

Dissolution of calcitic marble and dolomitic rock in high iron concentrated acid mine drainage: application to anoxic limestone drains

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Abstract Oxidation of sulphide mining waste can generate acid mine drainage (AMD) that has the potential to seriously affect the ecosystems. Acid mine drainage is characterised by a high acidity, high concentrations of sulphates and metals. To reduce the environmental impacts due to AMD, neutralisation using limestone drains is an option proposed in the literature and used around the world. The present study focuses on the influence of the carbonate rock mineralogy and their particle size on the neutralising capacity. The tests were performed in two different anoxic conditions: in batch reactors, and in columns having a hydraulic retention time of 15 h. The results showed that the neutralisation capacity of calcite was more important than for dolomitic rock, and smaller particle size gave higher alkalinity production (fine calcite dissolved faster in contact with AMD). A characterization of metal precipitate in sludge and in limestone coating was performed and demonstrated that gypsum, lepidocrocite and goethite were the predominant secondary minerals to be formed. Finally,

this study underlines that anoxic limestone drain cannot be used alone to treat high iron concentrated AMD.

Keywords Mine water treatment · Acid mine drainage · Passive systems · Anoxic limestone drains

Introduction

Acid mine drainage formation and treatment with anoxic limestone drains

Mine drainage is the result of water movement through the components of a mine site, such as mine openings, waste rock dumps, low grade ore piles, and tailings impoundments (e.g. Morin and Hutt 2001). In the absence of a sufficient neutralising potential from the mine waste, mine drainage can become acidic and is then called acid mine drainage (AMD). The production of AMD can be described by a series of chemical reactions catalyzed by bacterial activity (see the following references for more information on these reactions: Kleinmann et al. 1981; Blowes and Ptacek 1994). Briefly, sulphide minerals oxidize and produce sulphuric acid that lowers the pH when the neutralization potential of the waste due to carbonates or silicates is absent or exhausted (Benzaazoua et al. 2004). The low pH of AMD also increases the solubility of some metals and metalloids that can be found in concentrations greater than current regulation criteria.

During mining operations, chemical agents are usually used to treat AMD collected from the mine site (Ritcey 1989). However, in the context of sustainable development, active chemical treatment is not usually considered as a viable option for the long-term rehabilitation of AMD-generating sites. The other water treatment options available

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are the use of passive treatment methods, such as bioreactors with sulphate-reducing bacteria (e.g. Neculita et al. 2007), wetlands (e.g. Skousen and Ziemkiewicz 2005; Barley et al. 2005), and oxic and anoxic limestone drains (e.g. Cravotta 2003); this paper focuses on anoxic limestone drains (ALDs) which is used to treat highly contaminated AMDs, typical of those found in many Canadian hard rock mines.

Anoxic limestone drains are trenches filled with crushed limestone (or carbonate rock) with high calcite content, covered with an impermeable material to ensure top sealing. The stream of contaminated effluent flows under anoxic conditions into the drain by gravity. The AMD dissolves the limestone leading to a calcium and bicarbonate release that reduces the acidity, and increases the pH and alkalinity of the effluent (Hedin et al. 1994; Cravotta and Trahan 1999; Cravotta 2003). The anoxic environment in ALD prevents oxidation of dissolved metals (mainly iron) inside the drain avoiding massive precipitation and drain clogging. Metal precipitates, such as iron oxyhydroxides, are consequently formed at the exit of the drain due to the direct oxidation with oxygen.

Carbonate rocks used in ALD

The most important criteria to select the carbonate rock that constitutes the ALD are the alkalinity production and the neutralisation rate (Cravotta and Watzlaf 2002; Cravotta 2003; Cravotta et al. 2008). Hence, it is usually assumed that carbonate rock used in ALD must have the highest unit surface area possible and a high calcium carbonate content (more than 90% according to Watzlaf and Hedin 1993); unit surface area depends mainly on particle size and internal rock porosity (Morse 1983, suggested that carbonate rock should have a grain diameter below 5 cm). A high unit surface area allows a better neutralization of acidity (Morse and Arvidson 2002) and a high purity in calcium carbonate induces faster neutralization rates (Hedin et al. 1994). However, the high purity of the limestone used in ALD can be detrimental in the long term. Indeed, gypsum precipitates could be formed at the surface and passivate the calcite (Hammarstrom et al. 2003; Huminicki and Rimstidt 2008; Soler et al. 2008). To reduce the influence of this gypsum coating, Huminicki and Rimstidt (2008) recommend using dolomite to neutralize AMD with a very low pH. Although dolomite dissolves more slowly than calcite (Herman and White 1985; Langmuir 1997; Liu et al. 2005), the production of dissolved calcium is less important, and the gypsum formation is reduced. The most successful ALD tests to neutralize AMD reported in the literature used calcite (Cravotta et al. 2008). However, Potvin (2009) showed that dolomite can also be used to neutralize a very acidic AMD.

Objectives and content

Anoxic limestone drains have been applied mainly for the treatment of AMD coming from coal mines (Hedin et al. 1994; Cravotta and Trahan 1999; Cravotta 2003). For this type of AMD, the existing literature shows that ALD can efficiently treat the contaminated water. However, there is only few data on the effectiveness of ALD to treat AMD from hard rock base metal mines, which usually contain higher concentrations of dissolved metals and sulphate (Aubertin et al. 2002) than AMD from coal mines (Bernier 2005).

Therefore, the main objective of this paper was to evaluate at the laboratory scale using batch and column (dynamic) tests, the lifetime and the capacity of ALD to treat highly contaminated AMD from hard rock base metal mines. The influence of different parameters on the performance of ALD was evaluated namely particle size and mineralogy of the crushed carbonate rock, and the characteristics of AMD. The effect of coating on the neutralisation potential of the carbonate rock tested was also investigated.

Moreover, since the recent literature proposes to combine ALDs with other passive systems like sulphate reducing biofilters and peat biofilters to treat highly contaminated AMD (Champagne et al. 2005; Figueroa et al. 2007), the present study provides crucial information on the potential contribution of ALD in a multi-step passive treatment system as an alkalinity-generating step.

Materials and methods

Synthetic AMD solution tested

The tests (batch and columns tests) were carried out using two AMD having characteristics given in Table 1. The

Table 1 Characteristics of the two influent synthetic acid mine drainage solutions (in mg/L except pH)

Component	Used salt	AMD Light	AMD Lorraine
Al	Al ₂ (SO ₄) ₃ ·18H ₂ O	7	7
Cd	CdSO ₄ ·8H ₂ O	1	1
Cr	CrK(SO ₄) ₂ ·12H ₂ O	2	2
Fe	FeSO ₄ ·7H ₂ O	1,600	6,900
Mg	MgSO ₄ ·7H ₂ O	100	100
Mn	MnSO ₄ ·H ₂ O	21	21
Ni	NiSO ₄ ·6H ₂ O	7	7
Pb	Pb(NO ₃) ₂	1	1
SO ₄ ²⁻	Na ₂ SO ₄ ·10H ₂ O	4,200	15,000
Zn	ZnSO ₄ ·7H ₂ O	2	2
pH	HCl/NaOH 1N	55	35

metallic salts used (see Table 1) in the preparation of AMD were dissolved in tap water. The AMD composition given in Table 1 is representative of observed concentrations near AMD generating sites located in Quebec and Canada (e.g. Aubertin et al. 2002). The oxydo-reduction potential of AMD was positive (>500 mV) in both cases. To illustrate the variability of AMD, a highly contaminated (based on a real case called AMD Lorraine; see Potvin 2009, for more details) and less contaminated (called AMD Light) AMD were tested. The AMD Lorraine had a pH of 3.5, a high iron concentration (above 6,900 mg/L) and a sulphate concentration of 15,000 mg/L. The AMD Light had a pH of 5.5, an iron concentration of approximately 1,600 mg/L and a sulphate concentration around 4,200 mg/L.

