

# The Use of Limestone as a Strategy to Remove Sulphate from Mine Waters with Sulphate Concentrations Below the Limit Defined by Gypsum Solubility

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## Abstract

The precipitation of sulphate, iron and aluminium is the main factor accounting for armouring during limestone treatment of acid mine drainages, which renders the acidity neutralization processes ineffective. Based on this observation, limestone is proposed herein as a sorbent for sulphate removal, from neutral mine drainages. Therefore the present work investigated sulphate removal from a pH 6.5 mine water through sorption on limestone. Batch equilibrium tests showed that sulphate loading on limestone can be described by the Langmuir isotherm with a maximum loading of 0.248mmol/g. Fixed-bed experiments were utilized to produce breakthrough curves at different bed depths (15cm-25cm) and flow rates (2mL/min-10mL/min). The Thomas model was selected to describe the breakthrough data and revealed sulphate loadings of up to 0.21molSO<sub>4</sub><sup>2-</sup>/L-bed as the flow rate increased. Sulphate sorption on limestone might be a cost-effective alternative to treat mine waters with sulphate concentrations below the values set by gypsum solubility (1500-2000mg/L) and for which only more expensive processes are available.

Key words: Sulphate, mine water, limestone, bed length, sorption models.

## Introduction

Sulphate is a major anion in effluents of the industries which utilize sulphuric acid in their processes (Mulinari and da Silva 2008; Roonasi and Holmgren 2009) and is also produced during acid mine drainages (AMD) (Cao *et al.* 2009). In drinking water, sulphate can affect taste and have laxative effects at concentrations in excess of 600mg/L (Haghsheno *et al.* 2009). In mine waters, sulphate is of less concern than both acidity and metal content notwithstanding environmental agencies in mine countries establish regulations to control sulphate, usually by setting a limit between 250mg/L and 500mg/L in different type of effluents. Even when there is not a specific guideline for sulphate, total dissolved solids are usually specified, which include sulphate concentrations (INAP 2003).

Sulphate-bearing wastewaters or mining drainages are usually treated by different techniques such as ettringite precipitation, ion exchange and membrane techniques. The selection of the process aiming at treating such effluents is defined by several factors such as chemical availability, local regulations, commercialization of the produced water and process economics (INAP 2003), but gypsum precipitation is usually applied as the first step, particularly when acidity needs to be controlled. One good example is the production of drinking water from AMD originated from different sites by the eMalahleni Project in South Africa. AMD is first treated by oxidation and precipitation prior to being subject to ultrafiltration and reverse osmosis to produce a <200mg/L total dissolved solids water

(Hutton *et al.* 2009). Sulphate removal by shrimp peelings (Moret and Rubio 2003), modified zeolites (Oliveira 2006) and coconut pith (Namasivayam and Sangeetha 2008) has also been investigated.

Limestone is an inexpensive material widely available in many parts of the world, which has been the primary option for treating mine-affected waters containing high acidity and dissolved metals, particularly iron and manganese (Sun *et al.* 2000). Limestone consumes acidity according to equation 1, increasing the drainage pH and then inducing metal removal (Rose and Elliott 2000) through precipitation and/or adsorption (Komnitsas *et al.* 2004). However, its efficiency as acidity neutralizer is reduced if the mine water is only mildly acidic. Also contributes to this lower reactivity the precipitation of either iron and aluminium oxy-hydroxides or calcium sulphate on the limestone surface, which create a layer of inert material strongly reducing its reactivity (the so-called armouring effect).



The formation of calcium sulphate on the limestone surface can be utilized to devise a new process for sulphate removal from neutral mine waters (in which acidity is low) based on sorption principles. This process does not have the drawback of the high residual sulphate concentrations observed when gypsum precipitation is used for sulphate precipitation from mine waters, usually in the 1500-2000mg/L range. Therefore, a new approach is proposed in the current work whereby limestone is applied for sulphate sorption, particularly in those mine waters with moderate anion concentrations (below 1500mg/L), which are above the discharge limit set by environmental agencies.

