

# Stability of metal-rich solids from laboratory multi-step treatment system for ferriferous acid mine drainage

M. Jouini<sup>1\*</sup>, T.V Rakotonimaro<sup>1</sup>, M. Benzaazoua<sup>1</sup>, T. Genty<sup>1</sup>, C.M. Neculita<sup>1‡</sup>

<sup>1</sup> Research Institute on Mines and Environment (RIME), University of Quebec in Abitibi-Temiscamingue (UQAT)

<sup>‡</sup>Corresponding author: RIME-UQAT, Professor, 445 Boul. de l'Université, Rouyn-Noranda, QC, Canada, J9X5E4. Phone: +1 819 762 0971 ext. 2278, Email: [Carmen-Mihaela.Neculita@uqat.ca](mailto:Carmen-Mihaela.Neculita@uqat.ca)

## Abstract

Acid mine drainage (AMD), characterized by low pH and high concentrations of metals and sulfates is preferably treated with passive treatment systems. However, metal-rich residues (solid precipitates) with variable chemical composition and physical properties can be generated. Hence, their characterization is required to better anticipate the fate (stability for disposal, potential recovery, or reuse). In this context, the present study aims to evaluate the leaching potential of solids from a laboratory passive multi-step treatment for Fe-rich AMD. To do so, post-testing solids from three units [Fe-pretreatment reactor (50% wood chips and 50% wood ash- WA50), passive biochemical reactor - PBR for  $\text{SO}_4^{2-}$  treatment (30% inorganic materials, 70% organic substrate), and polishing unit (50% calcite and 50% wood chips - C50)] of a pilot passive treatment system were sampled. Then, physicochemical and mineralogical characterizations, as well as static leaching tests were performed. Results showed that all solids had high neutralizing potential. Significant metal concentrations were particularly found in WA50. Metals in all solids were precipitated in the form of oxyhydroxides, oxyhydroxy-sulfates, carbonates, sulfides, sulfate and native sulfur. Fe was not a problematic contaminant. However, a probable new formation of contaminated neutral drainage by Ni and Zn could occur from WA50. C50 had the most significant acid neutralizing capacity and could therefore resist to acid aggression. PBR and C50 were considered as non-hazardous and a potential co-disposal with municipal wastes could be a storage option. Further studies should be undertaken by testing other leaching and kinetic tests to assess long-term metal stability.

## Keywords

Mine water treatment residues, mine residue, waste management, TCLP, acid neutralizing capacity

## Introduction

Exploitation of mineral resources can generate large quantities of waste, including process sludge and tailings. These materials can generate contaminated drainage such as the acid mine drainage (AMD), which is characterized by low pH and high concentrations of metals, metalloids and sulfates [1]. The AMD is caused by the oxidation of pyrite and other sulfidic minerals in presence of water and oxygen [2]. This acidic water is highly toxic and may have harmful effects on humans, animals and plants once mixed with groundwater, surface waters or soils [3, 4]. AMD is a worldwide issue in mining with significant environmental impacts that require responsible management [5]. Passive treatment systems (chemical/biological) are presently preferred to treat AMD impacted-waters in closed and/or abandoned mine sites, particularly as a multi-step system or a combination of several passive treatment units with high contamination [6–8, 11, 12]. However, these systems have a limited effectiveness due to hydraulic issues by decreasing the permeability (clogging), passivation and formation of preferential flow [13]. In order to limit these issues, the use of dispersed alkaline substrate (DAS) such as  $\text{CaCO}_3$ -DAS [14–16],  $\text{MgO}$ -DAS [17, 18],  $\text{CaMg}(\text{CO}_3)_2$ -DAS and wood ash (WA)-DAS [16] was proposed. At the same time, passive treatment systems generate residues (metal-rich solid precipitates) with variable chemical composition and physical properties, depending on water quality to be treated [3, 19]. As their stability is inconsistent, a case by case management approach is often necessary. Indeed,

the analysis of Fe-rich solids from passive biochemical reactors (PBRs) showed that Fe was precipitated as sulfides and oxyhydroxides, which must be stored under water with a near neutral pH [8]. It was also recommended that metal-rich solids (Fe, Al and Zn) from DAS systems used for AMD passive treatment should not be disposed in landfill and have to be stored in a dry environment [3]. A proper management of metal-rich residues generated during the treatment of AMD is then necessary to control and prevent the possible metals release. The toxicity characteristics leaching procedure (TCLP) is commonly used to identify if a pre-treatment of the residues is necessary before their disposal [20]. The TCLP is also used to evaluate the possible co-deposition of different residues and for the classification of hazardous waste [3, 20]. However, the TCLP has the disadvantage to take into account only As, Ba, Cd, Cr, Ni and Pb while other pollutants such as Fe, Zn, Al are not considered. The pH-dependent leaching test ( $\text{pH}_{\text{stat}}$ ) is therefore used to evaluate the potential disposal and the stabilization effectiveness of solid residues (mining waste, soil, sludge, combustion residues, sediments, stabilized materials, construction) [21, 22].

In this context, the main objective of this study was to evaluate the leaching potential of the solids from a laboratory passive multi-step treatment for Fe-rich AMD composed of DAS-based and PBR units, to better anticipate their potential fate (stability for disposal, potential recovery, or reuse).

## Materials and methods

### *Sampling*

Solid residues resulting from a multi-step passive treatment system were sampled in order to evaluate the stability and potential environmental risks [13]. These solids were sampled after being tested in long-term (over 1-year period) for the treatment of a highly contaminated AMD which was characterized by  $1.6 \pm 0.6$  mg/L Al,  $2350 \pm 330$  mg/L  $\text{Fe}_{\text{tot}}$ ,  $33.5 \pm 3.8$  mg/L Mg,  $8.2 \pm 1.0$  mg/L Mn,  $0.7 \pm 0.4$  mg/L Ni,  $0.2 \pm 0.1$  mg/L Pb,  $0.2 \pm 3.0$  mg/L Zn,  $430 \pm 5$  mg/L Ca,  $5073 \pm 407$  mg/L  $\text{SO}_4^{2-}$  and pH  $3.04 \pm 0.45$ . Results showed that the pH increased 8.09, and Fe and sulfate removal exceeds 99% and 46-74%, respectively. More details including the initial characterization of solids are provided elsewhere [13]. Precisely, the samples originated from a Fe-pretreatment reactor WA-SAD (50% wood chips and 50% wood ash- WA50), a PBR for  $\text{SO}_4^{2-}$  treatment (10% sand, 40% wood chips, 20% chicken manure, 10% compost and 20% calcite), and a polishing unit  $\text{CaCO}_3$ -SAD (50% calcite and 50% wood chips - C50). Prior to their analysis, the solids were stored at  $T < 4^\circ\text{C}$ , carefully identified and sealed in a double sealed containers (ziploc). Handling of solids from the PBR was performed in a controlled atmosphere (anaerobic) chamber to avoid the potential changes in metal and sulfur speciation.

