

## ON THE USE OF LIMESTONE DRAINS IN THE PASSIVE TREATMENT OF ACID MINE DRAINAGE (AMD).

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### ABSTRACT

Most systematic studies carried out on passive treatment systems incorporating the use of limestone drains, under aerobic or anaerobic conditions, essentially deal with the treatment of effluents from mines in the USA. A limestone drain typically comprises a trench filled with crushed limestone rocks surrounded by impervious materials. In the case of anoxic drains, the trench is generally isolated under a geomembrane liner covered with soil. Contaminated mine effluents flow by gravity towards these limestone drains where the passive treatment consists in bringing the carbonates into solution, thus increasing the pH and alkalinity. Factors to be considered in the design are: chemistry of the contaminated mining effluent ([metals, [Al], [sulfates], dissolved oxygen, acidity, pH), desired residence time, nature of the rock, grain size, density, void ratio and mass of the limestone rock used, alkalinity, life span and hydraulic behaviour of the drain. Certain secondary effects (saturation by sulfates, co-precipitation, adsorption) may either be beneficial (lowering the sulphate and metal load) or harmful (armoring the limestone rock and clogging of the drain). This paper gives a brief status report on the available knowledge on the use of limestone drains for passive treatment of mining effluents heavily loaded with metals. Examples given include the old Lorraine mine (Ni-Cu), Témiscamingue, where limestone and dolomite rock drains were installed in 1998 when a cover with capillary barrier effects was placed over the tailings site.

### RÉSUMÉ

La plupart des études systématiques réalisées sur les systèmes de traitement passif du DMA incorporant l'utilisation de drains à base de pierres calcaires, en condition aérobie ou anaérobie,

portent essentiellement sur le traitement des effluents des mines de charbon des États-Unis. Un drain calcaire est typiquement formé d'une tranchée remplie de pierre calcaire, ceinturée de matériaux imperméables. Dans le cas des drains anoxiques, la tranchée est généralement isolée sous une géomembrane recouverte de sols. Les effluents miniers contaminés sont dirigés par gravité vers ces drains calcaires où le traitement passif consiste en la dissolution des carbonates, contribuant ainsi à l'augmentation du pH et de l'alcalinité. Parmi les facteurs à considérer lors du design, notons : la chimie de l'effluent minier contaminé ([métaux], [Al], [sulfates], [OD], acidité, pH), le temps de résidence souhaité, la nature de la roche, la densité, la granulométrie, l'indice des vides et la masse de la pierre calcaire utilisée, l'alcalinité, la durée de vie et le comportement hydraulique du drain. Certains effets secondaires (saturation en sulfates, co-précipitation, adsorption) peuvent à la fois être bénéfiques (diminution de la charge en sulfates et métaux) et néfastes (enrobage de la pierre calcaire et colmatage du drain). Le présent article dresse un bref état des connaissances actuelles sur l'application des critères de design des drains calcaires au traitement passif des effluents miniers à forte charge en métaux. Des exemples sont présentés dont celui de l'ancienne mine Lorraine (Ni-Cu) au Témiscamingue, où des drains de pierre calcaire et dolomitique ont été installés en 1998 lors de la mise en place d'une couverture à effets de barrière capillaire (CEBC) sur le parc à résidus.

## INTRODUCTION

During active and post closure mining activities, site management requires constant water quality monitoring, and treatment when necessary. One of the most often discussed problems in that regard is acid mine drainage (AMD), which results from sulfides oxidation in various mining wastes that lack a sufficient neutralization capacity. This leads to a net acid generation (reaction 1).



The treatment of effluents affected by acid mine drainage (AMD) is one of the major issues facing the Canadian mining industry, during and after closure of a mining site. Numerous abandoned mine sites didn't have a closure plan at the time of their operation and may thus induce considerable environmental impact.

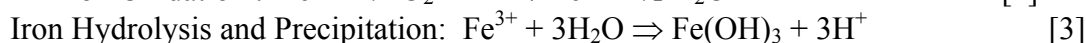
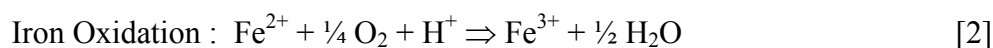
Passive methods for treating AMD have been principally applied to coal mines effluents world-wide since the late 1970. AMD treatment by various passive methods using limestone, including anoxic and oxic limestone drains (ALD, OLD), open limestone channel (OLC), successive alkalinity-producing system (SAPS), and limestone pond, have been reviewed by Kleinman (1989), Faulkner and Skousen (1994), Hedin and Watzlaf (1994), Martin et al. (1995), Gusek (1995; 2001), Ziemkiewicz et al. (1997), Cravotta and Trahan (1999), MEND (1999), DEP (2000), and Bernier et al. (2001). To date there are hundreds of passive treatment systems world-wide accepting acid mine waters. Some systems do not perform to design expectations while others have successfully operated relatively unattended for decades (Gusek, 2001). Many reasons can be inferred to explain the contrasting performances of passive systems including: lack of proper geochemical characterization of the AMD to treat (which may results from a cookbook approach for a wide range of AMD chemistries), a lack of care for hydraulic characterization and for the geometric design of the drain, and certainly in part, to the

misconception that low-maintenance is no maintenance and that passive treatment is a walk away solution. Inadequate characterization of the mine drainage chemistry prior to the design and implementation of a passive treatment system can result in inappropriate selection of unit operations and inappropriate sizing of the components of the treatment system.

The objectives of this paper are two folds: 1) to review the influence factors that can be used to optimize the passive treatment of AMD which integrate limestone drains and 2) to present the results of a monitoring study on the limestone drains at the Lorraine site, Témiscamingue.

## PASSIVE TREATMENT SYSTEMS

Historically, passive treatment systems have been considered mainly to reduce associated treatment costs in the long term post-closure collect-and-treat context, particularly for coal mine drainage (Rees et al., 2001). Two main objectives are generally considered in designing a passive treatment system : 1) generate sufficient alkalinity to neutralize the acidity and 2) decrease the metals loading through oxidation/hydrolysis, and precipitation mechanisms. There are various types of passive treatment systems including: open limestone channels (OLC), oxalic limestone drains (OLD), anoxic limestone drains (ALD), diversion wells, artificial wetlands, successive alkalinity producing system (SAPS), microbial reactor systems and reactive walls and biosorption systems; many of these systems have been reviewed in MEND (1999) Report 3.14.1. Limestone is being used with various configuration in many of these passive treatment systems to generate alkalinity. Iron is often the predominant contaminant of concern and its removal is promoted by the natural oxidation (reaction 2) of ferrous iron ( $\text{Fe}^{2+}$ ) to ferric iron ( $\text{Fe}^{3+}$ ) followed by hydrolysis (reaction 3) which generate in turn proton acidity ( $\text{H}^+$ ). Thus, the water being treated needs to provide sufficient alkalinity and buffering capacity to counteract the additional acidity produced during metals removal.



The difficulties of treating AMD with passive systems have been reviewed in details by Ziemkiewicz et al. (1994), Hedin et al. (1994), Gusek (1995; 2001), Barton and Karathanasis (1998), MEND (1999), Skousen (1999), Rees et al. (2001) and Brown et al. (2002). In order to successfully implement a passive treatment system that is suitably designed to treat a specific AMD, it is important to perform a good chemical characterization of the incoming AMD and have a good knowledge of metals removal mechanisms playing a role in passive treatment. The design of passive treatment systems is a somewhat inexact science due to the large variability of water chemistries requiring treatment and to the various type of materials that can be chosen in the construction process (Gusek, 2001). It should involve various testing stages including a laboratory scale, a bench scale and a field pilot scale test. All this information should be gathered and taken into account for the final full-scale design. The information available in the literature indicates that passive treatment technology has been proven to be effective in a variety of water chemistries, flowing conditions and climatic situations. However, cookbook design approaches should be implemented on a full-scale basis with caution (Gusek 2001). Each case is site specific and should be the object of a careful and detailed analysis.