Batch experiment description

Batch tests are frequently used as a preliminary procedure before the construction of full scale mine water treatment plant (Bernier 2005; Lindsay et al. 2008; Robinson-Lora and Brennan 2009). This type of test allows determining which materials have the best capacity to treat a given AMD (Neculita and Zagury 2008).

The experimental protocol used in this study was adapted from the one proposed by Bernier (2005). The main objective of this experiment was to compare the neutralizing potential of the different carbonate rocks and to observe the influence of particle size in batch tests. Each reactor consisted of a 1.5-L glass jar filled with AMD and the neutralizing material (calcite or dolomite). The reactor was hermetically sealed with a rubber seal and a top cap to maintain an anaerobic environment. The targeted liquid to solid ratio was 0.4. The first batch test series were performed during 150 h (≈ 6 days) under static anoxic conditions with AMD Lorraine to determine the time needed to reach a nearly constant pH. During this test, only the pH was measured. For the second series of batch test (41 h), the anaerobic environment was maintained for a period of 15 h, which corresponds to an optimal hydraulic residence time (HRT) for ALDs (e.g. Hedin et al. 1994). After this period, the treated water was transferred into an open recipient to allow the contact with oxygen and to promote the precipitation of iron hydroxides and gypsum. Parameters such as pH, alkalinity, metals and sulphate concentrations were monitored throughout the entire testing period of 41 h (at 0, 7, 15, 22, and 41 h). The last batch test series were made with coated carbonate rocks coming from column tests after dismantling (see Sect. 2.3.); these tests were performed to quantify the effect of coating on the neutralization capacity of carbonate rocks. The operating conditions were the same as described previously (15 h of anoxia with AMD Lorraine).

Column tests description

Column tests can provide information on the efficiency of treatment in a long term period and simulate more representative environmental conditions (compared to batch tests) that should be closer to a full scale plant (Neculita et al. 2008; Robinson-Lora and Brennan 2009). Five Plexiglas columns of 14 cm diameter and 70 cm height (10.7 L) were filled with the four carbonate rocks described in Table 2; one column (filled with calcite coarse) was run as a duplicate. According to the volume of liquid used to fill the columns, the porosities of the different columns was estimated to be 0.42 for the column with the fine calcite, 0.56 for columns with the calcite intermediate and coarse, and 0.53 for the column filled with the dolomite intermediate. Columns were fed from the bottom with AMD solution to allow constant anoxic conditions. A perforated plastic plate covered with a geotextile was placed at the bottom of the column to uniformly feed the column. The water upflow was set at 6 mL/min to ensure a HRT in the column of approximately 15 h. The flow was controlled by a peristaltic pump and was monitored on a daily basis. At the exit of the column, the effluent was aerated with compressed air before being sent to a clarifier tank. These steps had approximately a hydraulic retention time of 2 h for aeration and 27 h for clarification. As mentioned earlier, the last two stages were implemented to remove iron present in the effluent using the oxidation of ferrous iron to ferric iron, which then precipitate as iron hydroxides. Parameters such as pH, alkalinity, metals and sulphate concentrations were measured at the exit of the column and in the clarifier. A schematic representation of the setup is presented in Fig. 1. To assess the role of AMD characteristics on treatment efficiency, AMD Light and AMD Lorraine were used sequentially for 1 month on the same material.

Sampling and analytical method for water quality evaluation

Water samples were taken twice a week at the exit of columns and clarifiers. Samples were analysed for pH, alkalinity and dissolved metals. The pH was measured with an Orion Triode sensor coupled with a Benchtop pH/ISE Meter Orion model 920 (relative precision ± 0.01). The alkalinity concentration was obtained by titration with sulphuric acid 0.02 N (precision of 1 mg CaCO_3/L) (APHA 1995). Filtered water samples sent to the chemical analysis were preserved with 2% volume of nitric acid at 70% (w/w) before analysis; metal concentrations were evaluated with Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) technique using a Perkin Elmer OPTIMA 3100 RL (relative precision of 5%).

Table 2 Characteristics of carbonate rock used in the different columns (*column 3 and 4 are duplicates)

Type	Calcite			Dolomite
	Fine	Intermediate	Coarse	Intermediate
Mineral composition by XRD				
Calcite (wt%)	95	95	95	<MDL
Dolomite (wt%)	0	<MDL	<MDL	75
Quartz (wt%)	2.5	2.5	2.5	15
Hornblende (wt%)	2.5	2.5	2.5	0
Muscovite (wt%)	<MDL	<MDL	<MDL	9
Kutnahorite (wt%)	<MDL	<MDL	<MDL	0.5
Magnesite (wt%)	<MDL	<MDL	<MDL	0.5
Element abundance by ICP-AES				
Ca (wt%)	35	35	35	16.5
Mg (wt%)	0.5	0.5	0.5	8.7
Al (wt%)	0.01	0.01	0.01	0.9
Mn (wt%)	0.006	0.006	0.006	0.038
Fe (wt%)	0.07	0.07	0.07	0.7
S (wt%)	0.5	0.5	0.5	0.03
Physical characteristics				
Particle size minimum (cm)	0.03	0.8	1.3	0.8
Particle size maximum (cm)	0.8	1.9	3.8	1.9
Relative density of solid grain	2.72	2.67	2.69	2.54
Estimated unit surface area (m ² /m ³)	3,283	224	120	312
Estimated unit surface area (cm ² /g)	12.07	0.84	0.45	1.23
Column characteristics				
Number	1	2	3, 4*	5
Porosity	0.42	0.53	0.56	0.53
Carbonate rock mass (kg)	16.76	15.50	14.89	15.13

Method detection limit (MDL) is 1% for XRD quantification

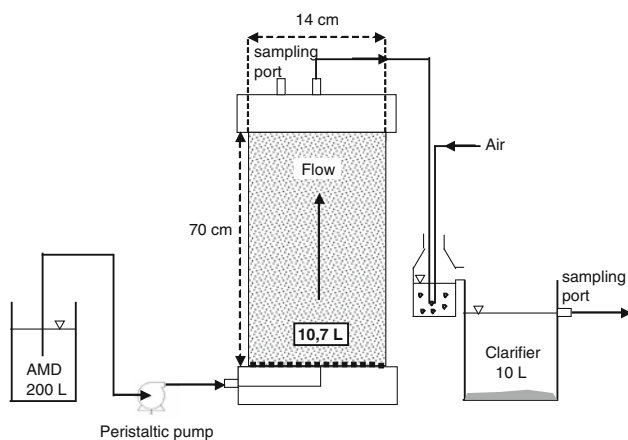


Fig. 1 Schematic diagram of the column laboratory setup (dimensions are not to scale)

Sampling and characterisation of solids

An X-ray diffractometer (XRD; Bruker axS D8 ADVANCE) was used to characterize the mineralogy of solid samples. The instrument is equipped with a Cu anticathode and

scintillation counter. Data treatment was done using Bruker axS EVA and TOPAS software packages. The proportion of minerals was estimated by the Rietveld method (precision of 0.5%). This method uses a least squares approach to refine a theoretical line profile until it matches the measured profile. At the end of the column experiments, coatings from carbonate rock were collected by scraping off the rocks. Recovered materials were then air-dried for 1 week at 35°C. Collected sludge from each clarifier was also air-dried for the same period. Dry samples of the coating and the sludge were crushed to 10 μm before XRD analysis.

However, because the coating and the sludge could be constituted of amorphous minerals, a thermogravimetric analysis (TGA) coupled with a differential scanning calorimetric analysis (DSC) was also performed on both materials using a SDT Q600 TA. This equipment allows simultaneous registry of weight loss and heat flow along thermal treatment. Thermal behaviours were registered in an inert nitrogen atmosphere at a rate of 10°C/min from ambient temperature up to 600°C, and then to 1020°C at 20°C/min. Tests were performed with approximately 35 mg of material placed in a 90-μl alumina cup and

covered by an alumina lid. The thermal behaviour of a given material is directly related to his mineralogy (e.g. Prasad et al. 2006).

