

The use of limestone, lime and MnO_2 in the removal of soluble manganese from acid mine drainage

A. Aguiar, G. Xavier & A. Ladeira

CDTN, Center for the Development of Nuclear Technology, Brazil

Abstract

Acid mine drainage (AMD) is one of the main environmental issues faced by the mining industry. The acid mine water generally contains metals above the permissible discharging levels. Manganese is particularly present in this effluent and its removal is notoriously difficult due to its high solubility over a wide range of pH. While most of the metals precipitate at a pH below neutrality, the pH necessary for manganese precipitation is very high, above 10. Most systems that effectively remove this element from mine waters use the oxidation of Mn (II) followed by precipitation at an elevated pH. Precipitation consumes a great amount of lime, which implies high operational cost. Besides, the process generates a large amount of sludge containing metals which have to be disposed of. The objective of this study is to optimize the removal of manganese by using a laboratory prepared acid solution and an acid effluent from Poços de Caldas uranium mine (Brazil), in order to achieve the Mn permitted level for discharging ($<1\text{mg/L}$) and to reduce the amount of sludge generated. The precipitation process has been studied using lime, limestone and a non-conventional catalyst/adsorbent (MnO_2 residue). The results obtained showed that both lime and limestone are effective in the removal of Mn in a pH higher than 10. However, there is a slight difference between the two reagents and lime shows a better performance. The volume of precipitate generated by the addition of lime was 50% smaller than that obtained when limestone was used. The use of the non-conventional material made the removal of almost 100% of the Mn possible as the concentration of manganese was reduced from 140mg/L to $<1\text{mg/L}$ at a pH near neutrality (6.8 to 7.2). The final effluent complies with the recommended value for manganese discharge.

Keywords: manganese, acid mine drainage, precipitation, manganese oxide.



1 Introduction

Manganese is a typical contaminant from mining effluents, as it is one of the constituents of gold, uranium and zinc ores. The contamination of surface water with manganese is increasing expressively due to mining activities. Specifically in acid mine drainage, manganese is particularly present in high concentrations much higher than the permissible levels for discharging. Acid mine drainage (AMD) has been considered one of the main environmental problems faced by the mining industry and it may contain 5 to 10mg/L of Mn but values higher than 50mg/L are not uncommon. The concentration depends on the amount of Mn-containing minerals and on the process used to treat these minerals [1]. The maximum admissible concentration of manganese in liquid effluents, according to Brazilian legislation is 1.0mg/L. There are pragmatic problems in attaining such low concentration [2] especially when the manganese is in the form of Mn (II), typical case of mine water. In that oxidation state, manganese is much more stable at higher pH than the oxidized form (Mn (IV)). Most systems that effectively remove manganese from mine waters use the oxidation of the Mn (II) species at an elevated pH followed by precipitation as sulphite or manganese oxides [2, 3].

It is well known that for decades most water contaminants have been removed by chemical precipitation. Chemical treatment can provide reasonable remediation treatment for AMD, however, it has been contested, both technically and economically, due to its high operational and environmental costs incurred from the formation of large amounts of sludge which need to be disposed of [4, 5]. In general, the removal of Mn (II) is carried out through the addition of lime, which demands an excessive consumption of reagent as a result of high pH values required for its precipitation [3]. Even so, after the precipitation, the solution free of manganese cannot be discarded, as it generally has a pH above 10.0 [4]. Another difficulty related to the process of precipitation is the time-consuming kinetics in the formation of stable precipitates. Oxidizing reactions are usually kinetically too slow, which means a problem for large flows, as currently found in acid mine drainage (>50mg/L) [6, 7]. The practice of precipitation through the formation of hydroxides, although widely distributed and relatively simple, can be further optimized through studies aiming at achieving a faster, more practical and more effective removal.

Mn removal can be catalyzed by the use of some solids, including manganese oxide [6]. That is because many manganese oxides exhibit redox properties, which implies in high reactivity with respect to the sorption phenomena [8]. The U.S Environmental Protection Agency recognizes many commercially available Mn oxides as oxidizing and adsorptive media in industrial applications. Nowadays, the great challenge of the industry in the removal of manganese, especially when present in acidic effluents, is the low limit permitted for discharging (<1mg/L). This fact stimulates the development of new researches, aiming at the definition of technically and environmentally feasible processes.