In the following sections of this paper, we will describe the design concept behind the use of limestone drains integrated in a passive treatment system with a particular emphasis given to the alkalinity generation mechanisms and the influencing factors that can affect treatment performance.

## LIMESTONE DRAINS DESIGN CONCEPTS

The basic design of an ALD is a buried bed (or trench) of crushed limestone surrounded by impervious materials. The trench through which the unaerated acidic effluent flows in by gravity is often isolated under a geomembrane covered with soil (Figure 1). The passive treatment is initiated as the AMD begins dissolving the carbonates in the limestone drain (LD) thus generating some bicarbonate alkalinity and raising the pH. The sole purpose of a LD is to provide alkalinity that will change an acidic water into a net alkaline water. Keeping oxygen out the water helps to prevent oxidation of metals and armoring of the limestone.

### Anoxic Limestone Drain + Overlying Limestone Channel

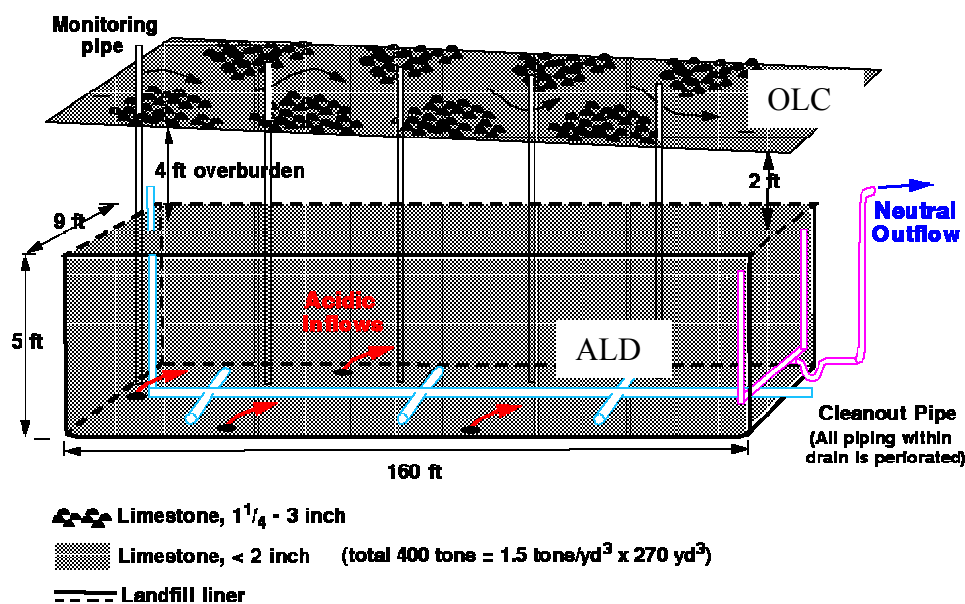


Figure 1 Combination of an ALD and OLC design proposed by USGS (<http://pa.water.usgs.gov/projects/amd/treatments.html>).

As carbonates dissolve, the  $\text{CO}_2$  partial pressure may increase within the drain, and further improve limestone dissolution and alkalinity generation (see reaction 5 below). OLD and OLC are more experimental and are similar to ALD except that Fe and Al hydroxides can form within the limestone drain and be periodically flushed out by temporarily increasing the pressure head and by releasing the water rapidly. Important influencing factors to consider in the design of passive treatment are: the AMD chemistry ([metals], [sulfates], pH, redox, acidity, DO), residence time, physical and chemical characteristics of the crushed stone used to generate alkalinity, and the geometry of the drain or channel (slope, profile, width, length, etc). Some

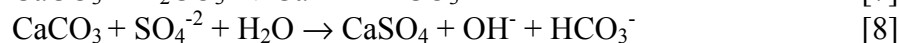
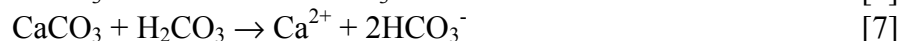
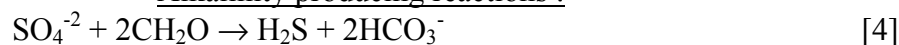
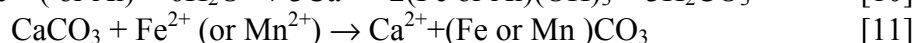
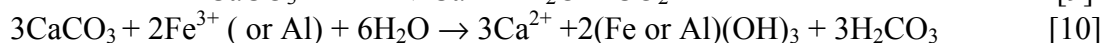
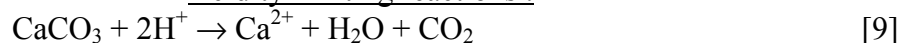
secondary effects (sulfates saturation, co-precipitation, sorption) can be beneficial (decreases in sulfates and metals loading) while others are detrimental (armoring of the limestone by secondary minerals, voids plugging) (Bernier et al., 2001).

**Required Mine Effluents Characteristics:** Selecting the appropriate passive-treatment system layout is a site specific process governed by the AMD chemistry and by whether the system relies on aerobic or anaerobic reactions or both (Hedin et al, 1994; Gusek, 1995, 2001). For example, the passive treatment of an acid mine influent entering an ALD will be effective only if it has a low dissolved oxygen (DO) concentration (<2mg/L) and low Fe (with < 10% Fe<sup>3+</sup>) and Al (<25 mg/L) concentrations. Numerous decision making charts have been proposed for passive treatment system design considerations (Hedin et al., 1994; Brown et al., 2002). A general flowchart for designing passive mine drainage treatment systems can be summarised as follows:

1. Determine flow rate, analyse water chemistry and calculate sulfates and metals loading.
2. If the water is alkaline, direct the water flow to a settling pond and then into an aerobic wetland.
3. If the water is acidic, determine the DO status and ferrous/ferric iron ratio and determine into which one of the following three categories the acidic water belongs:
  - 3.1. DO<2mg/L, Fe<sup>3+</sup><10% of total Fe, Al<25 mg/L,
  - 3.2. 2<DO<5 mg/L, 10%<Fe<sup>3+</sup><25% of total Fe, and
  - 3.3. DO>5 mg/L and Fe<sup>3+</sup>>25% of total Fe.
4. *Category I mine Water:* Increase the alkalinity by treating with an ALD.
  - 4.1 If after passing through the ALD the water is net alkaline, then send into a settling pond and aerobic wetland treatment.
  - 4.2 If the water remains acidic after the ALD treatment, aerate before sending in the settling pond and aerobic/anaerobic wetland.
5. *Category II mine water:* Treat in a aerobic/anaerobic wetland to strip DO and precipitate Fe<sup>3+</sup> before treating into and ALD, then proceed with steps 4.1 and 4.2.
6. *Category III mine water:*
  - 6.1 If pH>4 then aerate and direct toward a settling pond before the aerobic/anaerobic wetland treatment.
  - 6.2 If pH<4 send directly into the aerobic/anaerobic wetland.

For passive treatment described in 4, 5, and 6 above, verify if the water meets the effluent limits before discharging. At this point, additional chemical treatment may be necessary to meet the regulation limits. In order to be effective and applicable, the passive treatment of AMD requires flow rates generally less than 250 L/h because of size and area limitations (Skousen, 1999). A key mechanism that controls the effectiveness of a passive treatment is alkalinity generation.