### *Physicochemical and mineralogical characterization*

The physicochemical characterization consisted of determining the paste pH and chemical composition. The paste pH was measured in deionized water using a solid to liquid ratio of 1:10 (Method D4972-95a) with a double junction electrode Orion GD9156BNWP of Thermo Scientific coupled with a VWR SympHony SB90M5 multimeter (relative accuracy  $\pm 0.01$  pH) in order to provide rapid and inexpensive preliminary information about the acid generation or neutralization potential [23]. Chemical composition was analyzed on dried ( $60^\circ\text{C}$ ) and homogenized samples (150  $\mu\text{m}$ ) after their digestion (with  $\text{HNO}_3$ ,  $\text{Br}_2$ ,  $\text{HCl}$ , and  $\text{HF}$ ). The digestate was analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; relative precision of 5%) using a Perkin Elmer OPTIMA 3100 RL. In order to assess metal removal mechanisms, mineralogical characterization was also carried out using a scanning electron microscope (SEM) equipped with Energy Dispersive X-ray Spectroscopy probe (EDS) HITACHI S-3500N (voltage of 20 kV, amperage of 140 A, pressure around 25 kPa and work distance of 15mm). Prior to SEM-EDS analyses, samples were dried in a glovebox (model 855-AC PLAS LABS, Inc.), which was operated under controlled atmosphere (sparging with  $\text{N}_2$ ) to maintain anaerobic condition and prevent moisture. Images,

elemental maps and chemical composition were recorded with a data processor INCA (Oxford Energy 450). Crystalline phases of the secondary precipitates were analyzed by a X-ray diffractometer (XRD) (Bruker axs D8 ADVANCE) equipped with a Cu anticathode and a scintillation counter. The XRD analyses were carried out on dried (in a glovebox at room temperature) and grinded (10  $\mu\text{m}$ ) samples (detection limit <1% w/w). The data was collected and interpreted for minerals identification and quantification with Bruker axs EVA and TOPAS software packages.

### *Leaching tests*

Two static leaching tests, including TCLP and  $\text{pH}_{\text{stat}}$  tests were performed. The TCLP, which is a single-batch method, evaluated the potential mobility of inorganic contaminants in solids [20, 24]. In order to select the appropriate leaching medium, a pre-test was carried out, consisting of mixing and stirring for 5 minutes of a wet sample with 96.5 mL of deionized water, then adding 3.5 mL of HCl (1N). The mixture was then heated at 50°C and agitated continuously. After cooling, the pH was measured with the same equipment as previously presented. If the  $\text{pH} < 5.0$ , the leaching medium number 1 ( $\text{pH} 4.93 \pm 0.05$ , prepared with sodium hydroxide dissolved in deionized water and mixed with the acid glacial acetic acid) was used. If the  $\text{pH} \geq 5.0$ , the leaching medium number 2 ( $\text{pH} 2.88 \pm 0.05$ , prepared with glacial acetic acid and deionized water) was used. After the pre-test, the TCLP tests (duplicated) were then performed, using the previously selected leaching solutions in a liquid to solid (L/S) ratio of 20:1 and stirred for 18 hours at room temperature. Afterward, the pH, Eh, electrical conductivity (EC) and chemical composition of the eluates were measured. The Eh redox potential (values were corrected to standard hydrogen electrode (SHE)) was measured using an Orbisint CPS12-OPA2GSA Pt/Ag/ AgCl electrode related to a Benchtop Meter Symphony B30PCI ( $\pm 0.1$  mV). The EC was measured using a portable Oakton Acorn CON 6 ( $\pm 0.001$  mS/cm). The eluate (after centrifugation) was filtered (0.45  $\mu\text{m}$ ) and acidified (2%  $\text{HNO}_3$ ) for elemental analysis by ICP-AES. The  $\text{SO}_4^{2-}$  concentration was determined on filtered samples (0.45  $\mu\text{m}$ ) with a DR/890 HACH colorimeter (Method 8051 [44]). The  $\text{pH}_{\text{stat}}$  leaching test aims to determine the buffering capacity or the acid neutralizing capacity (ANC) of the solids as well as to better evaluate the contaminants' chemical speciation and behavior under changing environmental conditions as a function of pH [21, 25]. The  $\text{pH}_{\text{stat}}$  tests were performed with nine parallel batch according to the Method 1313 [20], consisting of mixing the solids with water, with diluted acid ( $\text{HNO}_3$ ) or with diluted base (NaOH) to obtain leachate pH ranged from 2 to 12 [25]. The leaching parameters (dry mass of solid, contact time and volume of the extraction bottle) depend on the particle size of the tested material. The mixtures were placed in rotated beakers at a constant speed of  $28 \pm 2$  rpm with L/S of 10:1 (at room temperature). Afterward, the pH was measured and the leachate was centrifuged, filtered (0.45  $\mu\text{m}$ ) and then acidified (2%  $\text{HNO}_3$ ) for elemental analysis by ICP-AES. Because using only the TCLP limits are insufficient to classify the solids [3,4], results from the TCLP tests were compared to different threshold limits: 1) Québec's provincial regulation D019 [26], 2) Canadian discharge limits as specified in the metal mining effluent regulation (MMER) [27], 3) worldwide or universal treatment standard (UTS) [28] and, finally, 4) the criterion of continuous concentration (CCC) [29]. Results from the  $\text{pH}_{\text{stat}}$  were compared to both D019 and MMER threshold limits.

## **Results**

### *Physicochemical characterization of solids from the treatment system*

Results showed that all solid residues presented a neutral to weakly basic paste pH of 6.8–8.5. Solids from the WA50 showed the lowest pH value (6.9–7.8), and C50 the highest (8.1–8.5). The low paste pH of WA50 was explained by the acidic water (AMD) that fed this pre-treatment unit. As expected, due to the high contaminant load in the AMD [13], metal concentrations in the WA50 were very high and explain the important role of this Fe-pretreatment unit. The As, Cr, Cu, Mn, and Zn concentrations were below the detection limit (<5 mg/kg) in PBR and C50. High Fe concentration was found in WA50 ( $42000 \pm 900$  mg/kg). The Al was also found in all solids with the highest value in WA50 with a mean

of  $2600 \pm 2500$  mg/kg for WA50,  $5476 \pm 408$  mg/kg for PBR and  $966 \pm 300$  mg/kg for C50. Noteworthy, Mn was mainly found in WA50, around  $1300 \pm 300$  mg/kg, which was attributed to the high buffering capacity of the mixture during the first phase of the treatment [30]. Similarly, Cr, Cu and Zn were only detected in WA50, as a confirmation that these elements were originating from the wood ash. Total S in all solids varied from 7600 to 17000 mg/kg, with the highest value of  $11000 \pm 500$  mg/kg found in WA50, probably due to a reduction of sulfates or to the formation of sulfate based precipitates. The high concentration of Ca in C50 (mean of  $364 \pm 16$  mg/kg) showed an important dissolution of neutralizing material (calcite).

#### Mineralogical characterization of solids from the treatment system

Mineralogical quantification by XRD was complex to carry out because of detection limit of the method (5%, depending on the mineral crystallinity) and the solids contained significant amorphous phases as well as a high content of organic matter. For solids from the WA50, the identified peaks mainly correspond to silicate (quartz, albite and orthoclase), Fe-oxyhydroxides (hematite and magnetite), carbonates (magnesium calcite and siderite), sulfates (anhydrite), Fe-hydroxysulfates (jarosite), sulfide minerals (troilite) and native sulfur (Fig. 1). These results were not in agreement with the results previously reported during the treatment of ferriferous AMD, where a XRD analysis detected no peaks of Fe-oxyhydroxides because of their poor crystallinity [30]. The potential cause of this inconsistency could be explained by the difference of the operating time (2 months, Rakotonimaro *et al.* [30] versus 1 year in this study). For solids from PBR and C50, XRD showed that quartz and calcite were predominantly present in the crystalline fraction (Fig. 1).