## Experimental

A calcite limestone sample assaying 53.7% calcium and 0.28% magnesium had its particle size between 0.42mm and 0.59mm (0.774 m<sup>2</sup>/g specific surface area) selected for a series of fixed-bed experiments performed with neutral mine water (pH 6.5) samples assaying 588.0mg/L sulphate, 45mg/L Mn and 2.4mg/L Fe.

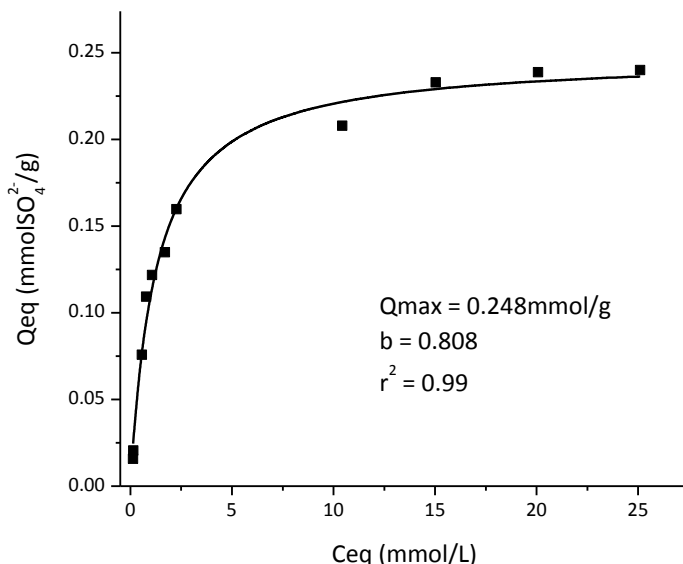
The fixed-bed experiments were performed with limestone particles with an average diameter of 505µm. The solid particles were transferred to a glass column (20mm diameter) to produce bed depths ranging from 15cm to 25cm. The column diameter/particle size ratio enabled the wall effect to be neglected during experiments. Subsequently the particle bed was washed with distilled water to remove fine particles. During the experiments, the column was fed upwards by peristaltic pumps and the flow rate (Q) was varied between 1 and 10mL/min, regulated by a constant-speed pump (Milan). From the column effluent, samples were collected regularly for analysis as total sulphur in an ICP-OES (Varian, 725). Such concentration was assumed to represent sulphate in the both the mine- and treated water. Sulphate loading on limestone was determined by mass balance and the experiments were carried out at 23±1°C.

For modelling purposes, a pseudo adsorption isotherm was produced using synthetic sulphate solutions. The procedure comprised shaking (at 300min<sup>-1</sup>) limestone particles (0.42mm-0.59mm) added to 250mL Erlenmeyer flasks containing 120mL of sulphate solutions. The anion concentration varied from 50.0mg/L to 3000.0mg/L at (pH 9.6-9.8), the pulp contained 25.0g/L solids and the experiments run for 9 hours. Sulphate (as S<sub>tot</sub>) was analysed in an ICP-OES (Varian, 725) and the loading on limestone was determined by mass balance.

## Results and discussion

The precipitation of calcium sulphate on the limestone surface has been demonstrated during the characterization of armoured limestone beds treating typical AMD (pH 2.9, 2200mg/L sulphate) (Hammarstrom *et al.* 2003). Therefore sulphate sorption by limestone would be an option for lowering the anion concentration, particularly from neutral mine water in which there is negligible limestone dissolution and the solid beads would behave like a solid substrate for sulphate sorption (either sorption or precipitation). This approach is not constrained by gypsum solubility and thus mine waters with moderate sulphate content (below  $\pm 1500\text{mg/L}$ ) could be treated. Such value is not high enough to enable gypsum precipitation, but remains above the discharge limit (usually  $250\text{mg/L}$ ) set by environmental agencies