**Alkalinity generation in passive systems:** Alkalinity can be generated through sulfates reduction in a reducing environment such as in a wetland (reaction 1). Other reactions controlling the formation of alkalinity involve bicarbonates alkalinity (HCO<sub>3</sub><sup>-</sup>) produced by carbonates dissolution (reactions 4-8). Carbonates dissolution reactions (Hedin and Watzlaf, 1994) can also limit the acidity of a solution by neutralizing protons (H<sup>+</sup>) and precipitating Fe, Mn and Al hydroxides (reactions 9-11).

Alkalinity producing reactions :Acidity limiting reactions :

In aqueous carbonate systems, the alkalinity is defined by Equation (12) and represent the acid neutralizing capacity (ANC) of an aqueous solution:

$$\text{Alkalinity (mg/L CaCO}_3) = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad [12]$$

Other aqueous species that can contribute to alkalinity in natural waters may be important in constructed passive treatment system. A more complete definition of alkalinity is given by equation (13) (Stumm and Morgan, 1996):

$$\begin{aligned} \text{Alkalinity (mg/L CaCO}_3) = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{NH}_3] + [\text{HS}^-] + 2[\text{S}^{2-}] \\ & + [\text{H}_3\text{SiO}_4^-] + 2[\text{H}_2\text{SiO}_4^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{Org}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] - [\text{H}_3\text{PO}_4] - [\text{H}^+] \quad [13] \end{aligned}$$

An alkalinity calculator is available at: <http://oregon.usgs.gov/alk/>.

Ferric iron and aluminium precipitate to form hydroxides whereas ferrous iron and manganese may form secondary carbonates. The calcium concentration in the solution increases as it is being released by reactions 5-7 and 9-11, which also increase the potential formation of gypsum. Aqueous metals hydrolysis generally contribute to a decrease in alkalinity.

**Carbonates dissolution:** The equilibrium dissolution of pure calcite (and dolomite) is fairly straightforward (reactions 5 to 9) and thermodynamic data are available which allow equilibrium thermodynamic modelling using specialised software such as Visual Minteq (<http://www.lwr.kth.se/english/OurSoftware/Vminteq/index.htm>). The buffering capacity of calcite and dolomite has been modelled by the first author of this paper with VMINTEQ (Figure 2). The software allows to do a virtual titration of water containing 1 mole/L calcite ( $\text{CaCO}_3$ ) or dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) with a solution of sulfuric acid (0.2mol/L) for a closed system (partial pressure of  $\text{CO}_2$  is allowed to increase) and for an open system (partial pressure of  $\text{CO}_2$  = atmospheric, 0.00035atm).

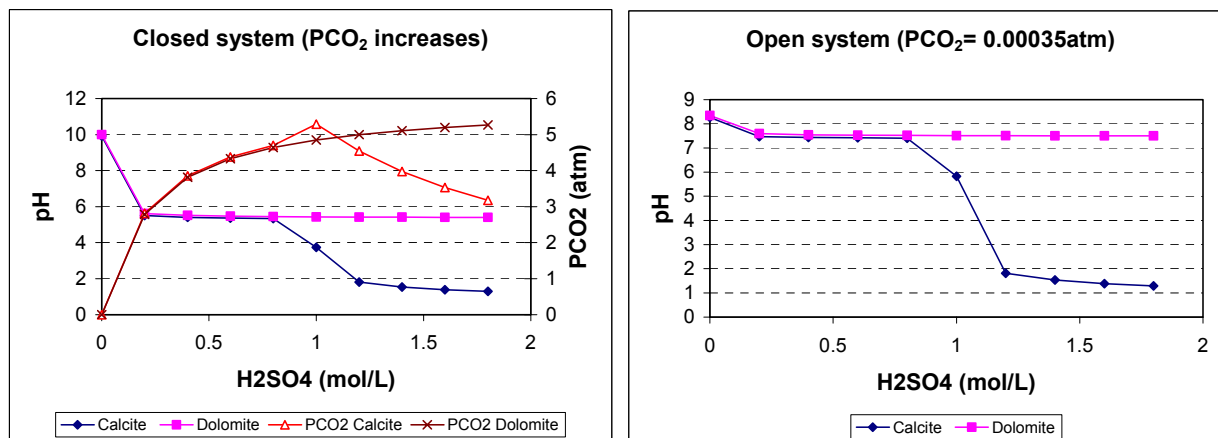



Figure 2. Comparison of buffering capacity of calcite and dolomite for open and closed systems in thermodynamic equilibrium. One mole of finite solids per litre is titrated with a solution of sulfuric acid (0.2 ml/L).

As can be seen from Figure 2, both calcite and dolomite can buffer the solution, but the range of pH variations depends on the nature (closed or open) of the system chosen. The lower buffering pH observed for the close system ( $\sim 5.5$ ) compared to an open system situation ( $\sim 7.5$ ) is due to the additional acidity attributed to dissolved carbon dioxide concentration (Stumm and Morgan, 1996). Because 1 mole of calcite weights 100.1g compared to 184.4g for 1 mole of dolomite, the calcite get exhausted before the dolomite after 0.8 mol/L sulfuric acid is added. Then the buffering capacity of calcite is superseded and the partial pressure of  $\text{CO}_2$  begins to drop in a closed system situation, whereas it continues to rise for the dolomite. An increase in partial pressure of  $\text{CO}_2$  will favour carbonate dissolution (reaction 5) which would be the ideal case for a perfectly anoxic limestone drain where no exchange occurs with the atmosphere. These results do not account for dissolution kinetics. Carbonate minerals that may offer some buffering capacity are indicated in Table 1 in order of decreasing solubility (Smith et al., 1994; Blowes and Ptacek, 1994). The rate of carbonate depletion is controlled partly by mass-action constraints and by kinetic limitations.

**Table 1 Solubility of Carbonate Minerals (25°C)**

|               |   |  |
|---------------|---|--|
| Nesquehonite  | $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ | <b>Decreasing<br/>solubility</b><br> |
| Magnesite     | $\text{MgCO}_3$                           |  |
| Calcite       | $\text{CaCO}_3$                           |  |
| Strontianite  | $\text{Sr CO}_3$                          |  |
| Dolomite      | $\text{CaMg}(\text{CO}_3)_2$              |  |
| Ankerite      | $\text{CaFeMg}(\text{CO}_3)_2$            |  |
| Rhodochrosite | $\text{MnCO}_3$                           |  |
| Smithsonite   | $\text{ZnCO}_3$                           |  |
| Siderite      | $\text{FeCO}_3$                           |  |
| Cerussite     | $\text{PbCO}_3$                           |  |

Another modelling of carbonate dissolution was done with VMINTEQ for an open system condition to compare the buffering capacity of calcite, dolomite (ordered and disordered), and magnesite (Figure 3). Chrysotile, a serpentine mineral which has a paste pH around 10, was also included as it is believed to offer some potential for the treatment of AMD.

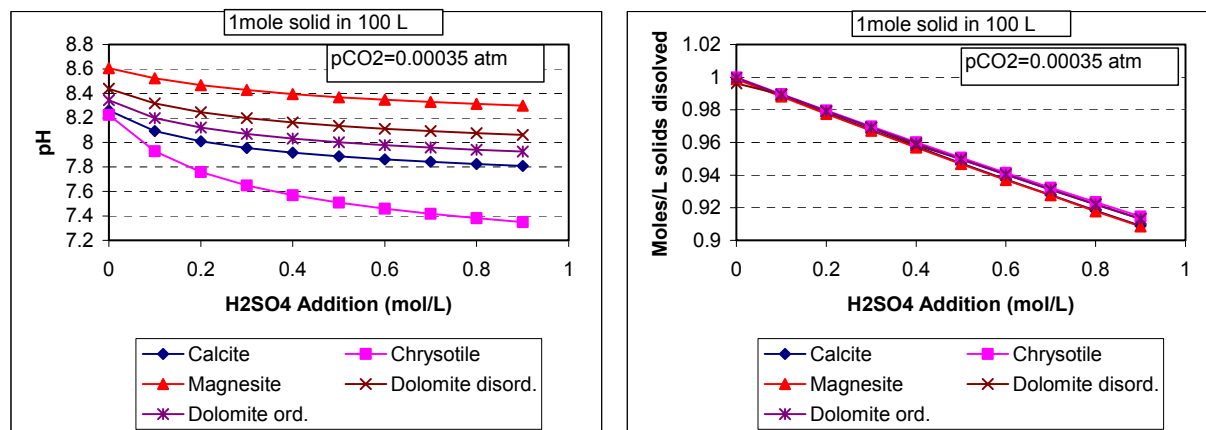


Figure 3 Comparison of carbonates and chrysotile buffering capacity in neutralizing sulfuric acid (open system). One mole of finite solid per 100 L was titrated with a sulfuric acid solution at a concentration of 0.1 mol/L under atmospheric condition ( $PCO_2=0.00035$  atm).