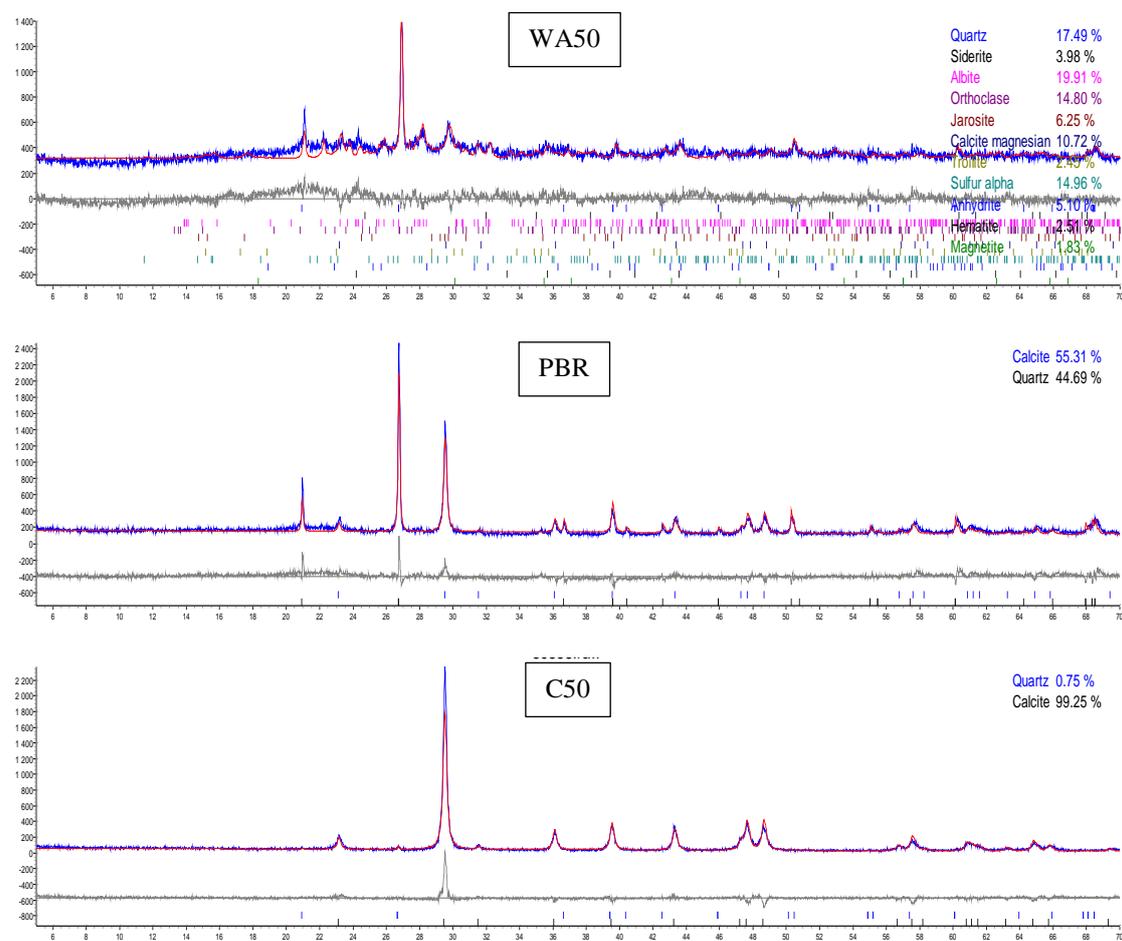


Fig. 1. Results of X-ray diffraction (XRD) analysis the collected solids WA50, PBR and C50

Mineral phases were also observed with the SEM-EDS. In solids from WA50, mineral phases such as quartz, albite, and orthoclase were detected with SEM-EDS (Fig. 2). Fe precipitates such as goethite, hematite, magnetite, jarosite and schwertmannite have been also identified. The  $\text{SO}_4^{2-}$  was identified as calcium sulfate such as anhydrite and bassanite. The surface of wood chips collected from WA50 was partially covered by secondary precipitates of Fe-oxyhydroxides. Oppositely to what was found in other studies, Fe sulfides (mackinawite -FeS and greigite- $\text{Fe}_3\text{S}_4$ ) have not been detected [11]. Nevertheless, similar observations were also reported by Genty *et al.* [31] and Rakotonimaro *et al.* [30]. In addition, carbonate minerals resulting from the precipitation of Fe in the form of siderite ( $\text{FeCO}_3$ ) was not identified as well, contrary to what was found in previous study [30]. The potential cause of this inconsistency could be also explained by the difference of the operating time as previously mentioned.

Elemental mapping of solids from the PBR showed a superposition of Fe, O, Al and C. This observation confirms the precipitation of oxyhydroxides phases of Fe or Al on the surface of organic matter (Fig. 2 & 3). Elemental sulfur (native S) have been also observed (Fig. 4), resulting from bacterial activity with an indirect reduction of Fe (III) that reacts with  $\text{H}_2\text{S}$  [30].