A Hitachi 3500-N scanning electron microscope (SEM) was used to characterize the microstructure and texture of coating samples. The main characteristics of the SEM-EDS during measurements on coatings were: voltage of 20 keV; amperage of 140 A; pressure of approximately 25 Pa; and work distance of 15 mm.

To determine the samples chemistry, solids were digested in HNO₃, Br₂, HCl, and HF. Then, the liquid resulting from this treatment was analysed for metal by ICP-AES (relative precision of 5%).

Finally, saturation indices of the main secondary minerals that could influence the water quality at the exit of the columns and clarifiers were calculated using Vminteq version 3. Vminteq is a chemical equilibrium model used to calculate metal speciation and solubility equilibriums. It is probably the most widespread model for these purposes today, and it is renowned for its stability (KTH 2010).

Carbonate rock characteristics

Calcitic marble (called calcite hereinafter) used in this study comes from the quarry of Perth, Ontario (Canada), while the dolomitic rock (called dolomite) comes from the Témiscamingue region in Quebec (Canada). This dolomitic rock contains some detrital silicated minerals. The main characteristics of the two type of carbonate rock are given in Table 2. Particle size distribution was determined using different sieve sizes (see Fig. 2). The particle size analysis shows that dolomite intermediate and Calcite intermediate were relatively similar in term of grain size distribution (minimum and maximum particle size between 0.8 and 1.9 cm). This similarity was useful to compare the influence of the rock source towards treatment efficiencies. The calcite fine and calcite coarse had minimum and maximum particle sizes between 0.03 and 0.8 cm, and 1.3 and

3.8 cm, respectively. The XRD analysis showed that the calcite used was 95% pure in CaCO₃, and contained a small proportion of quartz and hornblende. Dolomitic rock was composed mainly with 75% of dolomite (CaMg(CO₃)₂), 15% of quartz (SiO₂) and 9% of muscovite. Identified gangue minerals (quartz, hornblende and muscovite) were considered inert with respect to AMD neutralization. The elemental abundance showed that calcite contains approximately 35% of calcium and that dolomite contains 16.5% of calcium and 8.7% of magnesium.

The unit surface area A_s can be determined using the distribution of particles size of carbonate rocks and the porosity n ($n = V_v/V_t$; V_v is the void volume and V_t is the total volume).

The parameter A_s (m²/m³ or m⁻¹) can be approximated with Eq. (1) (Monoret 2001):

$$A_s = (1 - n) \int_0^{+\infty} \frac{6}{d_p} f(d_p) dd_p \tag{1}$$

with d_p the diameter of a particle (m) and $f(d_p)$ the frequency of the diameter d_p observed in the particle size distribution (adimensional). Equation (1) can be simplified into Eq. (2) considering the diameter of two consecutive sieves and disregarding the residual part (Monoret 2001):

$$A_s = \frac{(1 - n)}{\Gamma} \sum_i^n \frac{12}{(d_{i+1} + d_i)} \frac{m_i}{M} \tag{2}$$

with the following parameters: d_{i+1} and d_i the diameter of two consecutive sieves (m), Γ a form factor (adimensional), m_i mass of carbonate rock in the sieve i (g), M total mass of carbonate rock (g), and n the number of sieve.

According to Monoret (2001), the form factor for gravel could be approximated to 0.8. The estimation of the unit surface area by Eq. (2) gave the following results: 3283 m²/m³ for calcite fine (or 12.07 cm²/kg considering a measured relative density of 2.71), 224 m²/m³ (or 0.84 cm²/kg considering a measured relative density of 2.66) for calcite intermediate, 120 m²/m³ (or 0.45 cm²/kg considering a relative measured density of 2.69) for calcite coarse and 312 m²/m³ (or 1.23 cm²/kg considering a measured relative density of 2.54) for dolomite intermediate. Other approaches could have been used to estimate A_s (e.g. Chapuis and Légaré 1992) but Eq. (2) was considered adequate in this study.

Carbonate rock dissolution model

Carbonate rock dissolution rate is an important data to assess the lifetime of an ALD. This kinetic data allows determining the carbonate rock weight loss with time, which is recognized as a better parameter than the alkalinity production rate to evaluate the performance of an

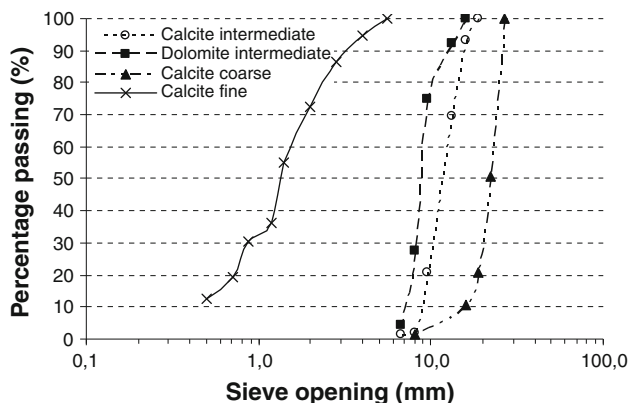


Fig. 2 Particle size distribution of materials

ALD. Indeed, alkalinity cannot be determined if the pH is below 4.5 and most of the time, calcium concentration is measured more accurately than alkalinity (Cravotta and Watzlaf 2002).

Cravotta and Watzlaf (2002) propose to evaluate the dissolution kinetic constant assuming that the flow rate is constant between two measurements of calcium concentration in the effluent and influent of ALD. Therefore, the mass flux of dissolved carbonate rock J_{CaCO_3} in mol/day can be approximated by the following equation considering that 1 mol of dissolved carbonate is equal to 1 mol of calcium in water:

$$J_{\text{CaCO}_3} = Q \cdot ([\text{Ca}]_e - [\text{Ca}]_i) \quad (3)$$

with Q in L/day, $[\text{Ca}]_e$ the calcium concentration in mol/L in the effluent and $[\text{Ca}]_i$ the calcium concentration in mol/L in the influent. Equation (3) allows estimating the daily carbonate rock mass loss.

In order to determine the kinetic constant for the carbonate rock dissolution, it is often assumed that a first order equation appropriately represents adequately the phenomenon (Cravotta and Watzlaf 2002; Cravotta 2003; Mukhopadhyay et al. 2007):

$$\frac{dM}{dt} = -kM \quad (4)$$

with M the carbonate rock weight and k the kinetic constant. The integration of Eq. (4) gives:

$$M_x(t) = M_0 \times e^{-kt} \quad (5)$$

with $M_x(t)$ the carbonate rock weight at the time t and M_0 the initial carbonate rock weight. Then, the kinetic constant k is determined by plotting the logarithm of M/M_0 versus time. Kinetic constant values are valid for a given carbonate rock, hydraulic retention time, temperature, and pressure.

Statistical validity of results

The aim of statistical analysis performed in the present section was to ascertain whether two sets of data from two similar column tests (columns 3 and 4) come from the same population. The statistical approach is similar to the one detailed in the work of Demers et al. (2011). The use of student's t distribution was justified by the relatively limited available data. To compare two series of data, the "Paired-difference test" as a two-tailed test at 95% confidence interval was used (Demers et al. 2011). The method hypothesis was that the difference between the two means of two series of data from two columns was null.