As one can see from Figure 3, magnesite is more soluble than calcite and dolomite, a result consistent with the relative ranking given in Table 1. However, dolomite appears to be slightly more soluble than calcite. This may depend on the solubility products used in the VMINTEQ thermodynamic database because some discrepancy of dolomite solubility products ( $10^{-16.5}$  to  $10^{-19.5}$ ) have been reported by different investigators (Stumm and Morgan, 1996). Nevertheless, the kinetics of dolomite dissolution is slower than that of calcite has shown in Figure 4, and a disequilibrium is commonly observed (Blowes and Ptacek, 1994). As can be seen from Figure 4, the kinetics of calcite dissolution are strongly influenced by the degree of undersaturation. Calcite dissolution is fast for highly undersaturated waters ( $pH < 4$ ), but decreases dramatically as the solution approaches saturation at higher pH (Hedin and Watzlaf, 1994). In addition, Berner (1978) demonstrated that calcite dissolution is diffusion-controlled (rapid) in solutions of  $pH < 4$ , but surface reaction-controlled (slow) for  $pH > 6$ .

The kinetics of dissolution and precipitation may differ substantially for a given mineral as shown experimentally for siderite and rhodochrosite. These carbonates are much less soluble than calcite (Table 1) and are often reported as supersaturated in natural anaerobic aquatic environments. This may be an artefact of their slow precipitation kinetic (Jensen and al, 2002). In the case of an iron-rich AMD solution incoming an ALD, situations where siderite becomes supersaturated may be encountered. Because of its slow precipitation kinetics, siderite may not precipitate within the drain and not contribute to limestone armoring. It is important to recall that if the ALD is perfectly anoxic and that incoming AMD has no ferric iron, secondary iron hydroxides should not form within the drain and armour the limestone (which would ultimately clog the drain). Thus, there are a number of influencing factors that may affect the performance of a limestone drain. Some of them are discussed in the next section.

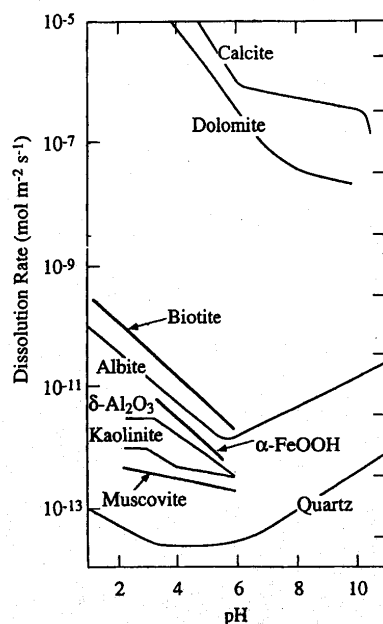


Figure 4 Dissolution rates of various minerals, T=25°C, P=1 atm. (from Stumm and Morgan, 1996).

**Influence factors:** A number of influence factors can affect the performance of a limestone drain, such as the type and mass of filling calcareous stone used, the residence time, the lifetime expectation, the drain geometry (slope, length, width, profile) and hydrobiogeochemical interactions occurring at the surface of the crushed carbonate rocks. Hedin and Watzlaf (1994) have proposed an ALD sizing method that accounts for the drainage flow rate, the anticipated carbonate dissolution rate, the desired lifetime and the minimum retention time required to achieve the maximum of alkalinity. This equation can be written as follow:

$$M = \frac{Q\rho_b t_r}{V_v} + \frac{QCT}{x} \quad [14]$$

where  $t_r$  is the residence time (h),  $M$  is the mass of stone filling the drain,  $V_v$  is the decimal bulk void volume (0-1),  $\rho_b$  is the bulk density ( $\text{kg m}^{-3}$ ),  $C$  is the predicted concentration of alkalinity ( $\text{mg/L CaCO}_3$ ),  $T$  is the lifetime of the proposed treatment period (h),  $x$  is the calcium carbonate content of the stone used in decimal form (0-1), and  $Q$  is the volume flow of the AMD ( $\text{L h}^{-1}$ ). As the limestone dissolves, the hydraulic integrity of the drain should decrease but it is difficult to predict the ensuing performance. Furthermore, equation (14) does not account for the demands of reactions generating alkalinity through retention of  $\text{Fe}^{3+}$  and Al (reaction 6), which have the potential to significantly and adversely affect the performance of LD by clogging the drain with secondary mineral precipitates (Hedin et al. 1994). Other acid consuming reactions that are not accounted by this mass equilibrium approach are the dissolution of minor minerals (silicates, sulfides) from in the limestone that can release Al, Fe, Mn and other elements. If precipitation of hydrous Fe and Al minerals occurs, they could dissolve and contribute to the release of Fe, Al and sorbed metals. In addition, proton could be adsorbed onto mineral surfaces and contribute to release, desorbed or ion-exchanged elements (Smith et al., 1994).

Another important sizing factor mentioned previously is the internal porosity and surface area of the crushed limestone rocks filling the drain. A value of 50% void space is typically chosen for laboratory work, which was questioned by Cravotta and Trahan (1999) who found that actual pore space determined *in situ* was 14% in ALD installed at Orchard mine, USA. A realistic range in porosity is probably between 0.25 and 0.50. Hence, although equation (14) is useful for the preliminary design stage and pilot-scale testing, it fails to represent the transient state of AMD flowing within a drain. The use of a single hydraulic conductivity or a single porosity is also questionable. These hydraulic design issues are currently being addressed by the third author of this paper.

**The potential effect of armoring limestone:** The amount of limestone needed for a passive treatment system is typically determined by multiplying the annual acid load by the desired lifetime of the system. This mass equilibrium approach suffers some limitations because AMD neutralization systems are typically not at equilibrium. Also, insoluble mineral precipitates may form on the limestone surface and hinder limestone dissolution, a process known as metal armoring. The same deleterious armoring process may be active in a limestone drains that would not be perfectly anoxic. Once armored, limestone is assumed to cease dissolution and acid neutralization. A laboratory titration study conducted by Ziemkiewicz et al. (1997) indicated that armored limestone was 2 to 45% less effective in neutralizing hydrochloric acid solution as fresh limestone. Furthermore, another laboratory container study indicated that armored limestone was 90% as effective in neutralizing AMD as unarmored limestone. Cravotta and Trahan (1999) have shown that despite surface encrustation by Fe and Al hydroxides, OLD and OLC can still be effective for AMD remediation.

Sun et al. (2000) performed an empirical study on the effects of armoring on limestone neutralization of AMD. As mentioned previously, the limestone dissolution is controlled partly by mass-action constraints and by kinetic limitations. In this regard, they demonstrated that particle size has a marked effect on surface area and dissolution rates determined in the laboratory. As can be seen in Figure 5A, both solutions have an identical initial and final pH for an identical mass of limestone, but the limestone having the higher surface area reaches the final pH at a faster rate. Despite the importance of surface area in limestone dissolution rates and acid neutralization capacity, surface area is rarely considered in the design of AMD passive treatment system.