To prove such a concept a pseudo-sorption isotherm was produced using synthetic solutions containing different sulphate concentrations at pH 6.5 as depicted in figure 1. Figure 1 indicates that sulphate sorption on limestone can be described by the Langmuir isotherm ( $r^2 = 0.99$ ) with a maximum sulphate loading of  $0.25\text{mmolSO}_4^{2-}/\text{g-limestone}$ . Several adsorbents have been applied to remove sulphate from industrial effluents and it may be cited as example chitin flakes in which sulphate sorption was also described by the Langmuir isotherm with  $1.6\text{mmolSO}_4^{2-}/\text{g}$  as maximum capacity (Moret and Rubio 2003). Another example is sulphate uptake by the strong base ion exchange resin PuroLite A500, which also followed the Langmuir isotherm and the maximum uptake was  $0.61\text{mmol/L-resin}$  (Guimarães and Leão 2014). Likewise, sulphate sorption in the Lewait K6362 resin produced good fittings to both the Langmuir and Freundlich and the maximum loading was  $1.73\text{mmolSO}_4^{2-}/\text{g}$  (Haghsheno *et al.* 2009).



**Figure 1.** Sulphate sorption isotherm (a) and effect of bed depth on sulphate sorption. Experimental conditions:  $23\pm 1^\circ\text{C}$ , initial pH 6.5; particle size 0.42-0.59mm; 10mL/min;  $C_0 = 6.12\text{mmolSO}_4^{2-}/\text{L}$ .

A good fitting to the Langmuir isotherm as observed herein implies in a chemisorption process, characterized by the presence of a monolayer on the sorbent surface. Bonding between sulphate and calcium ions present on the limestone surface would account for the formation of such monolayer (Hammarstrom *et al.* 2003).

Fixed bed sorption was selected for further sulphate sorption studies. It is very often applied in mine water treatment because of both (i) its high selectivity and efficiency and (ii) the removal of harmful species even at very low concentrations (Reynolds and Richards 1995). Again a neutral mine water (containing 6.12mmol/L  $\text{SO}_4^{2-}$  at pH 6.5) was used in the fixed-bed tests with limestone as the sorbent. In this particular series of experiments the effects of flowrate and bed depth on the sulphate breakthrough curves were assessed. Subsequently, fixed-bed sulphate sorption was modelled according the Thomas model, which provided the solid loading and the rate constant of the sulphate sorption process.

The Thomas model for fixed-bed columns assumes that sulphate sorption on limestone can be described by the Langmuir kinetic equation (eq. 2) (Chu 2010). At equilibrium equation 2 is converted to the familiar Langmuir expression.

$$\frac{\partial q}{\partial t} = K_{T1} C(q_m - q) - K_{T2} q \quad (2)$$

In equation 2,  $q_m$  represents the sulphate loading in limestone (mg/g);  $K_{T1}$  and  $K_{T2}$  are rate constant and  $q$  is the limestone loading (mg/g) at time  $t$ .

Being  $v$  the axial velocity (cm/s) and  $\varepsilon$  is the bed porosity, a mass balance for a fixed-bed column in the absence of axial dispersion is:

$$v \frac{\partial C_t}{\partial Z} + \frac{\partial C_t}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_t}{\partial t} = 0 \quad (3)$$

An analytical solution for equation 3 was proposed by Thomas (1944) as follows:

$$\frac{C_t}{C_0} = \frac{J\left(\frac{n}{r}, nT\right)}{J\left(\frac{n}{r}, nT\right) + \{1 - J\left(\frac{n}{r}, nT\right)\} \exp\left\{\left(1 - \frac{1}{r}\right)(n - nT)\right\}} \quad (4)$$

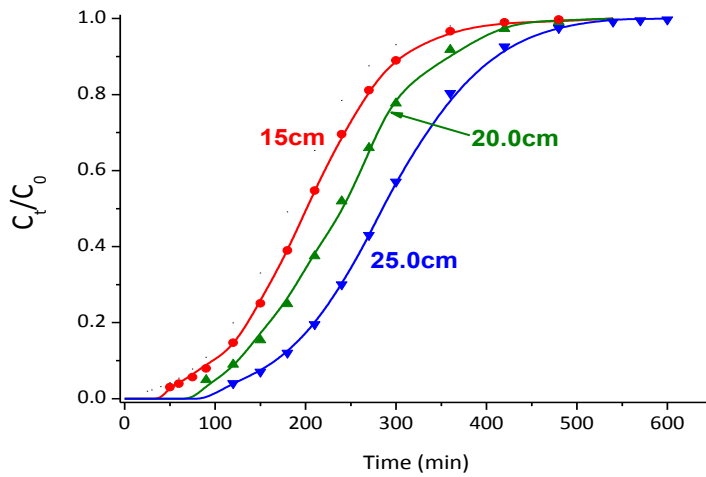
Where  $r = 1 + bC_0$  (5)