The t test notation became:

$$t = \frac{\bar{d}}{s_d/\sqrt{n}} \quad (6)$$

where \bar{d} was the mean of the paired differences, n was the number of paired differences and s_d was the standard deviation of the paired differences. The hypothesis (data come from the same population) was rejected when the t value obtained with the Eq. (6) was above a pre-determined value (determined in statistical tables for a two-tailed test at 95% confidence interval, $n - 1$ was the degree of freedom). Statistical analyses were performed on alkalinity concentration at the exit of the columns since this parameter is considered representative of carbonate rocks dissolution. Then, the Fischer–Snedecor (Mendelhall and Beaver 1994) was used to compare calcite and dolomite columns (columns 2 and 5). Result were statically different if the ratio between the variance of alkalinity in column 3 and the variance of alkalinity in column 5 was higher than a predetermined value $F_{a,b}^{0,05}$ (function of a the degree of freedom of alkalinity in column 3, b the degree of freedom of alkalinity in column 5, and for a confidence interval of 95%) which can be found in statistical table.

Results

Batch tests

Figure 3 presents the evolution of AMD Lorraine's pH after contact with the four types of carbonate rock during 150 h (anaerobic conditions). The pH after 15 h of anaerobic conditions reached 6.0 for calcite fine, 5.8 for calcite intermediate, 5.7 for calcite coarse, and 5.5 for dolomite intermediate. Between 15 and 150 h, the pH did not evolve significantly. Hence, the value of 15 h recommended in the literature (Hedin et al. 1994) as the optimal HRT is in agreement with results obtained in the present study.

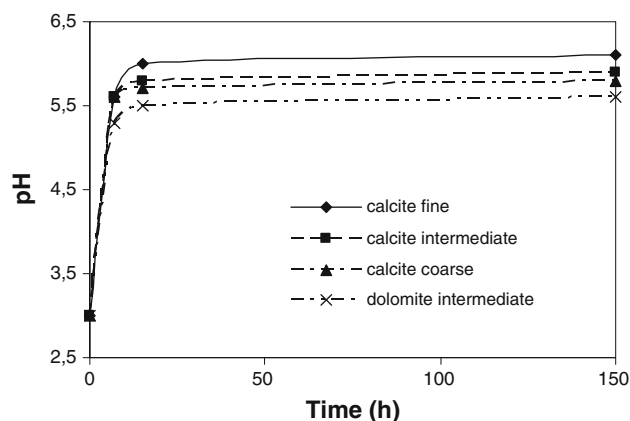


Fig. 3 pH evolution for treatment of AMD Lorraine for an anoxia period of 150 h for the batch test

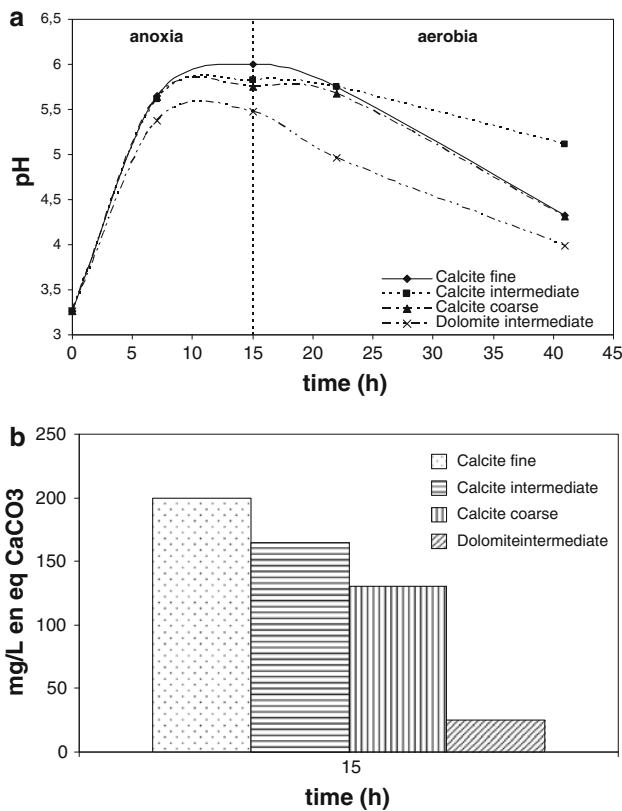


Fig. 4 Chemical parameters measured in batch test experiments for AMD Lorraine, **a** pH evolution and **b** alkalinity concentration (in mg/L CaCO₃) at the final time of anoxia $t = 15$ h (initial alkalinity was below method detection limit of 1 mg/L CaCO₃ in AMD)

The main results of the second series of batch tests, which include an aerobic period, performed with the different carbonate rocks and the two AMDs are presented in Figs. 4 and 5. With the AMD Lorraine (Fig. 4a), there was a rapid increase in pH during the first 7 h of anoxic conditions (from 3.3 to 5.6 for all calcite materials, and from 3.3 to 5.4 for the dolomite). Then, during the next 8 h, a difference in the neutralisation potentials between each calcite was observed; the water quality of the jar filled with calcite fine reached a pH of 6 while the jars filled with the calcite intermediate and calcite coarse reached a pH of 5.8 and 5.7, respectively. For the jar filled with dolomite, the pH reached 5.5 at the end of anoxic period (15 h). After 40 h of treatment (with 25 h of aerobic treatment), the pH decreased to 5.1 for calcite fine, to 4.4 for calcite intermediate and coarse, and to 4.0 for dolomite intermediate. After 15 h of anaerobic conditions (for the AMD Lorraine), the alkalinity (Fig. 4b) increased from 0 to 200 mg/L CaCO₃ for the calcite fine, from 0 to 160 mg/L CaCO₃ for the calcite intermediate, from 0 to 140 mg/L CaCO₃ for the calcite coarse, and from 0 to 20 mg/L CaCO₃ for the dolomite intermediate.

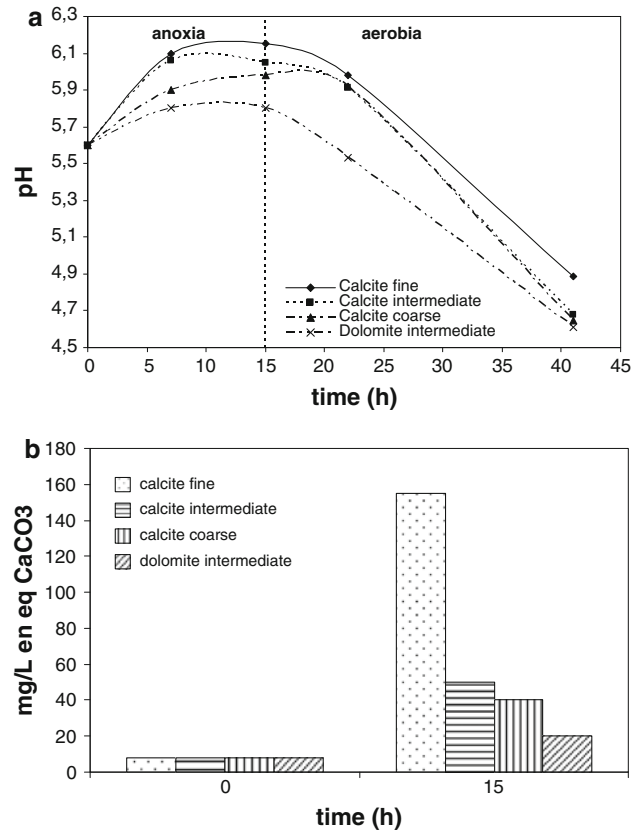
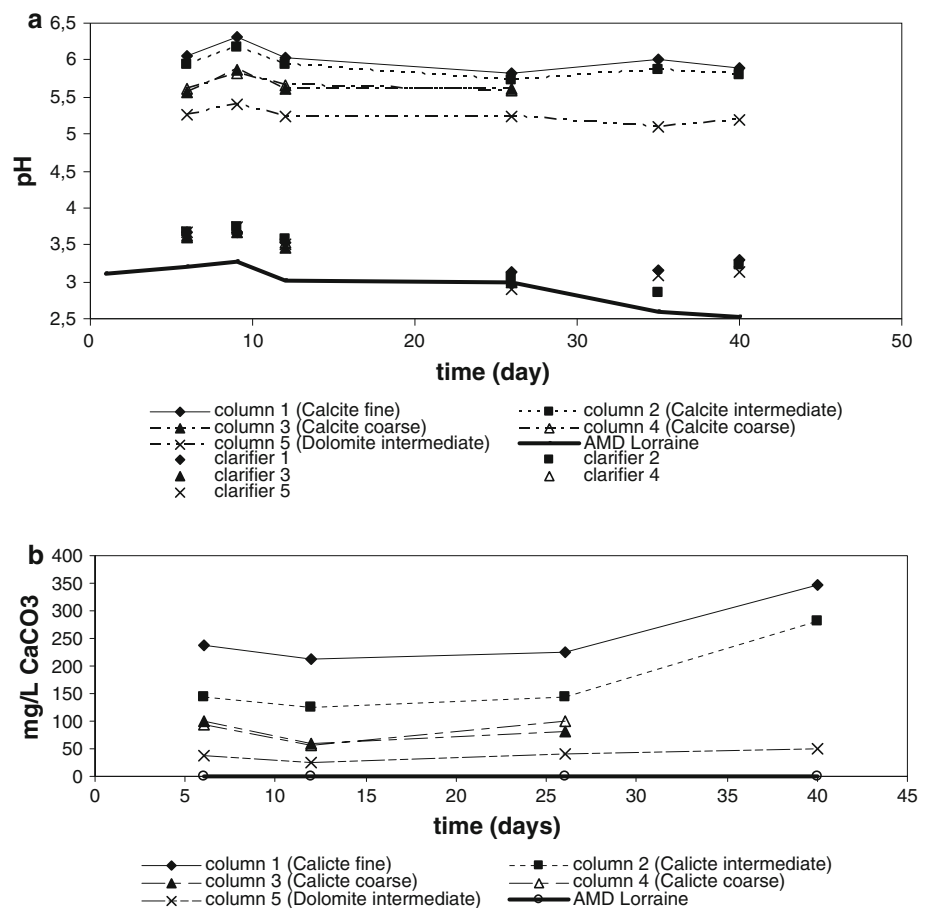