In their study, Sun et al. (2000) have also shown that an increase in iron concentration (from 28 mg/L to 225 mg/L Fe) increases the lag time before neutralization begins and the time required to reach a final pH (Figure 5B).

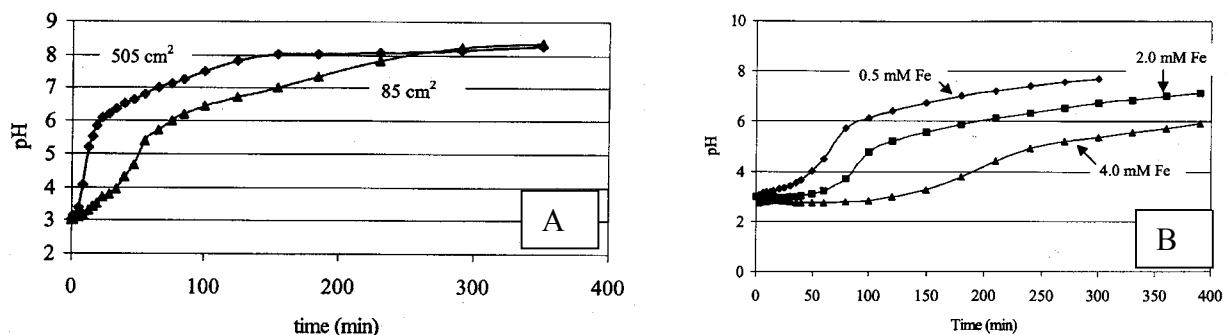


Figure 5 A) Effect of limestone surface area (per g of limestone) on the neutralization of an acid in the absence of iron (from Sun et al. 2000). B) Effect of iron concentration on the neutralization rate of acid solutions by limestone (from Sun et al., 2000).

Sun et al (2000) have derived an empirical equation for their range of experimental data typical of coal AMD to consider the influence of various factors including: surface area, initial pH, initial Fe<sup>3+</sup> concentration, final pH and coating thickness. Their equation was formulated as follows:

$$t = e^{0.0654b} \left[ (-78.08 pH_f + 338.27) + 0.8053 pH_f^{3.5346} \right] * A_{MS}^{(-0.1305 pH_f + 0.6185) pH_f + (0.7365 pH_f - 4.5918)} + (24.538 pH_f^2 - 272.44 pH_f + 765.29) [Fe] \quad [15]$$

where  $t$  is the reaction time (h),  $b$  is the thickness of the iron oxide coating ( $\mu\text{m}$ ),  $pH_f$  is the final pH,  $pH_i$  is the initial AMD pH,  $A_{MS}$  is the specific surface area of limestone ( $\text{cm}^2/\text{g}$ ) and  $[Fe]$  is the initial iron concentration (mM where 1mM Fe=55.85g). An application of Equation (15) in combination with equation (14) is illustrated in Figure 6 assuming a flow discharge of 1000L/min of a solution with an initial pH of 3, an initial iron concentration of 55 mg/L and a lifetime of 10 years for a given mass of limestone (Sun et al 2000).

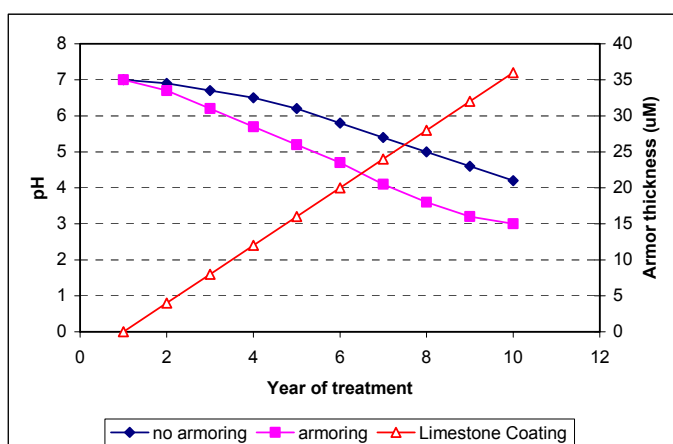


Figure 6 Comparison of two scenarios for a 10 year AMD passive treatment with limestone. Data from Sun et al. (2000).

Two scenarios are compared in Figure 6, no armoring effect and armoring effect by addition of 4  $\mu\text{m}/\text{yr}$  armoring thickness. From the results depicted in Figure 6, it can be seen that even without armoring effect, the system is expected to fail (when  $\text{pH} < 5.5$ ) after 6 years instead of the planned 10 years lifetime and second, when the iron armoring is considered, the expecting lag time for system failure is 4 years. A mine drainage is considered acid when its pH is less than 5.5. This modelling indicates that kinetics effects in the neutralization process and other influencing factors such as armoring should be considered in the sizing method developed. Equation (15) has some limitations as it is empirically derived and can only be used within the range of each parameter used. It was developed for the treatment of coal mine AMD which typically has much lower metals and sulfates loading than AMD derived from the oxidation of base metals mines tailings.

The above review has shown that current sizing methods for limestone drains used in passive treatment systems design are not incorporating all influencing factors and more field-oriented and experimental works are required to develop adequate sizing methods that incorporates all influencing factors described previously.

## PASSIVE TREATMENT SYSTEMS INTEGRATING THE USE OF LIMESTONE

A few examples of treated coal mine drainage with different types of passive systems using limestone are given in Table 2 for a range of initial conditions (flow rate and water chemistry). As can be seen from Table 2, the various AMD treated in passive systems can vary widely in water chemistry, pH and flow rates and are strongly site specific.

**Table 2 Examples of coal mine drainage treated in passive systems with limestone.**

| Coal mine<br>Drainage<br>Site | AMD influent |            |            |                         | Treated effluent |            |            |                         | Flow rate<br>L/h | Type |
|-------------------------------|--------------|------------|------------|-------------------------|------------------|------------|------------|-------------------------|------------------|------|
|                               | pH           | Fe<br>mg/L | Al<br>mg/L | SO <sub>4</sub><br>mg/L | pH               | Fe<br>mg/L | Al<br>mg/L | SO <sub>4</sub><br>mg/L |                  |      |
| 1                             | 3.38         | 787        | 12.6       | 3034                    | 6.47             | 37.3       | 0.2        | 1352                    | 240              | SAPS |
| 2                             | 3.5          | 1.8        | 0.89       | 215                     | 6.6              | <0.003     | 0.08       | 200                     | 1246             | OLD  |
| 3                             | 2.3          | 1416       | 486        | 6719                    | 6.2              | 202        | <1         | 2227                    | 48               | ALD  |
| 4                             | 4.3          | 589        | 5          | 2825                    | 5.5              | 507        | 3          | 2655                    | 6900             | ALD  |

1: Renovated failed Jones branch wetland, Kentucky USA. (Barton and Karathanasis, 1999)

2: Abandoned Orchard mine, Pennsylvania USA (Cravotta and Trahan, 1999)

3: Rid-2L, Appalachia USA (Hedin and Watzlaf, 1994)

4: REM-R, Appalachia USA (Hedin and Watzlaf, 1994)

A failed constructed wetland in McCreary County, Kentucky, USA was renovated to improve treatment efficiency. The renovation was designed incorporating two ALD (site 1, Table 2) and a series of anaerobic subsurface drains that promote vertical flow of mine water through a successive alkalinity producing system (SAPS) of limestone beds overlain by organic compost. Details of this passive treatment configuration are given in Barton and Karathanasis (1999). Overall, the mean iron concentrations at site 1 have decreased from 787 to 37 mg/L, pH increased from 3.38 to 6.5 mass removal rates averaged 98% for Al, 95% for Fe, 94% for acidity and 94% for acidity and 55% for sulfates.