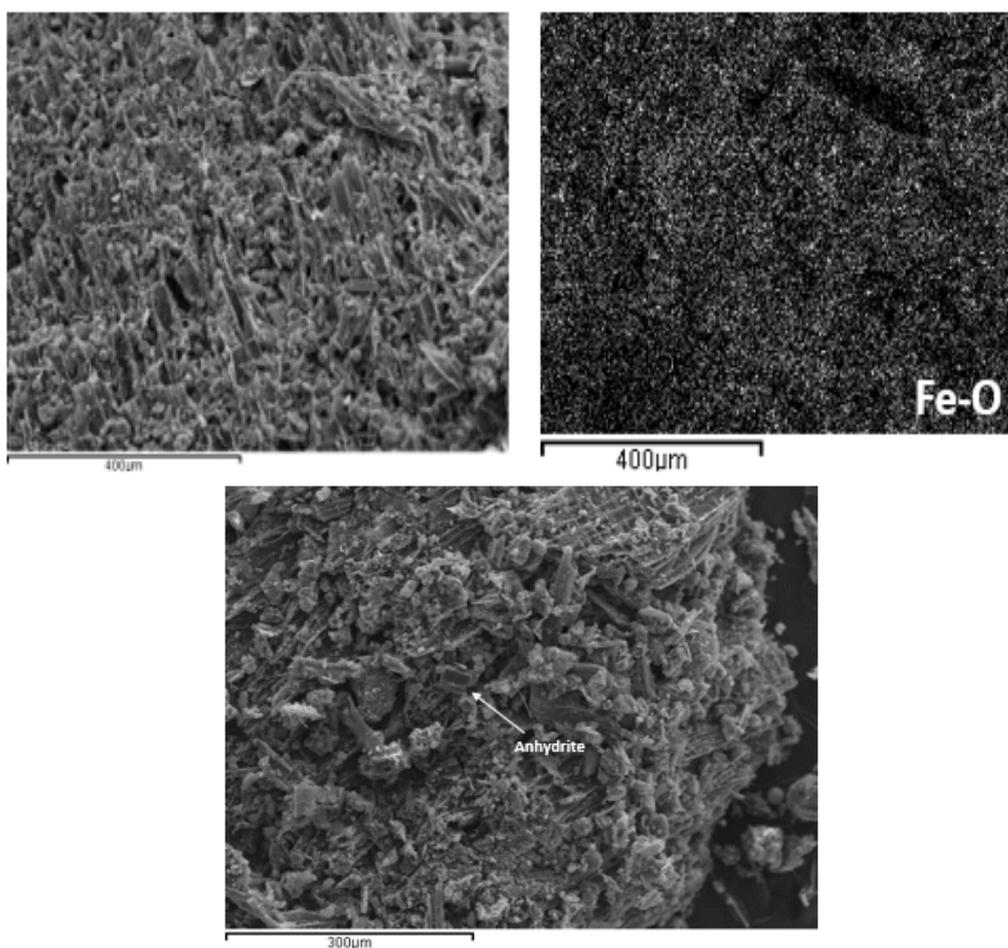


Fig. 2. SEM-EDS image of Fe-oxide/hydroxide and anhydrite in WA50

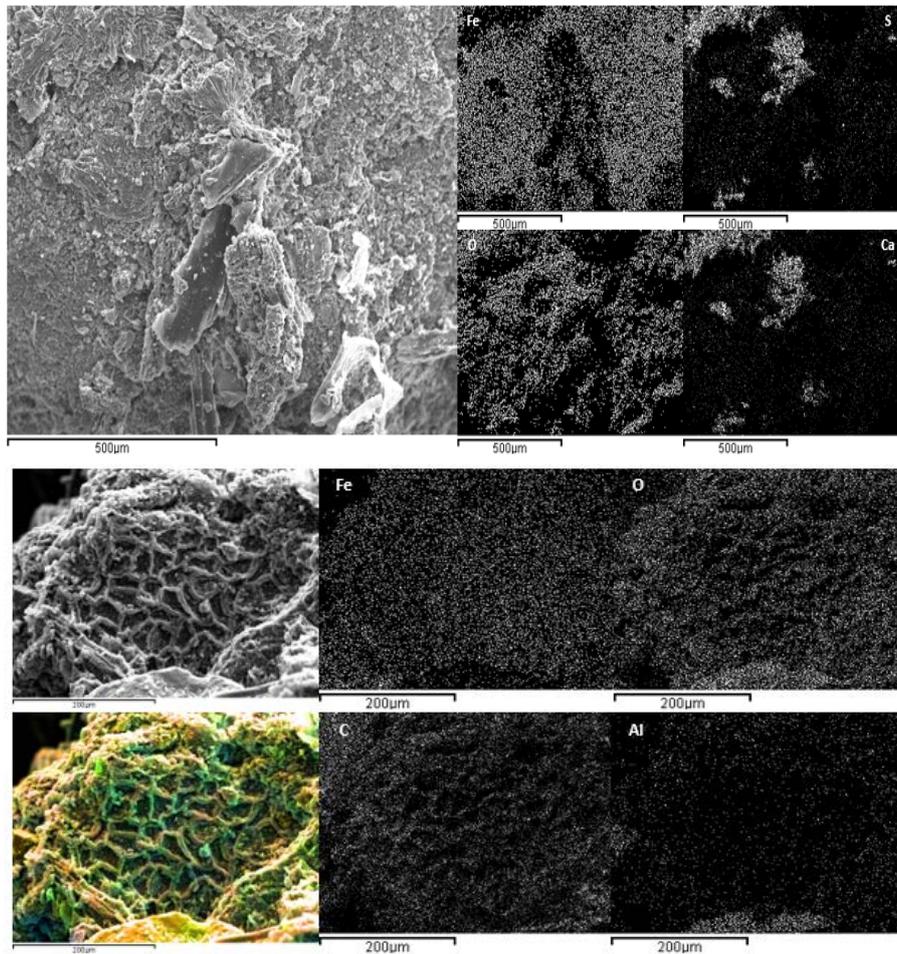


Fig. 3. SEM-EDS image of Fe/Al-oxide/hydroxide phases on wood chips on solids from PBR

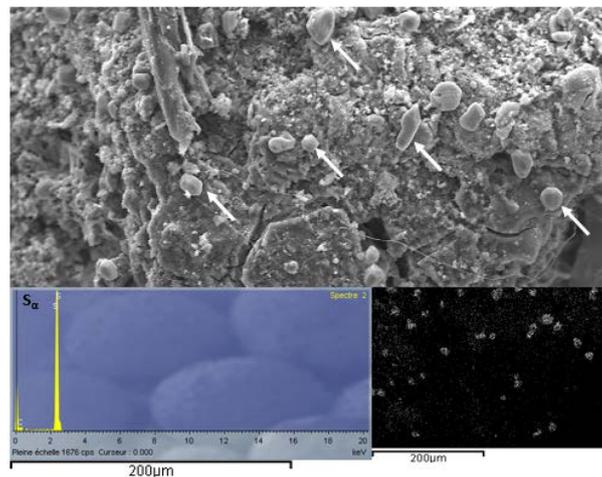
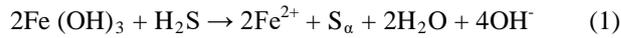


Fig. 4. Image SEM-EDS of native sulfur on solids from the PBR

For solids from C50, Fe-oxyhydroxides were under the form of magnetite, hematite and ferrihydrite (Fig. 5). Gypsum was identified by the superposition of Ca, S and O, as shown by X-ray mapping, in the form of needle and amorphous crystals. Native  $S_{\alpha}$  was also observed between the Fe (oxy) hydroxide layer and the limestone (Fig. 5). The formation of  $S_{\alpha}$  can be explained by the indirect reduction of Fe (III) that reacts with  $H_2S$  [30]. Indeed, if Fe concentration is low relative to that of  $SO_4^{2-}$ , i.e. the ratio  $Fe/SO_4^{2-}$  is low and the saturation index is negative, precipitation of Fe sulfide is not favored. Hence, the excess of  $H_2S$  (resulting from the activity of sulfate reducing bacteria in PBR

that reduces the  $\text{SO}_4^{2-}$  to  $\text{H}_2\text{S}$ ) in the PBR was transferred to the polishing unit (C50) where it was oxidized (Eq. 1) [22]:



It was also noted that Fe precipitates covered the calcite minerals, which could lead to the calcite surface passivation and a decrease in its dissolution rate and long-term reactivity (Fig. 5).

