With this technique, site managers use local residual materials to make a cover layer. The current project is therefore partly based on the cap and store approach. The cover layer recipes developed will be made up of BR and local inorganic and organic residual materials in varying proportions to meet the criteria of fertility (Gräfe & Klauber 2011) and of leaching of contaminants into the environment (MERN 2017). The two main obstacles to the design of a cover layer based on BR are their alkalinity, which creates a hostile environment for plants, and the risk of trace metal elements leaching (Di Carlo et al. 2019). One of the particularities of Vaudreuil BR is the presence of fluoride (F<sup>-</sup>). Fluoride is an element with a maximum standard concentration in effluents (MERN 2017). It is the most closely monitored element in this study. The granulometry of BR plays a major role in restoration. Indeed, particle size affects not only hydraulic conductivity (Wissmeier et al. 2011; Feng et al. 2017), but also the power of clay dispersion by sodium (Na) (Qadir et al. 2002). In addition, Thornber and Hughes (1987) related BR particle size distribution to their chemical composition. In the current study, two materials will be analysed: i) "Mud" being the unmodified residues collected at the filter press exit, and ii) the "Coarse Mud" being the particles > 45  $\mu$ m obtained by wet sieving of the "Mud" and representing approximately 15% of "Mud". After the extraction of aluminium (AI), the sodium in the form of oxide (Na<sub>2</sub>O) makes up between 2 and 12% of BR (Snars & Gilkes 2009) and needs to be neutralised. Then, BR can be amended with organic matter, in order to create a favourable environment for plant growth. Neutralisation methods, which aimed of neutralising BR to pH below 9, have been widely documented, including those using acid, seawater, carbon dioxide (CO<sub>2</sub>), superphosphate and calcium (Ca) additions (Rai et al. 2017). The optimum pH for Glenister & Thornber (1985) is 8 as some of the adsorbed Na is released, the alkalis are neutralised, and the toxic metals remain insoluble. As a source of Ca, Gypsum (CaSO<sub>4</sub>) is the most common agent used to neutralise BR (Barrow 1982; Wong & Ho 1993; Gräfe et al. 2011; Courtney et al. 2013). Nearby the Vaudreuil refinery, Rio Tinto operates also an aluminium fluoride production plant in Jonquiere, which generates annually about 80 kt of synthetic anhydrite (CaSO<sub>4</sub>). This calcium sulphate is the solid by-product of this plant coming from the chemical reaction of fluorspar (CaF<sub>2</sub>) with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). It consists of more than 95% CaSO<sub>4</sub>. Its purity, well above 90%, is comparable to that of a geological deposit. Calcium and sulphur (S) concentrations are 28% and 23%, respectively (Guérin et al. 2022). This product can be recycled in the construction industry, and also as an agricultural fertilizer and as a neutralizing agent in BRDA (Figure 1).



Figure 1 Application of calcium sulphate (CaSO<sub>4</sub>) from the fluoride plant to a bauxite residue disposal cell at Vaudreuil as a dust abatement and neutralisation agent

Beside the Al production, the regional economy of the Saguenay-Lac-Saint-Jean region is also based on the forest industry, which pulp and paper mills generate organic residues that are interesting products to use as inputs in the design of the Vaudreuil BRDA cover layer. In fact, pulp and paper mill sludge (PPMS) is a fertilizing residual material (FRM) resulting from the effluent treatment process in the pulp and paper industry (Primeau 2014; Faubert et al. 2016). Around 900 kt (wet basis) of these materials are generated in the province of Quebec every year, 51% of which are disposed of by landfill or incineration and 49% are recycled (Recyc-Québec 2021). These fibrous materials are relatively rich in nutrients and have a fairly high carbon content (Faubert et al. 2016). These by-products of the pulp and paper industry are widely used in agriculture (Camberato et al. 2006) for their effects on soil health, thanks to their contribution in organic carbon, nutrient content (nitrogen (N), phosphorus (P) and potassium (K)), pH, water content, cation exchange capacity and the stability of their aggregates. The efficiency of CaSO<sub>4</sub> and FRM to produce a BR-based topsoil that promotes plant growth has already been demonstrated (Jones et al. 2011; Santini & Fey 2018; Gagnon et al. 2021; Miura et al. 2023). However, no author has published work on the use of PPMS for the restoration of BRDA. Instead, PPMS have been applied to acid mine tailings sites (Calace et al. 2005). This study aims at characterizing BR (both "Mud" and "Coarse Mud") in terms of their granulometry, chemical composition, acidification curve and leachable  $F^{-}$ . The study also aims at analyzing the leaching of  $F^{-}$ , sulphate (SO<sub>4</sub><sup>2-</sup>) and trace metals as a function of "Mud" pH.