Fig. 5 Chemical parameters measured in batch test experiments for AMD Light: **a** pH evolution and **b** alkalinity concentration (in mg/L CaCO₃) at the initial time $t = 0$ and final time of anoxia $t = 15$ h

For the AMD Light, the effluent pH (Fig. 5a) increased during the anoxic period from 5.6 to 6.2 for the calcite fine jar, to 6.0 for the calcite intermediate jar, to 5.9 for the calcite coarse jar, and to 5.7 for the dolomite intermediate jar. A pH decrease was observed after 15 h (which corresponds to the beginning of the aerobic conditions). After 40 h of treatment, the pH dropped to a value of 4.9 for calcite fine, 4.7 for calcite intermediate and coarse, and 4.6 for dolomite intermediate. The pH decrease was mainly attributed to the hydrolysis of metal and precipitation of iron hydroxide. These results confirmed that the neutralizing potential is higher for calcite than dolomite. In addition, the finer the calcite particles were, the better was the neutralisation. For alkalinity (see Fig. 5b), a similar trend to the one of the AMD Lorraine was observed, but with lower alkalinity values: between 140 and 40 mg/L CaCO₃ for the three calcites, and 20 mg/L CaCO₃ for the dolomite intermediate. These results confirm that a higher production of alkalinity is obtained with fine carbonate rocks, and that dolomite does not generate alkalinity as much as calcite when exposed to a less contaminated AMD (AMD Light).

Fig. 6 Chemical parameters measured in column test experiments for AMD Lorraine: **a** pH and **b** alkalinity concentration (in mg/L CaCO₃). Columns 1, 2, 3, 4, and 5 are filled, respectively, by calcite fine, calcite intermediate, calcite coarse, calcite coarse (duplicate), and dolomite intermediate. Clarifiers 1 to 5 are linked respectively to columns 1 to 5



Columns tests

AMD Lorraine treatment

During the column tests, the dolomite could only increase the pH up to a value of 5.2. The pH increased to values up to 5.6, 5.8 and 6 for calcite coarse, calcite intermediate and calcite fine, respectively (Fig. 6a). These results also confirmed the impact of limestone grain size on the neutralizing capacity (the finer the calcite, the higher is the pH increase). They also showed the higher neutralizing potential of calcite as compared to dolomitic rock. Moreover, the results in columns 3 and 4 (duplicate columns) indicated that the experiments were reproducible. Indeed, statistical results showed that the alkalinity concentration came from the same population for the two duplicate ($t = 0.71$, the theoretical values of t was found at 2.44 for a confidence interval of 95% and a degree of freedom of 6). The alkalinity at the columns' exit ranged between 212 and 346 mg/L CaCO₃ for the calcite fine, 124 and 280 mg/L CaCO₃ for the calcite intermediate, 56 and 100 mg/L CaCO₃ for the calcite coarse, and 26 and 50 mg/L CaCO₃ for the dolomite intermediate (Fig. 6b). As observed in batch tests, the production of alkalinity was higher for

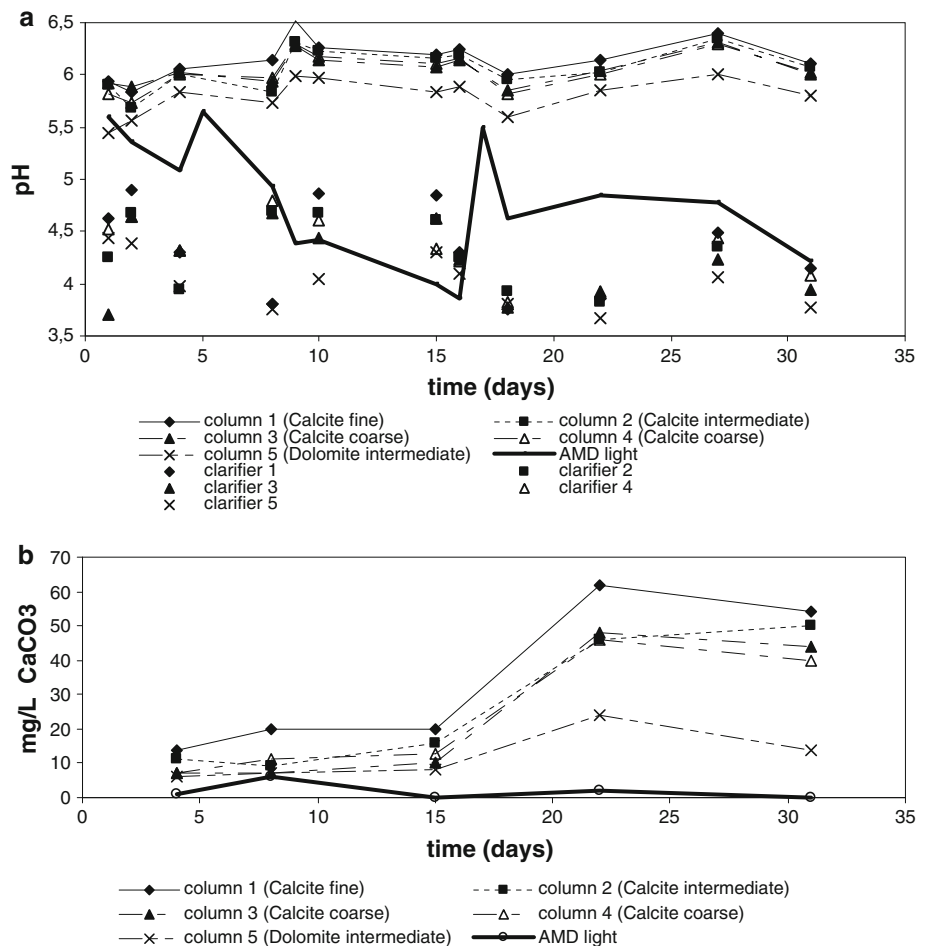
calcite than for dolomite, and fine calcite particles generated more alkalinity due to their higher unit surface area.