$$n = \frac{\rho_p q_m k_T Z (1-\varepsilon)}{\varepsilon v} \quad (6)$$

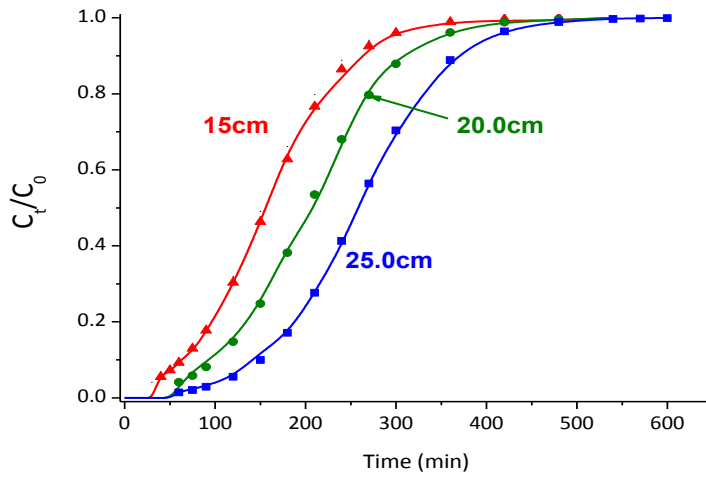
$$T = \frac{\varepsilon \left(\frac{1}{b} + C_0\right)}{\rho_p q (1-\varepsilon)} \left(\frac{vt}{Z} - 1\right) \quad (7)$$

And  $J(x, y) = \frac{1}{2} \left\{ 1 - \operatorname{erf}(\sqrt{x} - \sqrt{y}) + \frac{\exp(-(\sqrt{x}-\sqrt{y})^2)}{\sqrt{\pi} (\sqrt{y} + (xy)^{0.25})} \right\}$  (8)

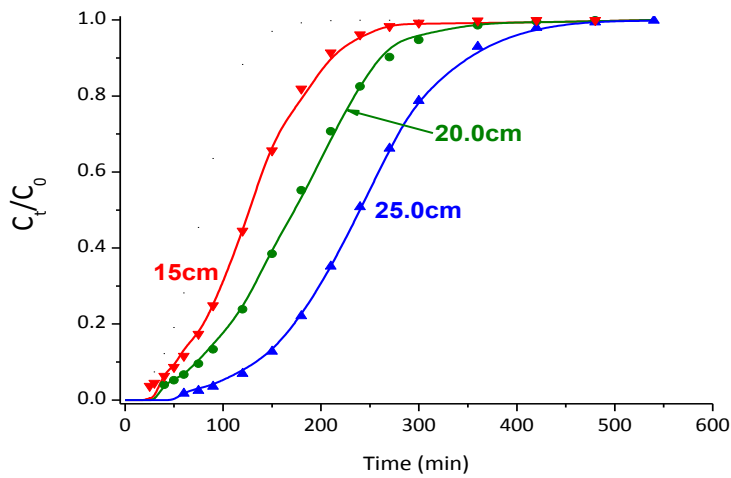
Equations 4-8 were solved using Mathematica 9.0 to produce the  $q_m$  and  $k_T$  values which resulted in the best fit between experimental and model data. As it can be seen in figures 2 - 4, Thomas equation reproduces fairly accurately the breakthrough curves for sulphate sorption on limestone under the experimental conditions investigated.



**Figure 2.** Breakthrough curves for sulphate sorption on limestone at different bed depths. Experimental conditions:  $Q = 2\text{mL/min}$   $23 \pm 1^\circ\text{C}$ , initial pH 6.5; particle size 0.42mm-0.59mm;  $C_0 = 6.12 \text{ mmolSO}_4^{2-}/\text{L}$ .