#### 2 Material and methods

To assess the geochemical behaviour of BR, samples of "Mud" were collected at the outlet of the filter press. One part of the "Mud" was sent for analysis, the other part was wet sieved using the liquor collected at the filter press. The larger particles retained by sieving are called "Coarse Mud".

#### 2.1 Granulometry and composition

The granulometry of the "Mud" and "Coarse Mud" was measured by laser particle size analysis using an Analysette 22 (Carter & Gregorich 2008). To measure leachable  $F^-$ , the "Mud" and "Coarse Mud" were diluted in 1:10 (solid-water) adjusted according to their moisture content, and then stirred for 18 hours with a magnet bar. The leachate was filtered to 0.45 µm and sent for analysis by ion chromatography using the Dionex<sup>TM</sup> ThermoFisher ICS-5000. The solids were analysed by X-ray fluorescence (XRF) using a Brucker S8. X-ray Powder Diffraction (XRD) analysis (DRX XPert) was carried out on the "Mud" at the filter press outlet. All tests were performed in triplicate.

#### 2.2 Description of acidification tests

To produce the buffering curve for the "Mud" and "Coarse Mud" fractions (8 grams), the material was diluted at a ratio of 1:5 (solid to water) (Courtney et al. 2013) and adjusted according to its moisture content (CEAEQ, 2014) in 150 mL beakers. Every 24 hours, an aliquot of 0.5 moles of 1N HCl per kg of solids was added, depending on the final targeted HCl dosage. Between each addition of HCl, the samples were shaken on an orbital table at 200 rpm. Once acidification was complete, the samples were stirred for 30 days to achieve pH stability. The pH was measured using a calibrated pH meter (Hanna HI 9813-6). All tests were repeated three times.

#### 2.3 Description of "Mud" leaching tests as a function of pH

To produce the buffering curve for the "Mud" fraction, 20 grams of material were diluted in solution in beakers at a ratio of 1:5 (solid to water) adjusted according to their moisture content (CEAEQ, 2014). Every 24 hours, an aliquot of 0.5 moles of 1N HCl per kg of "Mud" was added according to the final targeted HCl dosage. Between each addition of HCl, the samples were shaken on an orbital table at 200 rpm. Once acidification was complete, the samples were stirred for 10 days, and the pH was measured using a calibrated pH meter (Hanna HI 9813-6). A 10-day stabilisation period was selected because, when HCl was added, the pH of the solution decreased very quickly and then gradually increased again. The pH stabilisation was complete at 30 days but after 10 days, the variation in pH became negligible. The leachate was filtered at 0.45  $\mu$ m and divided in two parts. The first part was stabilised with HCl (2%, volume volume<sup>-1</sup>) for analysis to measure the concentration of the following elements by inductively coupled plasma atomic emission spectroscopy (iCAP<sup>™</sup> PRO XPS Duo): mercury (Hg), arsenic (As), selenium (Se), molybdenum (Mo), antimony (Sb), zinc (Zn), cadmium (Cd), lead (Pb), cobalt (Co), nickel (Ni), silicon (Si), manganese (Mn), iron (Fe), magnesium (Mg), vanadium (V), gallium (Ga), aluminium (Al), beryllium (Be), Ca, copper (Cu), silver (Ag), strontium (Sr), barium (Ba), Na, lithium (Li) and K. The second part of leachate was analysed by ion chromatography using the Dionex ThermoFisher ICS-5000 to measure the concentration of  $F^-$  and  $SO_4^{2-}$ . All tests were carried out in triplicates. However, these tests were not undergone according to the standard protocols (TCLP, SPLP and CTEU9) (MA. 100 - Lix.com.1.1) generally used to characterize hazardous materials. In these protocols, the pH is fixed and determined according to a methodology. The latter were therefore not appropriate for this stage of the project considering that we wanted to know the availability of metal and fluorinated ions following target pH range. Therefore, the results will not be representative of the leaching conditions encountered in the field.