Results of pH evolution in the clarifier showed that the pH dropped to a value usually between 3 and 3.7 for all columns. This pH drop results from the precipitation of metals which acidified water by metal (iron mainly) hydrolysis. As a result, at the end of the treatment, the pH was comparable to the pH of the initial AMD (pH of approximately 3).

AMD light treatment

The pH in the column filled with the calcite fine increased from 5.5 to a maximum of 6.5 while calcite intermediate increased the pH up to a maximum of 6.4, calcite coarse to 6.3 and dolomite intermediate to 6 (Fig. 7a). The pH of columns 3 and 4 (duplicate columns) gave similar results and confirmed that the experiments were reproducible. The pH in each clarifier varied from 3.7 to 4.8 whatever the type of carbonate rock; these values were lower than the initial AMD pH. AMD Light was prepared on a weekly basis and adjusted to pH 5.5. However, pH varied and decreased with time due to iron hydrolysis. The same observation was made by Neculita et al. (2008). The

Fig. 7 Chemical parameters measured in column test experiments for AMD Light: **a** pH and **b** alkalinity concentration (in mg/L CaCO₃). Columns 1, 2, 3, 4, and 5 are filled, respectively, by calcite fine, calcite intermediate, calcite coarse, calcite coarse (duplicate) and dolomite intermediate. Clarifiers 1–5 are linked, respectively, to columns 1–5



alkalinity reached a maximum concentration of 62 mg CaCO₃/L for calcite fine, 50 mg CaCO₃/L for calcite intermediate, 48 mg CaCO₃/L for calcite coarse and 24 mg CaCO₃/L for dolomite intermediate (Fig. 7b). Hence, the difference between each column towards the alkalinity production was less significant for AMD Light than for AMD Lorraine for calcite, but the difference between calcite and dolomitic rock stayed observable. In the case of AMD Light, the impact of particle size and carbonate rock mineralogy seemed to be less important than with AMD Lorraine.

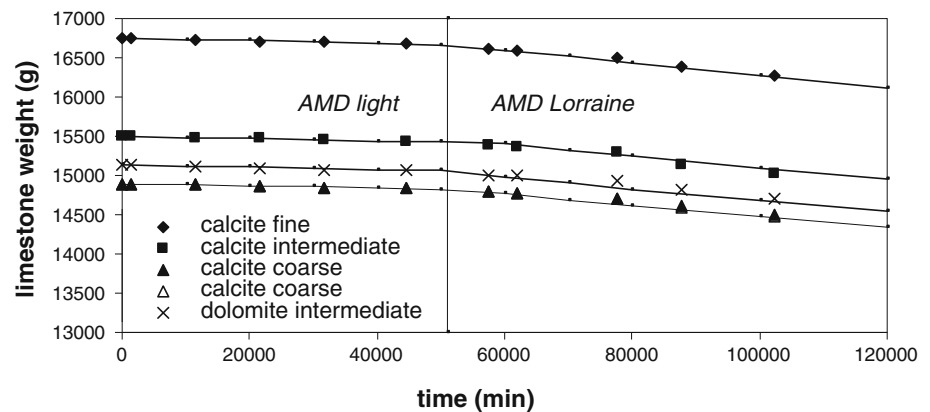
Results interpretation and discussion

Calcite and dolomite dissolution

Calcitic marble and dolomitic rock had not the same dissolution response toward AMD because alkalinity generation depends on the columns and on the AMD quality. This can be observed in Figs. 6 and 7, and is confirmed by statistical results that showed that alkalinity concentration

at the exit of calcite intermediate and dolomite intermediate columns were significantly different. More specifically, the ratio between the variance of alkalinity in column 3 and the variance of alkalinity in column 5 ($F_{7,7}^{0,05} = 3.8$) for a confidence interval of 95% and two degrees of freedom of 7. Calcium concentration (in average) for AMD Light increased up to 181 mg/L for calcite fine, 114 mg/L for calcite intermediate, 91 mg/L for calcite coarse, 62 mg/L for dolomite intermediate. For AMD Lorraine, calcium concentration reached 324 mg/L for calcite fine, 285 mg/L for calcite intermediate, 265 mg/L for calcite coarse, and 149 mg/L for dolomite intermediate (results not shown). Figure 8 represents the carbonate rock mass loss in each column during the experiment at 21°C. To calculate the carbonate rock mass loss, the following hypotheses were made based on VMinteq modelling, precipitation of calcium as gypsum in ALD systems was considered negligible as compared to the calcium dissolved (1 mol of calcium in solution was equal to 1 mol of carbonate rock dissolved); and Ca concentration and water flow were stable between two measurements. A significant slope change at 57,000 min

Fig. 8 Carbonate rock weight as a function of time. The calculation is based on the calcium concentration at the column exit (hypothesis: the number of moles of calcium at the column exit corresponds to the number of moles of dissolved carbonate rock). Continuous *black lines* represent the prediction of weight loss using Eq. (5) and kinetic constants given in Sect. 4.1



(950 h) was observed corresponding to the change of AMD treated, from AMD Light to AMD Lorraine. Whatever the type of carbonate rock or AMD, the curves were nearly linear and particle size did not seem to influence the dissolution rate.

However, as suggested in the literature, the weight decrease could be also approximated by Eq. (5) (see in Sect. 2.7) which is an exponential correlation with a first order kinetic (Mukhopadhyay et al. 2007).

The kinetic constants k for AMD Light was 0.060 y^{-1} for calcite fine, 0.054 y^{-1} for calcite intermediate, 0.050 y^{-1} for calcite coarse and 0.048 y^{-1} for dolomite intermediate (with a correlation between experimental determination of carbonate rock mass and the first order kinetic model of $R^2 = 0.99$ for all tested materials). For AMD Lorraine, the k values were: 0.26 y^{-1} for calcite fine, 0.27 y^{-1} for calcite intermediate, 0.25 y^{-1} for calcite coarse and 0.24 y^{-1} for dolomite intermediate (with a correlation of $R^2 = 0.98$). Kinetic constant values determined by Eq. (5) showed the important role of particle size on the dissolution rate since smaller particles had higher kinetic constants. Values obtained in this experiment were in agreement with other values found in the literature. For example, Mukhopadhyay et al. (2007) show that carbonate rock dissolution can be approximated by a first order reaction and that the kinetic constant varies around 0.42 y^{-1} and Cravotta and Watzlaf (2002) found values between 0.044 and 0.13 y^{-1} for a number of ALDs.

Then, considering the previous values of k , it was possible to express the following order for the carbonate rock dissolution: calcite fine > calcite intermediate > calcite coarse; Perth calcitic marble > Témiscamingue dolomitic rock (for a similar particle size); Carbonate rock dissolution in AMD Lorraine > carbonate rock dissolution in AMD Light. These previous conclusions are in accordance with the literature (e.g. Stumm and Morgan 1996; Langmuir 1997; Morse and Arvidson 2002; Hosten and Gulsun 2004; Liu et al. 2005; Potgieter et al. 2006).

Using Eq. (5), the carbonate rock weight lost with time in each column for both AMD was calculated. Calcite fine, intermediate and coarse, and dolomite intermediate would be totally dissolved (weight lost greater than 99%) after approximately 17.7, 17, 18.4, 19.2 years, respectively, with AMD Lorraine and after approximately 76.7, 85.3, 92.1, 95.9 years, respectively, with AMD light.