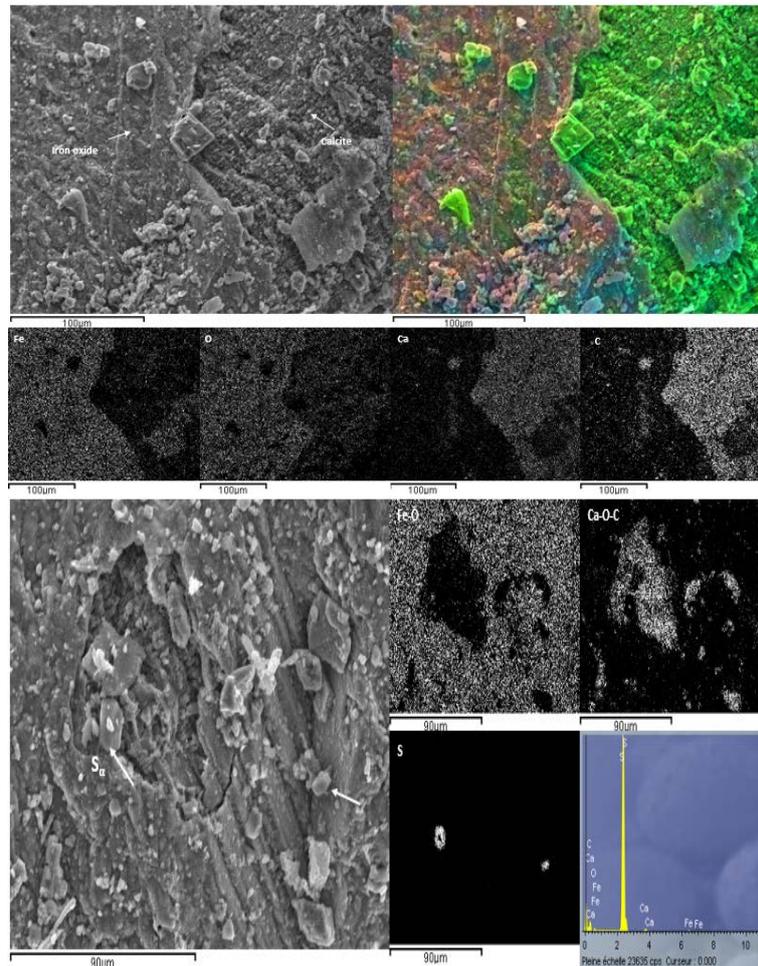


Fig 5. Image SEM-EDS of Fe oxide/hydroxide and gypsum crystals in C50 (left) and native sulfur (right)

#### *Results of the toxicity characteristics leaching procedure (TCLP)*

The leaching solutions used to perform TCLP tests were the leaching medium 1 ( $\text{pH } 4.93 \pm 0.05$ ) on WA50 and PBR and the leaching medium number 2 ( $\text{pH } 2.88 \pm 0.05$ ) on C50. The average pH values of the eluates from all solids varied between 6.80 and 7.82 (Table 1). Eluates from the C50 had the lowest pH value but remained very close to the neutrality despite the low initial pH of the leaching medium (2.88). The Eh values were positive and high (474–500 mV) in all collected eluates, indicating oxidized conditions. The EC was also high (6.07–6.88 mS/cm), showing high total dissolved solids in the eluates. It is noted that the leaching capacity is strongly related to the initial pH of the leaching medium; the lower is the leaching medium's pH, the higher is the transfer of elements to the liquid phase i.e. the eluates [32].

**Table 1.** Physicochemical characteristics of the eluates after TCLP tests

Parameters	WA50	PBR	C50
pH	6.80–7.58	7.45–7.82	6.88–6.92
Eh (mV)	486–500	474–479	493–495
Conductivity (mS/cm)	6.14–6.88	6.07–6.13	6.52–6.44
SO <sub>4</sub> <sup>2-</sup> (mg/L)	210–540	155–370	0

Regarding the chemical composition, Ca is the most mobile element in the eluates from C50, WA50 and PBR (2098±34 mg/L; 762±84 mg/L and 616±93mg/L, respectively). The high values of Ca from C50 were attributed to the dissolution of calcite (50%) in the mixture. The Mg concentration in the eluate from the PBR is higher than those in WA50 and C50 (44.07±30 mg/L, 23.15±4.4 mg/L, 8.65±0.7 mg/L, respectively). The leached Cu was assumed to be originated from the substrates (WA50, PBR and C50) because the AMD does not contain Cu [30]. However, Ni concentration in the pretreatment unit i.e. WA50 (0.52±0.77 mg/L) was higher compared to D019 and MMR limits (Table 2). Significant Zn concentration was also noted in the eluates from WA50 (6.80±10 mg/L), which exceeds the UTS' regulatory limit of 4.3 mg/L. Noteworthy, the high concentrations of Ni and Zn in the leachates are mainly due to high solubility at near neutral pH (6.8-7.82) [1, 34, 35]. Because of the existing heterogeneity of all solids, the relative standard deviations were low only for Ba and variable for Fe, Ni and Zn (Table 2).

**Table 2.** Concentrations of metals in the eluates collected after TCLP tests compared with standard regulations

Standard	Metals									
	Al	As	Ba	Cd	Cr*	Cu	Fe	Ni	Pb	Zn
WA50 (this study)	0.03±0.01	0	0.31±0.10	0	0.003±0.002	0.01±0.01	0.08±0.05	<b>0.52±0.77</b>	<b>0</b>	<b>6.80±10</b>
PBR (this study)	0.02±0.01	0	0.23±0.09	0	0	0.01±0.003	0.18±0.17	0.01±0.01	0	0.12±0.07
C50 (this study)	0.02±0.01	0	0.22±0.04	0	0	0.01±0.01	0.09±0.01	0.01±0.01	0	0.17±0.10
D019 <sup>1</sup> (mg/L)	-	0.2	-	-	-	0.3	3	0.5	0.2	0.5
MMER <sup>2</sup> (mg/L)	-	0.5	-	-	-	0.3	-	0.2	0.5	0.5
TCLP (mg/L)	-	5	100	1	5	-	-	-	5	-
UTS <sup>3</sup> (mg/L)	-	5	21	0.1	0.6	-	-	11	0.75	4.3
CCC <sup>4</sup> (µg/L)	87	150	-	720	74	-	1000	52	2.5	120

\*Limit value for CCC associated with Cr(III); total Cr for all other regulatory limits

<sup>1</sup> Québec's provincial regulation

<sup>2</sup> Canadian discharge limits as specified in the metal mining effluent regulation

<sup>3</sup> The worldwide or universal treatment standard (UTS)

<sup>4</sup> The criterion of continuous concentration (CCC)

According to the concentrations of As, Ba, Cd, Cr, and Pb in the eluates from all solids, WA50, PBR and C50 could be considered as non-hazardous wastes. These results were consistent with previous study where DAS residues rich in Fe, Al and Zn were classified as non-hazardous materials according to the TCLP limits (and compared with other regulatory limits), but should be treated before disposal [3]. Metal concentrations in the eluates from PBR and C50 are lower compared to all regulations' limits and do not require preliminary treatment before their release in the natural environment. Fe concentrations were very low from all solids and below all the existing regulation limits with values of 0.08±0.05 mg/L for WA50, 0.18±0.17 mg/L for PBR and 0.09±0.01 mg/L for C50 (Table 2). This could be due to the pH value of the leaching medium (4.93) for PBR and C50, where redissolution of Fe precipitates were limited (Fe mainly under the form of schwertmannite and goethite) [3, 36, 37].