Cravotta and Trahan (1999) studied oxic limestone drains (OLD) to treat AMD (site 2 in Table 2) at Orchard mine, Pennsylvania, USA. OLD are intended to generate alkalinity and remove metals simultaneously, as opposed to ALD which only aim at adding alkalinity with metal

removal being achieved subsequently in a settling pond or wetland. OLD were chosen because most of the iron was ferric and the water was oxygenated (4 mg/L DO). In this case, over 95% of the Fe and Al was removed with Mn, Ni, Cu, Zn, Co which were removed by co-precipitation. Limestone dissolution continued despite coatings of hydrous oxides on the crushed limestone surface. Removal of precipitate was achieved by incorporating a perforated subdrain pipe into the OLD. It was shown in this study that the combination of neutralization and hydrolysis processes within an OLD require less land area than conventional passive treatment using an ALD/oxidation pond configuration.

Sites 3 and 4 given in Table 2 relate to a study by Hedin and Watzlaf (1994) on 21 ALD treating coal mine drainage from Appalachian abandoned coal mines (USA). These two examples were chosen to illustrate contrasting flow rates and mine water chemistry treated by an almost similar mass of rock (114 and 124 mt). Better results were observed for the low flow rate (site 3, Table 2) even if metals and sulfates concentrations were much higher in the mine influent entering the ALD. Equation [14] was derived by Hedin and Watzlaf (1994) from this data set and introduced the residence time variable. They found that a minimum residence time of the mine waters in an ALD was 15 hours. These authors also observed that large changes in acidity resulted from retention of ferric iron and aluminium in the ALD studied. Equilibrium calculations indicated that the ALD effluents were undersaturated with respect to calcite but oversaturated with siderite. However, no significant retention of ferrous iron was observed which could reflect the slow precipitation kinetic of siderite discussed above. They also report that retention times over 23 hours did not markedly increased alkalinity concentrations.

### **MONITORING OF LIMESTONE DRAINS INSTALLED AT THE LORRAINE (Ni,Cu) MINE SITE TÉMISCAMINGUE.**

Most decision making charts used in selecting AMD passive treatment systems and sizing methods have been derived from coal mine drainage data. Few orphan base metal sites have implemented the use of ALD in the treatment of AMD. One such site is the remediated Lorraine mine site, Temiscamingue (Nastev and Aubertin, 2000; Bernier et al. 2001; Dagenais et al., 2001), which will be discussed in this section.

**Site history:** The Lorraine Cu-Ni ore body was discovered in 1961 at about 30km East of Lorrainville in the Gaboury Township, Témiscamingue. The ore zone was characterised by chalcopyrite, pentlandite, pyrrhotite and pyrite as the dominant sulphides and was hosted in a sequence of mafic volcanic rocks. The mine was operated between 1964 and 1968, and 600000 tons containing 1.08% Cu and 0.48% Ni were mined out (Lavergne 1985). The produced tailings were placed into a 155000 m<sup>2</sup> pond, with a thickness ranging between a few cm (to the north) up to 6 meters near the south dike (Figure 7A). The reactive tailings were left exposed to the atmosphere for 30 years allowing the formation of an oxidation front ranging between 15 and 120 cm in depth. An environmental impact study was initiated by the Ministère des Ressources naturelles du Québec (MRN) in 1994. It revealed limited impact related to AMD at the site. The acid base accounting (ABA) analysis done on the fresh tailings (below the oxidised zone) indicates a high acid generation potential (AP=223 kg CaCO<sub>3</sub> eq/t) and relatively low neutralisation and carbonate neutralisation potentials (NP=49 kg CaCO<sub>3</sub> eq/t; CNP=23 kg CaCO<sub>3</sub>

eq/t). Hence, the tailings have a negative net neutralisation potential of  $-174 \text{ kg CaCO}_3 \text{ eq}$ . The seepage observed south of the pond, analysed in 1996, was characteristic of AMD with low pH (between 2.3 and 2.6), high acidity (ranging between 1700 and 5900 mg/L  $\text{CaCO}_3$ ), and elevated concentrations (mg/L) of sulfates (3730-9190) and metals ( $\text{Cr}=0,008-0,096$ ;  $\text{Cu}=0,135-0,804$ ;  $\text{Fe}=838-3200$ ;  $\text{Mn}=9.2-18.3$ ,  $\text{Ni}=0,21-9,5$ ;  $\text{Pb}=0,14-0,49$  and  $\text{Zn}=0.19-1,0$ ).

A number of studies followed to determine the best course of action to prevent further tailings oxydation and AMD production; the remediation background was summarized in Bernier et al. (2001). The hydrogeological conditions of the site prior to restoration are given in details in Nastev and Aubertin (2000), which also modelled the cover behaviour prior to its construction. A multi-layered cover with capillary barrier effect (CCBE) was constructed in 1998 under the supervision of Dessau-Soprin (Fontaine, 1999). The CCBE has been instrumented to monitor the cover performance (Dagenais et al., 2001; Aubertin et al., 2002). In parallel with the construction of the CCBE, 3 limestone drains (LD) were constructed downward the slope of the south dike (Figure 7). These drains were filled with crushed dolomite rock (83.5% dolomite and 2.6% calcite; D-1, 2, 3) to treat the AMD collected below the south dike. A fourth LD filled with marble (98.2% calcite; C-1) was later constructed downward the slope of the west dike. Details on the drains characteristics are given in Bernier et al. (2001) and Bernier (2002). Basically, the LD are trenches enclosed by impervious materials filled with crushed marble and dolomite. Each trench is isolated under a plastic and geotextile covered with soil. The acid effluent flows in by gravity. The neutralised effluent is then evacuated in an open trench. Sampling tubes were installed at the entrance of each LD to monitor the influent quality and compare it with the treated effluent.

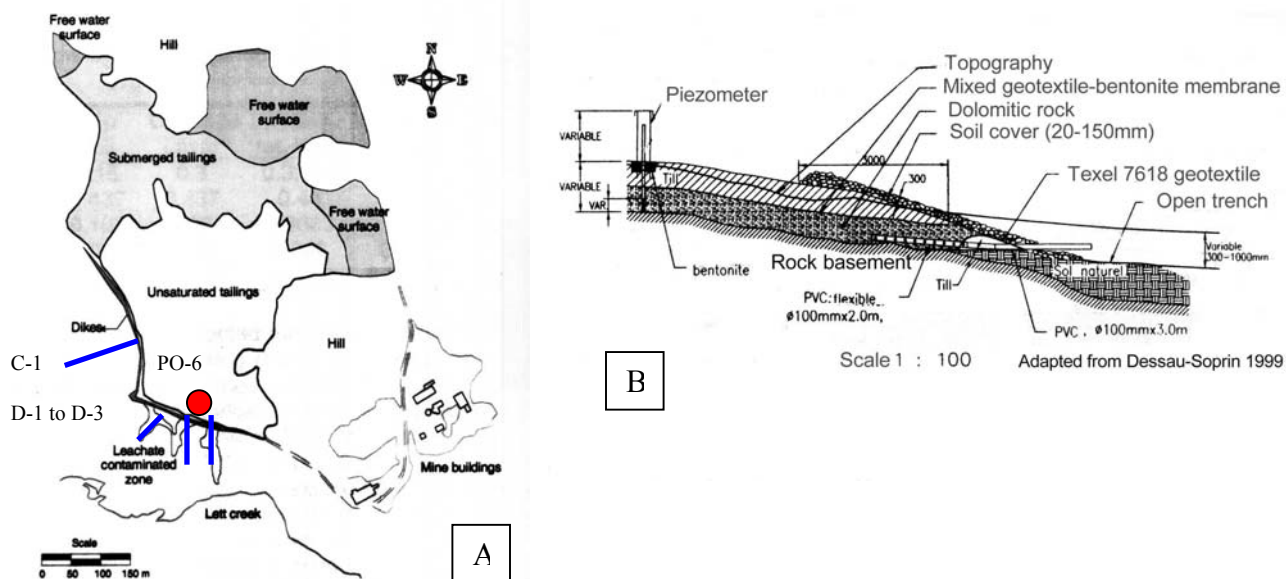


Figure 7 A) Plan view of the Lorraine mine site and tailings pond showing the location of the dolomitic (D-1 to D-3) and limestone (C-1) drains, PO-6 is a piezometer sampling the AMD in the oxidised tailings (adapted from Nastev and Aubertin, 2000). B) Longitudinal section of a limestone drain installed downward slope of the dikes at the Lorraine site (taken from Fontaine, 1999).