#### 2.4 Description of statistical analyses

The normality and homogeneity of the BR pH effect on the concentration of leached elements of the "Mud" was verified before statistical analysis. The homogeneity of the variance was tested using Fisher, whereas the normality was verified graphically (Minitab<sup>TM</sup> 19). Analysis of variance (ANOVA) was performed on the normal variables. The concentration means were statistically significant at a level of P < 0.05.

#### 3 Results and discussion

#### 3.1 Granulometry

The difference between "Mud" and "Coarse Mud" was primarily due to their particle size. The average particle size of the "Mud" fraction is 2  $\mu$ m, with 90% of its particles smaller than 20  $\mu$ m (Figure 2). The average particle size of the "Coarse Mud" fraction is 20  $\mu$ m, with 90% of its particles below 200  $\mu$ m (Figure 2).

In Figure 2, two Gaussians are identifiable for the "Mud", one centred at 2  $\mu$ m, the other centred at 16  $\mu$ m. For "Coarse Mud" there are three Gaussians, one centred at 2  $\mu$ m, like "Mud", one at 13  $\mu$ m, close to "Mud", and one centred around 180  $\mu$ m. This similarity comes from the fact that "Mud" is the parental material to "Coarse Mud". In a sodium-laden soil, it is interesting to have a coarser particle size to reduce clay dispersion and soil crusting during dry spells, improve Na leaching and increase soil water infiltration (Qadir & Schubert 2002; Luo et al. 2018) with coarse particle size and Na is preferable.



### Figure 2 Example of a particle size distribution curve for the "Mud" fraction and the "Coarse Mud" fraction.

#### 3.2 Composition

BR is mainly composed of iron oxides (in the form of haematite and goethite, which give it its reddish colour), sodium alumino-silicates, aluminium hydroxides, and silicon oxides (Table 1). It also contains, in smaller quantities, titanium oxides, various calcium and sodium compounds, etc. Bauxite residue contains residual NaOH and Na<sub>2</sub>CO<sub>3</sub>, two main components of the Bayer liquor used to extract alumina from bauxite. The latter two compounds make BR corrosive (Gräfe et al. 2011).

Mineral phases						
Haematite	Fe <sub>2</sub> O <sub>3</sub>					
Goethite	FeO(OH)					
Sodalite	$3(2SiO_2 \cdot Al_2O_3 \cdot Na_2O \cdot 2H_2O) \cdot Na_2CO_3$					
Anatase, rutile	TiO <sub>2</sub>					
Gibbsite	Al(OH)₃					
Boehmite	AIO(OH)					
Katoite	$3CaO \cdot Al_2O_3 \cdot 6H_2O$					
Quartz	SiO <sub>2</sub>					
Calcite	CaCO₃					