#### Results of the pH-dependent leaching tests

The pH<sub>stat</sub> curves showed the variation of ANC and the pH values of solids as a function of added acid (HNO<sub>3</sub> >0 meq/g dry solid) or base (NaOH <0 meq/g dry solid) (Fig. 6). Solids from the polishing unit (C50) had the highest ANC and WA50 the lowest (C50>PBR>WA50). The trend of C50 curve remained stable at approximately pH 6 (at 2–14 meq H<sup>+</sup>/g dry solid), which probably corresponds to

the consumption of the residual calcite in the materials, showing its higher buffering capacity (Fig. 6). The C50 could therefore resist upon acid aggression. In addition, the natural pH was slightly higher (7.9) compared to that of PBR and WA50 (7.3 and 6.9, respectively). These results are in agreement with the results of inorganic C which value was higher in C50 compared to PBR and WA50 (>10%, 3.8% and 0.3%, respectively). Above 14 meq H<sup>+</sup>/g, the pH of C50 drops to less than 2, meaning a loss of ANC. The pH slopes of PBR and WA50 showed that these materials have a low resistance to acid attack.

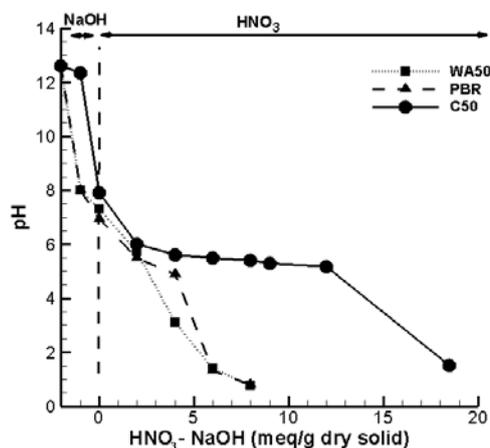


Fig 6. Buffering capacity of the three solids WA50, PBR and C50

The leaching of As, Al, Ca, Fe, Cu, Ni, SO<sub>4</sub><sup>2-</sup> and Zn increased when the pH decreased. Moreover, a significant amount of these elements has also been leached in the alkaline pH zone, in particular Al, Cu, Fe, Ni and Zn (Fig. 7). In general, for all elements, low dissolution was found at pH 7–9 (Fig. 7).

The leaching of Al from all solids occurred at pH<4 and pH>12. The Al leaching is mainly related to the dissolution of amorphous hydroxides at pH< 5 [31, 38, 39]. The Al originating from WA50 and PBR was strongly leached at pH<5 with the highest concentration from WA50 (about 30 times higher than from the PBR, 520 mg/L vs 20 mg/L, respectively). However, Al concentration was <1.1 mg/L over the entire pH range for C50 (Fig. 7). The minimum leaching of Al (0.01 mg/L) appears to be in neutral to slightly alkaline solutions (pH 7 to 8) for all the three types of solids. The Fe concentration was low (<0.2 mg/L) from all solids for pH 6.5–8. However, outside this range, the concentrations were significantly high (2–2000 mg/L). At pH <4, Fe concentration in WA50 was higher (1100 mg/L) compared to PBR and C50 (800 mg/L and 100 mg/L, respectively). The high concentrations of Fe under acidic conditions are probably due to the dissolution of oxyhydroxides of Fe (III), which are often poorly crystallized [40]. In addition, sorption phenomena play an important role for the release of Fe because it could be adsorbed to organic matter in PBR mixtures and wood ash [4, 31]. At pH>4, Fe concentration from PBR was higher compared to WA50 and C50. Low concentrations of SO<sub>4</sub><sup>2-</sup> (<100 mg/L) were found with pH>7. Conversely, at pH<5, high release of SO<sub>4</sub><sup>2-</sup> was detected from all solids. The As was weakly leached in PBR and C50 relative to WA50, which concentration exceeded the limits of D019 (0.2 mg/L) for pH value below 3 and greater than 11 while remaining below the MMR limits (0.5 mg/L) over the entire pH range. The leaching of As in WA50 was probably due to the dissolution of Fe-oxyhydroxides where As was co-precipitated and adsorbed [41–43]. The high concentration of Ca at pH<8 from all solids indicated the high and fast dissolution of carbonate to neutralize the acidity. High concentration of Ni was found at acidic and strongly basic pH for WA50 and PBR. Oppositely, Ni concentration from C50 was low and stayed stable in acidic zone, and even at pH>8, its concentration (< 0.02 mg/L) remains below the limits of D019 and MMR. Dissolution of Zn was maximal at pH <6, where WA50 presented the higher value (190 mg/L).

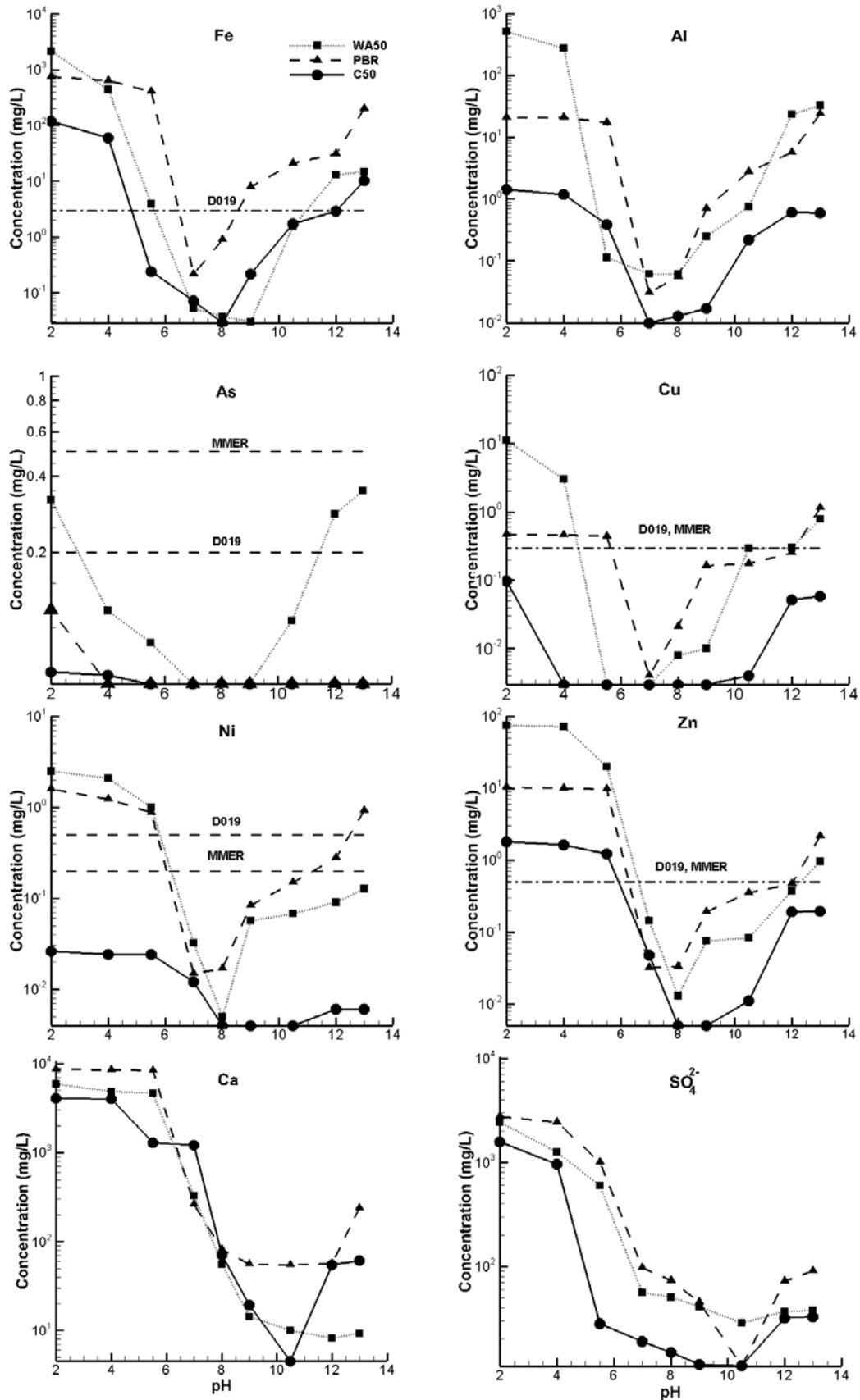


Fig. 7. Leaching of elements from WA50, PBR and C50 according to pH during pH<sub>stat</sub> test