**Treated effluent hydrogeochemistry:** A 3 year hydrogeochemistry monitoring program was initiated in May 1999 as part of a follow up study of the remediation plan. Water from a series of piezometers penetrating the tailings below the CCBE and the entrance of the limestone drains was sampled with the discharged treated effluent on a monthly basis between May and October of each year. The parameters measured during the field sampling to evaluate the drain performance are T, pH, redox, conductivity, flow rate; the water samples were also tested in the laboratory for alkalinity, acidity, hardness and ICP multi-elements analysis. At the end of the 3 year program, it was decided to continue the monitoring and the sampling and analysis were performed during the summer 2002.

The effluent variation in pH and alkalinity is considered a good indication of the passive treatment efficiency in treating AMD. The pH is an intensity indicator whereas alkalinity is a neutralising capacity indicator. The variation in pH, alkalinity and acidity with time are given in Table 3.

**Tableau 3 Influent and effluent average pH, alkalinity and acidity.**

| Sample    | 1999 (n=7)  |            |             | 2000 (n=6)  |            |            |
|-----------|-------------|------------|-------------|-------------|------------|------------|
|           | pH          | Alkalinity | Acidity     | pH          | Alkalinity | Acidity    |
| PO-6      | 3.17 (0.47) | 0          | 5239 (341)  | 3.78 (0.36) | 0          | 4525 (918) |
| Cal-1 out | 6.72 (0.08) | 470 (63)   | 0           | 6.82 (0.09) | 468 (32)   | 0          |
| Dol-1 out | 6.09 (0.14) | 145 (192)  | 116 (307)   | 6.19 (0.06) | 88 (25)    | 0          |
| Dol-2 out | 5.37 (0.17) | 8 (11)     | 2000 (1920) | 5.57 (0.14) | 4 (3)      | 0          |
| Dol-3 out | 4.44 (0.28) | 0          | 2407 (1114) | 4.70 (0.07) | 0          | 3478 (878) |
|           |             |            |             |             |            |            |
| Sample    | 2001 (n=6)  |            |             | 2002 (n=4)  |            |            |
|           | pH          | Alkalinity | Acidity     | pH          | Alkalinity | Acidity    |
| PO-6      | 3.81 (0.57) | 0          | 6293 (1125) | 4.16        | 0          | 8463 (382) |
| Cal-1 out | 6.77 (0.06) | 456 (47)   | 0           | 6.83 (0.08) | 529 (61)   | 203 (26)   |
| Dol-1 out | 6.14 (0.08) | 58 (31)    | 0           | 6.18 (0.1)  | 110 (70)   | 1076 (36)  |
| Dol-2 out | 5.64 (0.08) | 4 (6)      | 3160 (1614) | 5.49 (0.07) | 5 (10)     | 4865 (124) |
| Dol-3 out | 4.74 (0.16) | 0          | 3432 (986)  | 4.4 (0.08)  | 0          | 4760 (576) |

*Alkalinity and acidity are in mg CaCO<sub>3</sub>/L*

As can be seen, the pH of the treated effluents (Cal-1 out, Dol-1,2,3 out) are higher than the influent (PO-6). The drains Cal-1 and Dol-1 and Dol-2 have generated alkalinity since the beginning of the passive treatment whereas drain Dol-3 never generated alkalinity and the pH never raised above 4.75. The pH of the treated effluents has regularly increased during the first two seasons of passive treatment and remained fairly constant afterward (Figure 8 A). The concentration in Fe total, Al and SO<sub>4</sub> of the treated effluents are lower than in the influent (PO-6). It should be kept in mind that the role of an ALD is essentially to generate alkalinity and if the drain is perfectly anoxic, metals oxidation should be prevented in the drain. Measured concentrations of ferrous iron and total iron were done in the field in June 2001 using a spectrophotometer and calculated Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios varies considerably for the four drains treated effluents (Cal-1: Fe<sup>3+</sup>/Fe<sup>2+</sup>=0.26; Dol-1: Fe<sup>3+</sup>/Fe<sup>2+</sup>=0.20; Dol-2: Fe<sup>3+</sup>/Fe<sup>2+</sup>=0.57; Dol-3: Fe<sup>3+</sup>/Fe<sup>2+</sup>=0.63) indicating that most of the iron is in its ferrous state when entering drains Cal-1 and Dol-1 and is expected to oxidized in the trench once outside the drains (Figure 9). However, AMD entering drains Dol-2 and Dol-3 contain much higher Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios, limiting further oxidation in the open trench.

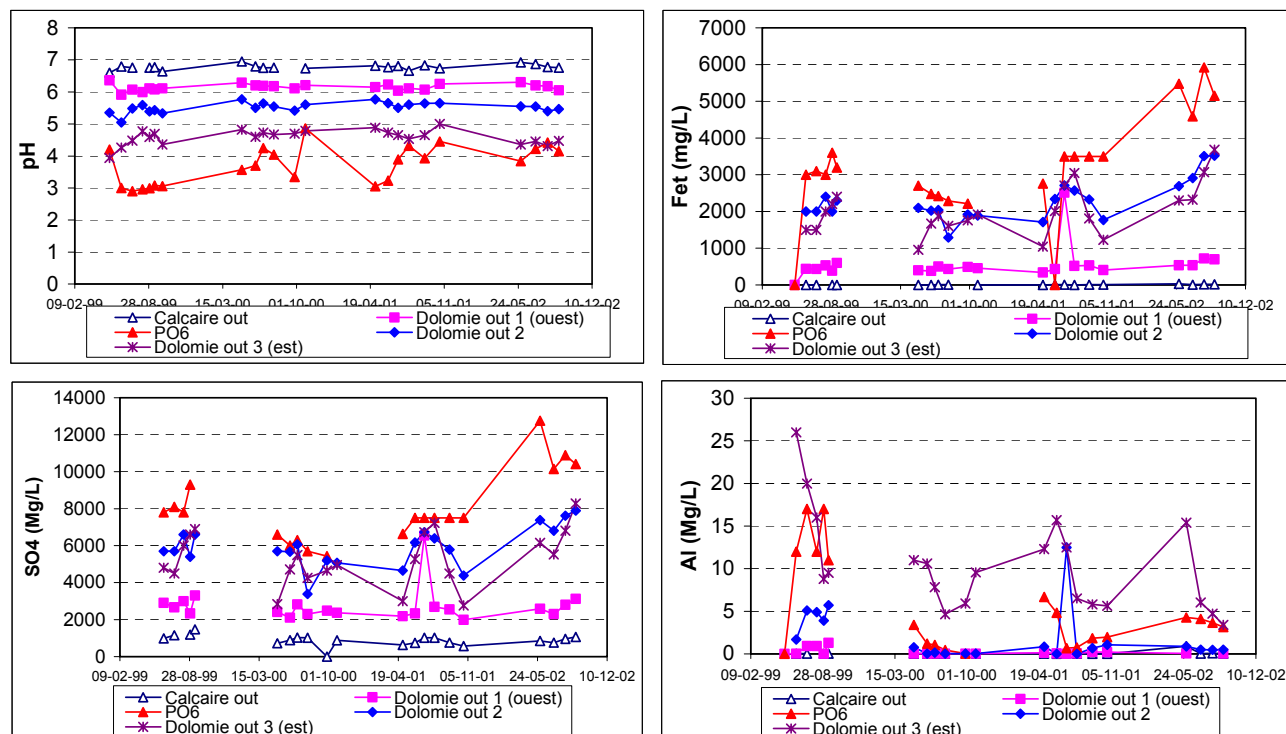


Figure 8 Variation of pH, Fet, Al and sulfate concentration in the influent (PO-6) and treated effluents.