#### Table 1 Vaudreuil press-filtered bauxite residue solid composition measured by XRD

"Mud" fraction contains (Table 2) 7.3% Na<sub>2</sub>O, 23.2%, Al<sub>2</sub>O<sub>3</sub>, 8.5% SiO<sub>2</sub>, 2.1% CaO and 45.3% Fe<sub>2</sub>O<sub>3</sub>. On the other hand, "Coarse Mud" contains (Table 2) 1.5% Na<sub>2</sub>O, 12.4% Al<sub>2</sub>O<sub>3</sub>, 6.8% SiO<sub>2</sub>, 2.0% CaO and 64.4% Fe<sub>2</sub>O<sub>3</sub>. The chemical composition fluctuates according to particle size, which coincides with the results of Thornber and Hughes (1987). They showed that Na<sub>2</sub>O is much more present in particles smaller than 20  $\mu$ m and as particle size increases, the proportion of Na decreases. Most of the Na<sub>2</sub>O in BR solids comes from desilication products (DSP) as sodalite or cancrinite (Gräfe et al. 2011). Since the Vaudreuil refinery uses a low-temperature process, cancrinite does not form. Therefore, a major part of Na<sub>2</sub>O is assumed to come from sodalite (3Na<sub>2</sub>O - 3Al<sub>2</sub>O<sub>3</sub> - 6SiO<sub>2</sub> - 4H<sub>2</sub>O) (Xu et al. 2010). By removing the finer particles of "Mud" samples to produce "Coarse Mud", it resulted in removing a major part of the sodalite and thus "Coarse Mud" is poorer in Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and richer in Fe<sub>2</sub>O<sub>3</sub> than "Mud".Compared with BR from other refineries (Figure 3), the "Mud" sample from Vaudreuil refinery contains the higher concentration of Na<sub>2</sub>O, and the "Coarse Mud" sample the lowest concentrations of Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. The "Coarse Mud" sample also has the highest Fe<sub>2</sub>O<sub>3</sub> concentration of all the BR presented in Figure 3. Similarly, in terms of particle size (Table 2), the "Mud" sample is the finest, while the "Coarse Mud" sample is the coarsest (Snars & Gilkes 2009). This agrees with the results of Thornber and Hughes (1987).

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Figure 3 XRF analysis of RB expressed as % oxides (adapted from Snars & Gilkes 2009), "Mud" and "Coarse Mud" values measured by Rio Tinto for the Vaudreuil refinery

"Mud" leaches more F<sup>-</sup> than "Coarse Mud" fraction (Table 2). The variation in granulometry could explain this difference. The "Mud" particle size is finer, which means it forms more interstices and contact surfaces to absorb the F<sup>-</sup> (Dumont-Frenette 2009). Once it has been put into solution and stirred for 10 days, some F<sup>-</sup> is released.

Refinery	рН	Particle size analysis %			Leachate mg.L <sup>-1</sup>	Composition %		
	(1:5)	< 2µm	2-20 μm	> 20µm	F <sup>-</sup>	Na <sub>2</sub> O	$AI_2O_3$	SiO <sub>2</sub>
"Mud"	12.04	50	43	7	31.8 ± 0.6	7.3	18.0	9.2
"Coarse Mud"	11.89	22	28	50	17.8 ± 1.2	1.5	12.4	7.8

Table 2 Summary of differences between "Mud" and "Coarse Mud"

#### 3.3 Acidification

The composition of "Mud" and "Coarse Mud" fractions was very different. This difference was reflected during the neutralisation with HCl. This can be seen in the buffering curves obtained for the two materials (Figure 4). Just under one mole of  $H^+$  per kg of solid was needed to reach pH 7, compared to 1.75 moles of  $H^+$  per kg for "Mud".

Both mud types showed similar starting pH around 12, mainly due to the residual caustic from the Bayer liquor (Gräfe et al. 2011). This assumption is confirmed by Figure 5. For acid addition up to 0.25 moles of H<sup>+</sup> per kg of Mud, the pH and free Na did not decrease significantly according to the ANOVA. There is likely no Na-based solid dissolved and that only the residual caustic is the cause of this pH level. Khaitan et al. (2009) and Wissmeier et al. (2011) observed on their numerical simulation a plateau around pH 10, which would correspond to the dissolution of tri-calcium aluminate (TCA) ( $Ca_3Al_2O_6$ ). In the present case, no plateau