### *Comparison of TCLP and $pH_{stat}$ tests with other regulation limits*

Based on the TCLP results and according to limits of TCLP, D019, MMER and UTS limits, solids from the PBR and C50 were considered as non-hazardous. The concentration of Ni and Zn were found high from WA50 than the regulations limit of D019 and MMER. Disposal in landfill could be considered as a storage option for WA50 because Zn is not an underlying hazardous constituent [33]. However, if Ni concentration was taken into account, WA50 is considered as a hazardous residue that could not be stored or co-disposed with municipal wastes. According to D019, MMER, TCLP and UTS regulations, PBR and C50 could be considered as non-hazardous waste. However, with the CCC limits, all solids could be hazardous with consideration of Zn concentration (and Ni concentration for WA50). Disposal of all solids in neutral to slightly basic pH areas is recommended. Based on the  $pH_{stat}$  test, disposal in a surface impoundment, waste pile or landfill could be considered for all solids and would respect the threshold values of D019 and MMER. at pH range of 7–8. Under these conditions, the solids could withstand environmental stresses and aging (absorption of carbon dioxide, contact with acid rain, mixing with other materials) often encountered in landfill sites. Outside the indicated pH range (7–8), all solids could be considered as hazardous materials and could be classified according to their environmental hazard as follows: WA50 > PBR > C50.

### **Conclusion**

In summary, the present study evaluated the leaching potential of contaminants from solid residues of a laboratory passive multi-step treatment for Fe-rich AMD. All solids had high neutralizing potential. Significant metal concentrations were measured in all solids, particularly in the pre-treatment unit (WA50). The TCLP tests showed that Fe was not a problematic contamination. The  $pH_{stat}$  results suggested that all solids should be stored in near neutral to slightly basic pH environment in order to prevent metal release. Comparison with regulation thresholds showed that contaminated drainage with significant concentration of Ni (in the pretreatment unit- WA50) and Zn (in all units) could occurred. The overall findings also suggested that a potential co-disposal with municipal wastes could be a storage option for solids from the PBR and C50. Further studies should be undertaken by testing: 1) other leaching tests (SPLP, CTEU-9, etc.), 2) kinetic test to assess long-term metal stability, 2) stabilisation/solidification approaches, and 4) options for metal recovery.

### **Acknowledgements**

This study was funded by the NSERC (Natural Sciences and Engineering Research Council of Canada), Canada Research Chairs Program and the industrial partners of the RIME UQAT-Polytechnique Montreal, including Agnico Eagle, Canadian Malartic Mine, Iamgold, Raglan Mine-Glencore, and Rio Tinto.

### **References**

- [1] Calugaru, I.L., Neculita, C.M., Genty, T., Bussière, B., Potvin, B., (2016) Performance of thermally activated dolomite for the treatment of Ni and Zn in contaminated neutral drainage. *J. Hazard. Mater.*, 310, 48-55.
- [2] Crane, R.A., Sapsford, D.J., (2018) Selective formation of copper nanoparticles from acid mine drainage using nanoscale zerovalent iron particles. *J. Hazard. Mater.*, 347, 252-265
- [3] Macías, F., Caraballo, M.A., Nieto, J.M. (2012) Environmental assessment and management of metal-rich wastes generated in acid mine drainage passive remediation systems. *J. Hazard. Mater.* 229-230: 107-114.
- [4] Macías, F., Pérez-López R., Caraballo, M.A., Canovas, R.C., Nieto J.M. (2017) Management strategies and valorization for waste sludge from active treatment of extremely metal-polluted acid mine drainage: A contribution for sustainable mining. *J. Clean. Prod.* 141: 1057-1066.
- [5] Park, I., Tabelin, C.B., Magaribuchi, K., Seno, K., Ito, M., Hiroyoshi, N. (2018) Suppression of the release of arsenic from arsenopyrite by carrier-microencapsulation using Ti-catechol complex. *J. Hazard. Mater.* 344: 322-332.