Relation between carbonate rock dissolution and unit surface area

Results presented in the previous section showed that whatever the AMD, the finer the calcite, the better the neutralization was. This property to generate more alkalinity is essentially due to the higher unit surface area. Calcite fine had the highest unit surface area (approximately $3282 \text{ m}^2/\text{m}^3$ or $12.07 \text{ cm}^2/\text{g}$) while calcite intermediate and calcite coarse had, respectively, a unit surface area of $224 \text{ m}^2/\text{m}^3$ ($0.84 \text{ cm}^2/\text{g}$) and $120 \text{ m}^2/\text{m}^3$ ($0.45 \text{ cm}^2/\text{g}$).

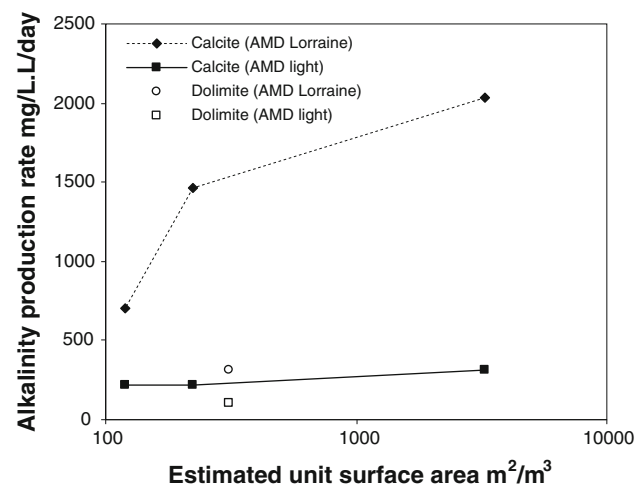


Fig. 9 Alkalinity production rate (in $\text{mg CaCO}_3/\text{day}$) versus the estimated unit surface area (in m^2/m^3)

The dissolution of carbonate rock is governed by physicochemical surface phenomena such as diffusion, adsorption, and reaction of reagents to the surface of the solid (Morse and Arvidson 2002). Thus, the dissolution rate of carbonate rock is greatly influenced by the unit surface area. Figure 9 presents the daily alkalinity generated for the different columns and for the two AMDs. The influence of the unit surface area on the alkalinity production was more significant for the more acidic AMD. In this case, the finer calcite produced 2000 mg/day of alkalinity while the coarser calcite produced 650 mg/day of alkalinity. For AMD Light, the influence of unit surface area on alkalinity production was less significant. Indeed, the alkalinity production rate varied between 400 (for the calcite fine) and 200 mg CaCO_3 /day (for the calcite intermediate and coarse).

The reactivity of carbonate rock was also a function of the AMD type and particularly of the AMD's pH. For a similar particle size, and thus for a similar unit surface area, the neutralizing potential was higher for calcite than for dolomite. Figure 9 shows that calcite intermediate produced, in the case of AMD Lorraine, 1463 mg CaCO_3 /day, while dolomite produced 317 mg CaCO_3 /day (which corresponds to a ratio of 4.6). Stumm and Morgan (1996) show also that dissolution constant of calcite is higher than dolomite. It was also interesting to note that for AMD Light, the difference between the alkalinity produced by dolomite and calcite was less important than for the highly contaminated AMD Lorraine. The alkalinity produced by calcite intermediate was 221 mg CaCO_3 /day while the one produced by dolomite intermediate was 105 mg CaCO_3 /day (which corresponds to a ratio of 2.1).

Treatment of metals in ALD

ALD is usually used to treat AMD with low concentration of metals (Hedin et al. 1994). In the context of AMD from hard rock mines typically found in Canada, AMD contains high concentration of dissolved metals, which is typically treated through active lime treatment (Ritcey 1989). Removal of metals contained in AMD was also assessed during the column tests. Results indicated that only lead, chromium, and aluminium were removed during AMD treatment. The possible mechanisms of Pb and Cr removal could be sorption onto iron oxyhydroxides of the coating. Indeed, Voges et al. (2001) and Genç-Fuhrman et al. (2008) observed Pb and Cr sorption onto iron oxyhydroxides. Thermodynamic modelling using VMinteq v.2.53 showed that aluminium could be removed by precipitation as hydroxides. For the other metals (Fe, Zn, Mg, Mn, Ni, Cd), the acidic pH in the clarifier did not allow an effective precipitation. Only magnesium concentration increased in the last column due to the dissolution of dolomite. These

observations confirmed that ALD should not be used alone to treat AMD with highly dissolved metal concentrations.

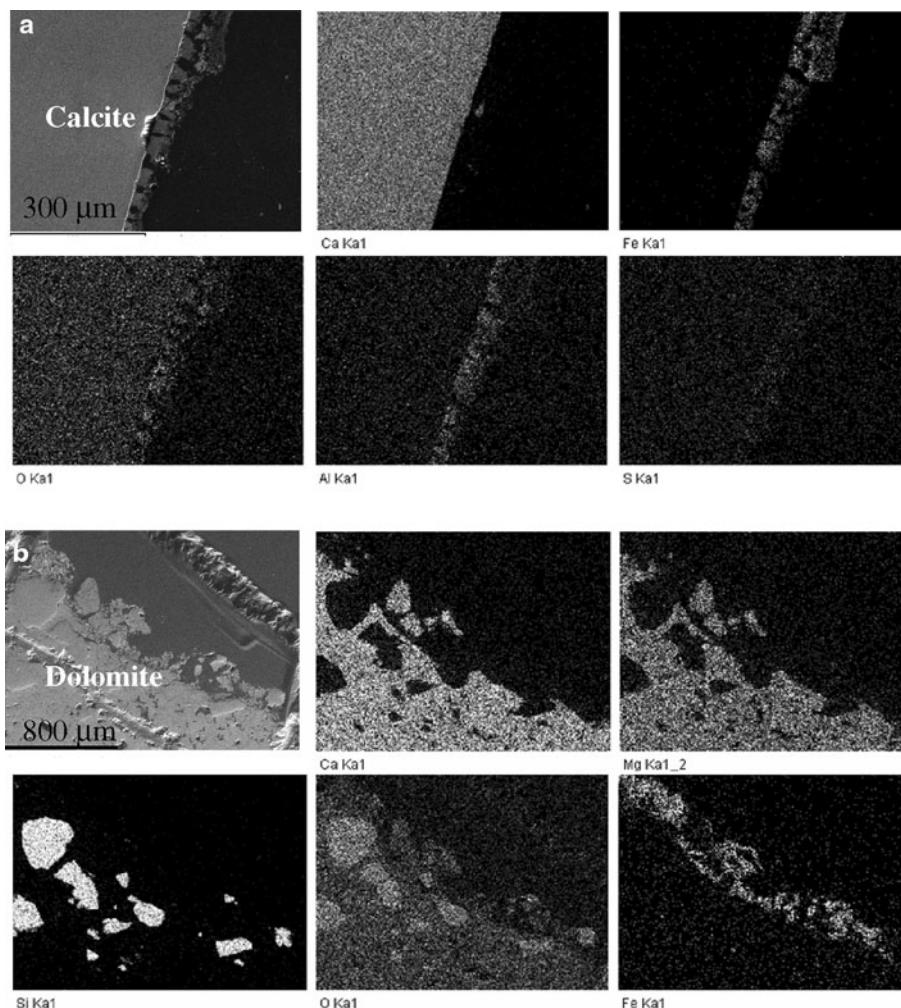
After columns tests, precipitated sludge in each clarifier was collected for analysis. The XRD analysis identified the main sludge minerals: 8% of gypsum, 8% of lepidocrocite, and 84% of goethite. In addition, the thermal analysis by TGA-DSC confirmed the precipitation of secondary minerals by goethite dewatering at 250°C (Prasad et al. 2006). The precipitation of iron hydroxide was also confirmed by thermodynamic modelling. The saturation indices of goethite and lepidocrocite were both positive (ranging from 2 to 4) for all carbonate rocks studied. However, the thermodynamic modelling results (using the water quality in the clarifier) were not in agreement with the precipitation of gypsum (negative gypsum saturation index). In fact, gypsum formation was observed only at the interface between water and air. The evapo-concentration at this interface could explain gypsum precipitation. In summary, even if iron concentration did not significantly decrease in the ALD, some iron precipitated as sludge in clarifiers and as coating on carbonate rock grains.