appeared on the buffering curves at this pH value. The absence of a plateau can be explained by the low quantity of CaO (Figure 3) in the BR from Vaudreuil refinery. It is known that TCA is formed in the Vaudreuil refinery process, but it may be in too small quantities to appear in this buffering curve (Figure 4). Figure 5 shows less than 10 mg  $L^{-1}$  Ca in solution at pH 10. The F<sup>-</sup> measured in the leachate comes from the calcium fluoride (CaF<sub>2</sub>) present in the Vaudreuil BR. According to Guo et al. (2020), CaF<sub>2</sub> dissolved around pH 9. In Figure 4, there is no clear plateau in the buffering curve of "Mud" and "Coarse Mud" for CaF<sub>2</sub> dissolution. The dissolution of CaF<sub>2</sub> at pH 9 can be observed in Figure 5, as the Ca concentration rises from less than 10 mg L<sup>-1</sup> to 170 mg L<sup>-1</sup>. The two materials, "Mud" and "Coarse Mud", exhibited a plateau between pH 7 and 8 (Figure 4). Around pH 8, calcite (CaCO<sub>3</sub>) dissolved and, around pH 7, sodalite dissolved (Snars et al. 2004, Thornber and Hughes, 1987). The dissolution of  $CaCO_3$  is well represented by the quantity of Ca, which increased up to pH 6.5 according to the ANOVA. Unlike Ca, Na dissolution peaked between pH 7 and 8 with an increase of more than 1,200 mg L<sup>-1</sup>. This shows that sodalite was indeed present. In "Coarse Mud", the sodalite was completely dissolved at one mole of H<sup>+</sup> per kg due to the sharp drop in pH. In the case of "Mud", no drastic drop in pH was observed. After 2.5 moles of H<sup>+</sup> per kg of "Mud", there was still some sodalite left. The fact that there was more sodalite in "Mud" than in "Coarse Mud" was consistent with the initial quantity of Na in the solids of "Coarse Mud" and" Mud" (Table 2).



Figure 4 Buffering curves for the two fractions of material as a function of the addition of hydrochloric acid (Moles of H<sup>+</sup> per kg of solid)



## Figure 5 Concentration of leached elements as a function of pH and theoretical buffering range of sodium (Na) and calcium (Ca) compounds. Concentration means followed by the same letter are not significantly different at the 5% level (p ≤ 0.05).

#### 3.4 "Mud" leaching

From all elements listed in the Material and Method section, only the following will be discussed:  $SO_4^{2-}$ , Mg, K, P, Sr, Li, Se Ga, As, Mo, V, Al and F<sup>-</sup>, since the others were in concentrations lower than those of the blank or at the detection limit (0.003 mg L<sup>-1</sup>). Two tendencies were observed in the concentration in the leachate as a function of pH: the concentration of some element decreased when the pH increased, while the concentration of others increased with the pH (Figure 6). On the one hand, Figure 6a shows the leachate concentration resulted for elements whose concentration decreased with increasing pH, such as  $SO_4^2$ , Mg, K, P, Sr, Li and Se. The sulphate, Mg, K and P concentrations increased might benefit the plant growth as they could be bio-available to plants (Mérelle 1998). Mg, K and P are contained in the initial bauxite. The sulphate mainly came from the use of sulphuric acid in the refinery and can be in solution or trapped in DSP (Khaitan et al. 2009). Concedering the size of the SO<sub>4</sub><sup>2-</sup>, it can be assumed they are located on the surface of the sodalite crystals The sulphate curve (Figure 6a) shows a stable concentration of free SO<sub>4</sub><sup>2-</sup> between pH 12 and 8, then the  $SO_4^{2-}$  concentration increased at the buffering pH range associated with sodalite dissolution. The sudden increase in  $SO_4^{2-}$  in the solution in the range of sodalite dissolution peak could be atributed to a temporary acid-base exchanges of  $SO_4^{2}$  with H<sup>+</sup> ions. The sulfates, upon binding with H<sup>+</sup> ions, would form sulfuric acid form ( $H_2SO_4$  or  $HSO_4^-$ ). As it forms, it would detach from the sodalite crystals, either releasing H<sup>+</sup> ions to form sodium sulfates (Na<sub>2</sub>SO<sub>4</sub>) or remaining in solution. The results of this study show that Se increased slightly with decreasing pH, in contradiction with Mishra et al. (2023) results. However, Tabelin et al. (2014) measured an increasing Se concentration at a pH of 6. In the range of pH targeted in this study (6.5 to 12), Se should not be of concern. Around pH of 9, Li and Sr concentrations in the leachate were detected. The more acidified the BR is, the more Li (Baştürkcü 2021; Gu et al. 2020) and Sr were released (Apak et al. 1995). On the other hand, the concentration of elements such as Ga, As, Mo, F<sup>-</sup>, Al and V was lower as the pH level in the solution decreased as they precipitated (Figure 6b). The behaviour of Ga, As, Mo and V has been confirmed in numerous articles (Altundoğan et al. 2002; Burke et al. 2012; Lehoux et al. 2013). At pH of 12, around 300 mg L<sup>-1</sup> of Al was measured in the leachate since the initial BR contains an unrecovered amount of Al from the Bayer process. Aluminium is also present in sodalite (Snars et al. 2004) and as the pH dropped, sodalite dissolved and released Al. The effect of Al leaching by sodalite dissolution did not appear in the solution. Indeed, at pH over 10.5, Al was in solution but when the pH was below 10.5, Al precipitated in the form of hydroxide or oxyhydroxide (Mérelle 1998), so the concentration of its dissolved form decreased. Aluminium can also trap the fluoride during its formatting into alumina (Equations 1 and 2). As BR can be used to capture F<sup>-</sup> in water purification processes (Çengeloglu 2002; Liang et al. 2014), some F<sup>-</sup> adsorption mechanisms are proposed in the literature. Even if F<sup>-</sup> is contained in BR itself, the same mechanisms apply. Fluoride can be adsorbed by metallic ions (M) such as Al, Fe and Si for example (Reyes Bahena et al. 2002; Çengeloglu 2002) as shows following equations:

$$MH_2^+ + F^- = MF + H_2O$$
 (1)

Or:

$$MH_2^+ + F^- = MOH_2 - F$$
 (2)

From pH 12 to 9, a slow diminution of  $F^-$  in the leachate was observed despite the possible dissolution of  $CaF_2$ . From pH 8.3 to below, there was an important drop in the concentration of  $F^-$  until the detection limit. Adsorption of  $F^-$  by BR is optimal at pH 5 and 6 (Sujana et al. 1998) and this absorption is probably due to the zero charge point of aqueous alumina (Reyes Bahena et al. 2002). Similar trend for Al species in the leachate was observed, probably due to the dissolution of sodalite.

In accordance with the Quebec Mining Act (MERN 2017), the cover layer for a residue disposal site must comply with certain standards. On the one hand, a cover layer must support vegetation and, on the other, it must comply with surface water quality standards. According to Gräfe and Klauber (2011), the optimum pH for plant growth is between 5.5 and 9. According to this study, in order to comply with Quebec's surface water quality standards, the optimum pH would be between pH 7.5 and 8.3, at which the F<sup>-</sup> and trace metal elements are at their lower level.

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Figure 6 Concentration of leached elements of bauxite residue as a function of pH, (a) element increases with decreasing pH, (b) elements decrease with decreasing pH. Concentration means followed by the same letter are not significantly different at the 5% level ( $p \le 0.05$ )

#### 4 Conclusion

The acidification test of BR for a cover layer development has shown that the biggest increase in Na in solution was observed at pH 7. After 2.5 moles of H<sup>+</sup> per kg of "Mud", the pH was at 6 and the Na is mainly in the form of sodalite. The significant increase in Ca in the leachate started at pH 9 and continued to rise slightly, suggesting that the Ca is more in the form of  $CaF_2$  and  $CaCO_3$  than TCA. The lower quantity of Na in the solids and less leachable F in the larger particle size fraction of BR makes the "Coarse Mud" the most interesting material for designing a BR-based cover layer. Nevertheless, the "Coarse Mud" would require an additional segregation process, which is for the moment an obstacle to its production at the industrial scale. The preliminary results of this study indicates that the F<sup>-</sup> and trace metal elements were present mostly in the solution at basic pH (≥ 8.3), and that the ideal pH for compliance with the agri-environmental standards was neutral-basic (pH 7.5 - 8.3). This pH is theoretical, as this study did not consider the action of either the neutralizing agent, organic matter, plants or microorganisms. However, since the variable studied in this paper is the effect of pH on contaminants leaching, the results were used to determine a pH range at which the level of leached contaminants was minimum. Management of leachate with the refinery will be also a challenge to be addressed. Following this first study, the next step of this project will be to aim for the pH target determined in this study by using anhydrite and FRM as neutralizing agents instead of HCl. New top soil with those matters should allow to create a favorable environment for plant growth but will also have impacts on the elements in the leaching. Thus, this study will serve as a guide line to evaluate the performance of materials combined with BR in terms of the resulting leachate. The same protocol will be used to determine the most effective solution, which will then be tested on-site.

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