- [6] Skousen, J., Zipper, C.E., Rose, A., Ziemkiewicz, P.F., Nairn, R., McDonald, L.M., Kleinmann, R.L. (2017) Review of passive systems for acid mine drainage treatment. *Mine Water Environ.* 36 (1): 133-153.
- [7] Lee, W., Lee, S., Yun, S., Lee, P., Hwang, Y.S., Kim, S., (2016) A novel method of utilizing permeable reactive kiddle (PRK) for the remediation of acid mine drainage. *J. Hazard. Mater.*, 301, 332-341.
- [8] Genty, T., Bussière, B., Benzaazoua M., Neculita, C.M., Zagury G.J., (2018) Changes in efficiency and hydraulic parameters during the passive treatment of ferriferous acid mine drainage in Biochemical Reactors. *Mine Water Environ.* 1-10
- [9] Neculita, C.M., Zagury, G.J., (2008) Biological treatment of highly contaminated acid mine drainage in batch reactors: long-term treatment and reactive mixture characterization. *J. Hazard. Mater.*, 157, 358–366.
- [10] Genty, T., Neculita, C.M., Bussière, B., Zagury, G.J. (2012) Environmental behaviour of sulphate-reducing passive bioreactor mixture. In: *Proc. of the 9th International Conference on Acid Rock Drainage (ICARD)*, Ottawa, ON, Canada, May 20-26.
- [11] Neculita, C.M., Zagury, G.J., Bussière B. (2008) Effectiveness of sulfate-reducing passive bioreactors for treating highly contaminated acid mine drainage: II. Metal removal mechanisms and potential mobility. *Appl. Geochem.* 23: 3545-3560.
- [12] Genty, T., Bussière, B., Dionne, J., Neculita, C.M., 2016. Passive biochemical treatment of ferriferous mine drainage: Lorraine mine site, Northern Quebec, Canada, *International Mine Water Association (IMWA) Annual Conference: Mining meets Water - Conflicts and Solutions*, Leipzig, Germany, July 11-15, 2016.
- [13] Rakotonimaro, T.V., Neculita, C.M., Bussière, Genty, T., B., Zagury, G.J. (2018) Performance assessment of laboratory and field-scale multi-step passive treatment of iron-rich acid mine drainage for design improvement. *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-018-1820-x>
- [14] Rötting, T.S., Caraballo, M.A., Serrano, J.A., Ayora, C., Carrera, J., (2008) Field application of calcite Dispersed Alkaline Substrate (calcite-DAS) for passive treatment of acid mine drainage with high Al and metal concentrations. *Appl. Geochem.* 23, 1660–1674.
- [15] Caraballo, M. A., Macías, F., Rötting, T.S., Nieto, J. M., Ayora, C., (2011) Long term remediation of highly polluted acid mine drainage: A sustainable approach to restore the environmental quality of the Odiel river basin. *Environ. Pollut.* 159, 3613–3619.
- [16] Rakotonimaro, T.V., Neculita, C.M., Bussière, B., Zagury, G.J., (2016) Effectiveness of various dispersed alkaline substrates for the pre-treatment of ferriferous acid mine. *Appl. Geochem.* 73, 13-23.
- [17] Ayora, C., Caraballo, M.A., Macías, F., Rötting, T.S., Carrera, J., Nieto, J.M., (2013) Acid mine drainage in the Iberian Pyrite Belt: 2. Lessons learned from recent passive remediation experiences, *Environ. Sci. Pollut. Res.* 20, 7837–7853.
- [18] Macías, F., Caraballo, M.A., Rötting, T.S., Pérez-López, R., Nieto, J.M., Ayora, C., (2012) From highly polluted Zn-rich acid mine drainage to nonmetallic waters: Implementation of multi-step alkaline treatment system to remediate metal pollution. *Sci. Total Environ.* 435, 323–350.
- [19] Genty, T., Bussière, B., Benzaazoua, M., Neculita, C.M., Zagury, G.J. (2017) Iron removal in highly contaminated acid mine drainage using passive biochemical reactors. *Water Sci. Technol.* 76: 833-1843.
- [20] USEPA (US Environmental Protection Agency) (1992) Method 1311: toxicity characteristic leaching procedure, SW-846: Test methods for evaluating solid waste - Physical/Chemical Methods. Washington, D.C. <https://www.epa.gov/sites/production/files/2015-12/documents/1311.pdf> (last access 16.04.18).
- [21] USEPA (2012) Method 1313: Liquid-solid partitioning as a function of extract pH using a parallel batch extraction procedure. <https://www.epa.gov/sites/production/files/2015-12/documents/1313.pdf> (last access 16.04.18).
- [22] Johnson, D.B., Hallberg K.B., (2005) Biogeochemistry of the compost bioreactor components of a composite acid mine drainage passive remediation system. *Sci. Total Environ.* 338: 81–93.
- [23] ASTM (American Society for Testing and Materials) 1995 Standard test method for pH of soils. In: *Annual Book of ASTM Standards D4972-95a*, Washington, DC.
- [24] CEAEQ (Centre d'Expertise en Analyse Environnementale du Québec) (2012) Protocole de lixiviation pour les espèces inorganiques, MA. 100 - Lix.com. 1.1. <http://www.ceaeq.gouv.qc.ca/methodes/pdf/MA100Lixcom11.pdf> (last access 16.04.18).

- [25] CEN/TS 14429, Characterization of waste – Leaching behaviour tests – Influence of pH on leaching with initial Acid/base addition, Comité Européen de Normalisation, Brussels, Belgium, 2005.
- [26] Ministère du Développement Durable, de l'Environnement et Lutte Contre les Changements Climatiques (MDDELCC) (2013) Critère de qualité de l'eau de surface. Direction de suivi de l'état de l'environnement. Bibliothèque et Archives Nationales du Québec, QC, Canada, 510p.
- [27] Ministry of Justice (MOJ) (2002) Metal mining effluent regulations (MMER). Fisheries act, SOR/2002-222. <http://laws-lois.justice.gc.ca/PDF/SOR-2002-222.pdf> (last access 16.04.18).
- [28] USEPA (2017) Land disposal restrictions, rules and regulations. <https://www.epa.gov/hw/land-disposal-restrictions-hazardous-waste> (last access 16.04.18).
- [29] USEPA (2016) National Recommended Water Quality Criteria. <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table> (last access 16.04.18).
- [30] Rakotonimaro, T.V., Neculita, C.M., Bussière, B., Zagury, G.J. (2017) Comparative column testing of three reactive mixtures for the bio-chemical treatment of iron-rich acid mine drainage. *Miner. Eng.* 111: 79-89.
- [31] Genty, T., Bussière, B., Benzaazoua, M., Zagury, G.J. (2012) Capacity of wood ash filters to remove iron from acid mine drainage: Assessment of Retention Mechanism. *Mine Water Environ.* 31, pp. 273-286.
- [32] Tsiridis, V., Samaras, P., Kungolos, A., Sakellariopoulos, G.P., (2006) Application of leaching tests for toxicity evaluation of coal fly ash. *J. Env. Toxicol.*, 21, 4, 409-416.
- [33] USEPA (2017) Land disposal restrictions, rules and regulations. <https://www.epa.gov/hw/land-disposal-restrictions-hazardous-waste> (last access 16.04.18).
- [34] Nordstrom, K., Blowes, D.W., Ptacek, C.J., (2015) Hydrogeochemistry and microbiology of mine drainage: an update *Appl. Geochem.*, pp. 3-16
- [35] Stumm, W., Morgan J.J., (1996) *Aquatic chemistry, chemical equilibria and rates in natural waters* (third ed.), John Wiley & Sons, Inc, New York, USA, p. 1022
- [36] Acero, P., Ayora, C., Torrento, C., Nieto, J.M., (2006) The behavior of trace elements during schwertmannite precipitation and subsequent transformation into goethite and jarosite. *Geochim. Cosmochim. Acta* 70, 4130–4139.
- [37] Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L., Wolf, M., 1996. Schwertmannite and the chemical modeling of iron in acid sulfate waters. *Geochim. Cosmochim. Acta* 60 (12), 2111–2121.
- [38] Caraballo, M.A., Rötting, T.S., Verónica, S., (2010) Implementation of an MgO-based metal removal step in the passive treatment system of Shilbottle, UK: Column experiments. *J. Hazard. Mater.* 181, 923–930.
- [39] Vadapalli, K., Klink, M., Etchebers, O., Petrik, L., Gitari, W., White, R., Key, D., Iwuoha E., (2008) Neutralization of acid mine drainage using fly ash, and strength development of the resulting solid residues. *South African J. Sei.* 104, 317-322.
- [40] Theng, B.K.G., Yuan G. D., (2008) Nanoparticles in the soil environment. *Elements*, vol.4, pp. 395-399.
- [41] Cappuyns, V., Swennen, R., (2008) The application of pHstat leaching tests to assess the pH-dependent release of trace metals from soils, sediments and waste materials. *J. Hazard. Mater.* 158, 185-195.
- [42] Razzouki, B., Hajjaji, S., Azzaoui, K., Errich, A., Lamhamdi, A., Berrabah, M., Elansari, L.L., (2015) Physicochemical study of arsenic removal using iron hydroxide. *J. Mater. Environ. Sci.* 6, 5, 144-1450.
- [43] Asta, M.P., Cama, J., Martínez M., Giménez, J., (2009) Arsenic removal by goethite and jarosite in acidic conditions and its environmental implications. *J. Hazard. Mater.*, 171, 965–972.
- [44] APHA (American Public Health Association), 2012. Alkalinity titration, Standard methods for the examination of water and wastewater, 22nd ed. Greenberg A. (Eds), Washington DC, USA.