Figure 9 A) View of drain Cal-1 output, May 1999. B) Idem, but in June 2001. C) View of drain Dol-3 output, May 1999. D) Idem, but in June 2001. E) View of drain Dol-1 output, June 2001. Notice the iron hydroxides precipitates in the trenches.

The data shown in Figure 8 indicates that metals and sulfates concentration appears to have increased during summer 2002. Monthly flow rates measurements are shown in Figure 10 for the 3 dolomite drains (Dol-1 to 3). Since September 13, 1999, the average flow rates have been as follow:  $238 \pm 81$  L/h for Dol-1,  $148 \pm 53$  L/h for Dol-2 and  $148 \pm 81$  L/h for Dol-3. However, a decrease in flow rates has been recorded during the dry summer of 2002. It is too early to interpret this decrease in flow rates. Nevertheless, two hypothesis can be proposed: 1) the decrease in flow rates could reflect a decrease in internal porosity due to secondary minerals precipitating within the drains and transport and filtration of suspended matter, 2) a lower input of diluting waters from rainfall infiltration. The good correlation observed between measured flow rates and  $Fe_{tot}$ ,  $SO_4$  concentrations and acidity (Figure 10) is in better agreement with assumption number 2.

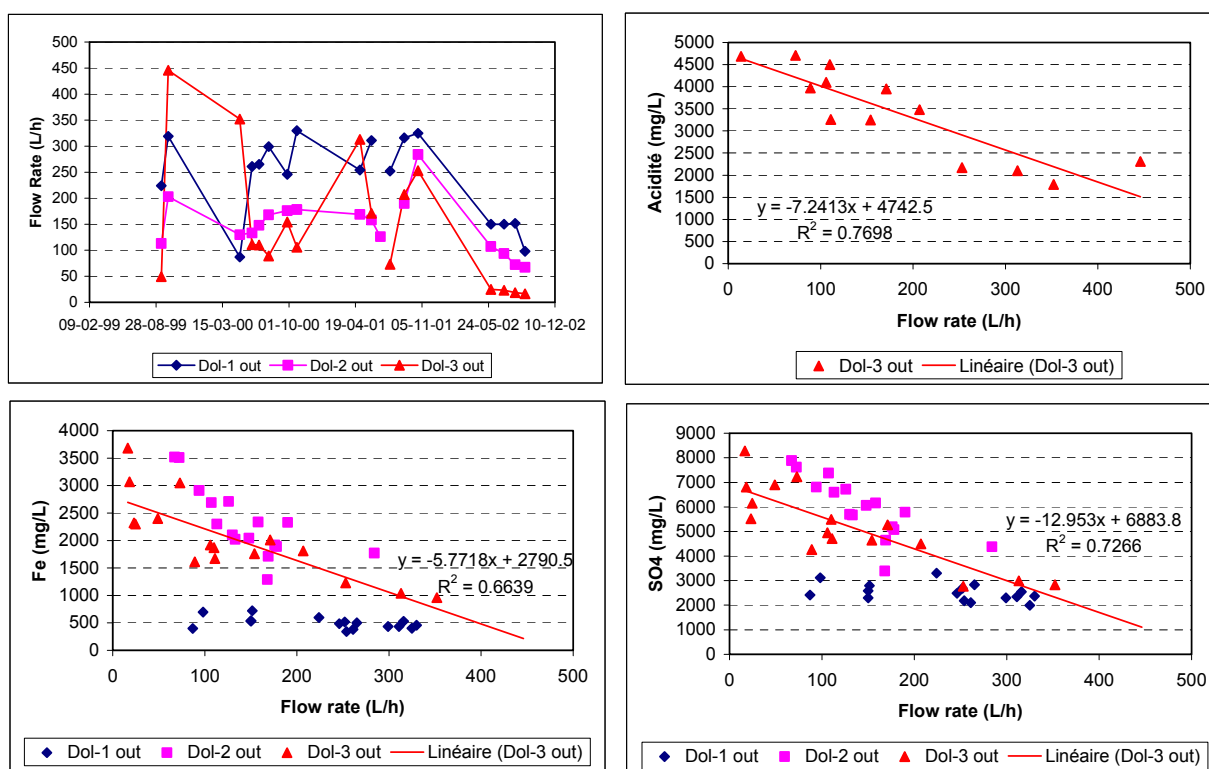


Figure 10 Seasonal variation in flow rates and correlation of flow rates with  $Fe_{tot}$ ,  $SO_4$  and acidity.

However, calculated mineral saturation indices indicates that outgoing treated effluents are over-saturated in gypsum, ferrihydrite and aluminium hydroxides which suggest these minerals may be slowly accumulating within the drains with time.

In summary, the interstitial AMD accumulated within that tailings pound at the Lorraine site prior to the CEBC construction has been substantially improved by the use of the limestone drains passive treatment when compared with the initial chemistry of resurgent AMD. The passive treatment of the Lorraine site effluents has to be considered on a long term basis because the average percolation rate through the CCBE is very slow (110 mm/y or less) and the volume

of AMD in the tailings is fairly large (465000m<sup>3</sup> with a porosity of 0.39; Nastev and Aubertin, 2000). The results obtained during the 3 years monitoring program are currently used to evaluate alternative designs and stone material to improve the passive treatment at the Lorraine site.

## CONCLUDING REMARKS

Since the development of passive treatment system in the late 1970s, the use of limestone has been frequently integrated in various systems such as open limestone channel (OLC), anoxic and oxic limestone (ALD, OLD) drains and successive alkalinity producing systems (SAPS). The increasing interest for passive treatment system has been driven mainly by lower treatment cost and also perhaps by a hope (so far unrealistic) that it may represent a walk away solution to AMD treatment. Current sizing methods are essentially based on mass equilibrium approaches which generally consist in determining the amount of limestone needed by multiplying the annual acid load by the desired lifetime of the system. Hence, this sizing method do not take into account the kinetics of carbonate dissolution, the surface area of the rock used, variations in hydraulic conditions, and the armoring effect. More research has to be done before these influencing factors can be successfully integrated in the sizing method. Alternative rock types that worth being evaluated in various passive treatment settings are other highly reactive dissolving minerals such as magnesite and brucite with fast weathering minerals such as magnesian olivine, serpentine, anorthite or nepheline. The geometry of a drain can be better engineered to take into account variable flow rates, armoring effects, and internal porosity to account for seasonal variations in hydraulic conditions and water chemistry. A good knowledge of the historical variations recorded in flow rates and metals loading is required in order to be able to design a passive treatment system that can perform successfully over many years. A multi-step approach is probably the key to successfully design passive system to treat AMD with a high acidity, and heavy metals and sulfates loads such as observed at the Lorraine mine site. New technology such as anaerobic sulfate reducing bacteria bioreactors also offer some interesting potential to treat AMD. Pre-restoration testing programs (various designs and materials) and site monitoring should be established to optimize long term system response.

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