**Figure 3.** Breakthrough curves for sulphate sorption on limestone at different bed depth. Experimental conditions:  $Q = 3\text{mL/min}$   $23 \pm 1^\circ\text{C}$ , initial pH 6.5; particle size: 0.42mm-0.59mm;  $C_0 = 6.12\text{mmolSO}_4^{2-}/\text{L}$ .



**Figure 4.** Breakthrough curves for sulphate sorption on limestone at different bed depths. Experimental conditions:  $Q = 10\text{mL/min}$   $23 \pm 1^\circ\text{C}$ , initial pH 6.5; particle size: 0.42mm-0.59mm;  $C_0 = 6.12\text{mmolSO}_4^{2-}/\text{L}$ .

The Thomas model revealed solid phase ( $q_m$ ) and bed loading ( $N$ ) values which were roughly independent of the bed depth at the same flow rate (table 1). Table 1 also shows that the bed capacity is increased when the influent flowrate ( $Q$ ) was also increased at the same bed depth,  $Z$  (e.g. 20 cm). Likewise, the rate constant ( $k_T$ ) decreased with increasing bed depth, at the same flow rate, implying in a larger resistance to mass transfer in the liquid phase. This reflected a change on the form of the breakthrough curves with bed-depth as also observed elsewhere (Srivastava *et al.* 2008; Chauhan and Sankararamkrishnan 2011; Patel and Vashi 2012). In addition there was also a small increase in the rate constant with flowrate (at the same bed length), which implies that chemical control may play a significant role on the sulphate sorption process. This is reinforced by the second-order kinetics observed in batch kinetics experiments carried out by Silva *et al.* (2012) with the same mine water and limestone. Furthermore, the presence of gypsum on the calcium sulphate surface was showed by Hammarstrom *et al.* (2003) and also Booth *et al.* (1997). The latter used sulphate containing neutral solution at pH 5-6 to demonstrate partial limestone dissolution prior to gypsum formation over the attacked rock surface.

**Table 1.** Parameters produced during fitting of the Thomas model to sulphate sorption on limestone.

Z (cm)	Q (cm <sup>3</sup> /min)	$k_T$ (mL.mmol <sup>-1</sup> min <sup>-1</sup> )	$q_m$ (mmol/g-limestone)	N (mol/L-bed)	SSE
15	10	4.916E-04	1.065E-04	2.00E-01	5.20E-03
20	10	3.840E-04	1.067E-04	2.00E-01	2.98E-03
25	10	3.711E-04	1.186E-04	2.22E-01	3.67E-04
15	3	3.779E-04	3.861E-05	7.24E-02	1.23E-03
20	3	3.528E-04	3.728E-05	6.99E-02	2.73E-03
25	3	3.508E-04	3.756E-05	7.05E-02	8.29E-04
15	2	3.639E-04	3.261E-05	6.12E-02	6.34E-04
20	2	3.359E-04	2.851E-05	5.35E-02	3.67E-03
25	2	3.257E-04	2.740E-05	5.14E-02	1.50E-04

Gypsum precipitation with lime still appears to be the best technical and economical alternative to reduce high sulphate loadings from mine waters because of its high efficiency in reducing the anion concentrations regardless of the pH of the process. Nevertheless, when the wastewater is undersaturated with respect to gypsum (sulphate concentrations below ~1500mg/L), sulphate sorption on limestone would be a cost-effective alternative to treat such waters in order to comply with environmental regulations. Such technology would be particularly suitable for those countries where water is widely available and where mine water treatment costs must remain as low as possible because there is no possibility to commercialize the treated water.

## Conclusions

Limestone is a promising low-cost adsorbent for sulphate removal from neutral mine waters containing low concentrations of metals such as iron and manganese. Sulphate removal, likely as gypsum sorbed onto limestone particles, suggests a chemisorption process described by the Langmuir isotherm with a maximum uptake of 0.248mmol/g. Such hypothesis was reinforced by the application of the Thomas model to breakthrough curves produced in fixed bed experiments, which revealed only a small effect of the flowrate on the rate constant.

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