Effect of particle coating on neutralization processes

Batch tests, similar to those presented in Sect. 2.1, were performed to compare the reactivity of coated and uncoated material on the neutralization of AMD. The coated carbonate rocks came from each column used previously, after dismantling. The pH increased from an average of 3.2 at the beginning of the batch test to an average of 6 for calcite and 5.7 for dolomite after 15 h for coated carbonate rocks. The comparison of pH results between the coated and uncoated materials showed that there was no significant change after 110 pore volumes (the test corresponded to 2 months or 110 pore volumes including the treatment of AMD Light and Lorraine in column tests). Alkalinity values were similar for coated and fresh material, for both calcite and dolomite.

Coating of carbonate rock is a local precipitation phenomenon at the water–rock interface due to the acid neutralization process and alkalinity production (Santomartino and Webb 2007). Figure 10a, b presents images for coated calcite and dolomite obtained by SEM on a polished section (carbonate rocks are cut transversely and polished to allow coating descriptions). BSE images indicated that the coating was porous and thus did not really affect the alkalinity production or acidity neutralization for the tested period; similar observations were reported by Santomartino and Webb (2007). The porosity of coating was approximated by SEM picture analysis (pixels count on height pictures) to 45% for dolomite and 24% for calcite. Hence, calcite seemed to coat more easily than dolomite. This hypothesis is also suggested by many authors (e.g. Hedin

Fig. 10 SEM images of a cross-section of coating and elemental maps (voltage of 20 keV, amperage of 140 A, pressure around 25 kPa, and work distance of 15 mm): **a** calcite grain and **b** dolomite grain



et al. 1994; Booth et al. 1997; Hammarstrom et al. 2003; Huminicki and Rimstidt 2008; Soler et al. 2008) who suggest that carbonate rock coating (due to metal hydroxide and gypsum precipitation within the drain) influence the reactivity in ALD systems. However, reactivity of carbonate rocks is not affected in the presented batch test conditions probably due to the porosity of coating.

Figure 10a, b show X-mapping of the main chemical elements observed on calcite and dolomite using the EDS technique. The X-mapping and corresponding EDS analysis indicated that the coating was mainly composed of iron oxides in both cases (calcite and dolomite), but there was also aluminium within the calcite coating. Calcium originates from the local gypsum precipitation and the aluminium presence could be explained by the precipitation of aluminium hydroxides like gibbsite during the neutralisation process (Santomartino and Webb 2007).

XRD analyses of the precipitates (extracted by shaking coated carbonate rock between two sieves) showed the presence of iron hydroxide and gypsum. More precisely, a goethite proportion of 7, 8, 38, 50% were

obtained for calcite fine, intermediate, coarse, and for dolomite intermediate, respectively. A lepidocrocite proportion of 4% was estimated for calcite fine, 2% for calcite intermediate, 6% for calcite coarse, 6% for dolomite intermediate. Higher gypsum concentrations were estimated by XRD analysis on coating fragments: 89% for calcite fine, 90% for calcite intermediate, 56% for calcite coarse, and 44% for dolomite intermediate. Moreover, the thermal analysis by TGA-DSC confirmed the formation of gypsum by a weight loss peak at 125°C corresponding to the gypsum dewatering (Dweck et al. 2000). Geochemical modelling using VMinteq suggested that the conditions were favourable for the precipitation of goethite and lepidocrocite for all cases. Gypsum was close to equilibrium with a saturation index slightly lower than 0.

In agreement with the findings reported in the literature (e.g. Hammarstrom et al. 2003; Huminicki and Rimstidt 2008; Soler et al. 2008), results obtained in this study confirmed that the use of dolomite can attenuate the risk of carbonate coating by gypsum.

ALD design considerations

Selection of an appropriate carbonate rock to treat AMD is a critical step for ALDs design. In this study, different particle sizes of carbonate and different mineralogy were tested to find the most efficient system. As seen in the previous section, the smaller the particle size, the greater was the alkalinity production. However, the coating contained more gypsum with fine particles of calcite than for coarse calcite. Although the coating did not affect the neutralisation performance during the present experiment, numerous authors suggest that coating, and particularly gypsum precipitation, may affect the treatment performance and could clog the system (Hedin et al. 1994, Booth et al. 1997; Hammarstrom et al. 2003; Huminicki and Rimstidt 2008; Soler et al. 2008). Other carbonate rocks like dolomite could be used to neutralize AMD. Although the kinetics of dolomite dissolution was lower, the pH of highly contaminated AMD (AMD Light and Lorraine) was increased from 3.5 to 5.5 for a 15 h retention time. Moreover, the alkalinity produced by dolomite was in the same order of magnitude than calcite for the AMD Light. These results suggest that anoxic dolomitic drains could be a viable alternative to anoxic calcite drains to neutralize a slightly contaminated AMD.

ALD using calcite or dolomite could not remove metals from a very contaminated AMD (see Sect. 4.3). With respect to governmental guidelines for mine water, ALD used alone is not an option. Some authors (e.g. Champagne et al. 2005, Figueroa et al. 2007), proposed a combination of ALD and sulphate reducing bacteria biofilters to treat AMD. Considering that sulphate reducing bacteria thrive at a pH near 5 (Neculita et al. 2007), Figueroa et al. (2007) propose to use ALD to increase the pH before the treatment in sulphate reducing bacteria biofilters. For the AMD tested in this study, dolomite or calcite could be used in ALDs before biofilters since both were able to increase the pH near 5. Consequently, the choice of carbonate rock would be mainly driven by the local availability of the material.

Conclusion

The role of an anoxic carbonate rock drain (ALD) aims mainly at increasing the pH and producing alkalinity. Results from batch and columns tests confirmed the capacity of the tested ALDs to do so. The AMD was neutralized to a pH between 5.5 and 6 whatever the type of carbonate rock used. Furthermore, all selected carbonate rocks were able to produce alkalinity, but at different rates. Calcite generated more alkalinity than dolomite for a similar grain size; the difference was more pronounced when a highly acidic AMD was treated. The grain size also

significantly influenced the rate of alkalinity production. The finer the carbonate rock, the greater was the alkalinity production. Again, the influence of grain size on the alkalinity produced was a function of the acidity of the AMD to be treated. The impact of grain size was more significant for the highly contaminated (Lorraine) AMD than for AMD Light.

Results of this study demonstrated the importance of the carbonate rock source in an efficient ALD. Indeed, mineralogical and particle size properties played an important role in the neutralisation of AMD. A carbonate rock with a fine particle size tended to dissolve more rapidly than a coarser carbonate rock, so the lifetime of the drain would be shortened. The calcitic marble would also be more reactive than dolomitic rock for the same particle size. Hence, particle size of the carbonate rock was a critical parameter for the design of an ALD since it governs water flow (or the hydraulic retention time) and neutralisation capacity of the system. In our study, coatings formed in the drains (goethite, lepidocrocite and gypsum) did not seem to affect carbonate rock reactivity. Indeed, the alkalinity production rate with coated carbonate rocks was relatively similar to those obtained with fresh carbonate rocks.

It is worth mentioning that an ALD alone cannot successfully treat metal from a highly contaminated AMD that has a low pH and contains high concentrations of dissolved metals. A one step treatment in ALD was not efficient to significantly decrease the pollution of high iron concentrated AMD as AMD (Lorraine and Light). Indeed, iron present in the ALD effluent could decrease the pH due to the oxidation of ferrous ions and the precipitation of iron oxyhydroxides. Multi-step treatment is required in this case. Therefore, to be efficient, ALD should be combined with other passive treatment methods such as sulphate-reducing bacteria bioreactors or engineered wetlands to remove metals.

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