This work presents a comparative study of manganese removal from acid solutions, including an acid mine effluent, by precipitation using lime and



limestone. The researches also assessed the influence of a non-conventional material (MnO_2) on promoting an efficient removal of manganese at pH lower than 10 which may reduce reagent consumption and, consequently, the amount of precipitate. MnO_2 was expected to act as a catalyst increasing the kinetics of the oxidation and also as an adsorbent of the Mn^{+2} .

2 Methodology

2.1 Reagents

A laboratory solution with Mn concentration around 150mg/L was prepared by dissolution of analytical grade $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. An acid mine effluent containing 144mg/L of Mn was supplied by Brazilian Nuclear Industry (INB). Samples of commercial lime and limestone reduced to size $<0.044\text{mm}$ were used as precipitants. The manganese oxide (MnO_2) was a residue supplied by the zinc industry. The MnO_2 specific surface area was $46.0 \text{ (m}^2/\text{g)}$ and was determined by BET method multiple point technique (Quantachrome Corp., NOVA-2200).

2.2 Batch experiments

Three distinct procedures were carried out in order to remove the manganese from the solutions:

Precipitation experiments: The volume of the laboratory solution was set at 200mL and the pH range was from 4.2 to 11, adjusted with lime or limestone. The suspension was magnetically shaken for 30 minutes after pH stabilization at room temperature (25°C). Subsequently, the suspension was filtered and the filtrate was analyzed for Mn through flame Atomic Absorption Spectroscopy (model AA240FS, Varian). The dissolved oxygen was monitored with the use of an oximeter (model DM-22, Digimed) during the process.

Batch Adsorption Experiments: The laboratory solution volume was fixed at 300mL with Mn content of 150mg/L. Different amounts of MnO_2 (0.75 to 3.00g dry basis) were added to the solution. The pH range adopted was set in the range of 6.8 to 7.2. Samples were collected every 2 hours, filtered and analyzed for Mn according to procedure 1. The Eh of the system was monitored using a platinum electrode.

Isotherms: The isotherms were obtained with the laboratory solution and the acid mine effluent. The pH of the Mn solutions was first adjusted to the pre-determined values (6.8-7.2), which leads to a decrease of the Mn concentration to values around 100mg/L, and then the solutions were filtered. Subsequently, different amounts of MnO_2 (0.2 to 1.5g dry basis) were added to 150 ml of the solution. The pH was adjusted to 6.8-7.2 when necessary with the use of 1.0M NaOH and 0.5M Na_2CO_3 for experiments with lime and limestone, respectively. The suspension was magnetically shaken for 24 hours at room temperature ($T=25^\circ\text{C}$). Afterwards, the suspension was filtered and the filtrate was assayed for manganese through Atomic Adsorption Spectroscopy (model AA240FS, Varian).



3 Results and discussion

3.1 Influence of the pH in the precipitation

As can be notice in figure 1 the manganese removal is very low at pH ranging between 4.0 and 8.0. For pH above 8.5, the removal increases significantly and reaches the value set by the protection standards (e.g. 1.0mg/L) at pH 9.1 for limestone and pH 10.0 for lime. According to literature [6, 9, 10] the formation of stable manganese oxides is obtained only at pH above 7.5 and the importance of the pH increase in the removal of Mn is extensively discussed. Figure 1 also shows that the curve for limestone stands below the curve for lime in almost the whole range of pH. It means that limestone shows a removal efficiency slightly higher than that presented by lime.

The mass of limestone used to attain the Mn limit recommended for discharge is greater than the mass of lime. This implies in the generation of an additional volume of residue in the treatment with limestone, which incurs an extra expense, namely disposal and/or storage. In industrial procedures, the viability of the use of limestone depends on the form it is used, which could be in fixed bed or column. This application has not been assessed yet.

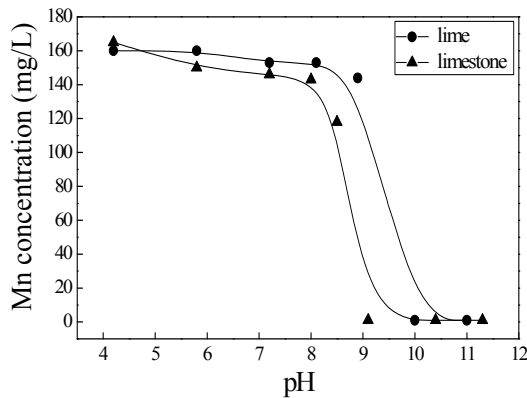


Figure 1: Mn concentration as a function of pH, without MnO_2 addition; $T=25^\circ\text{C}$.

3.2 The influence of dissolved oxygen

Figure 2 shows the correlation between the concentration of dissolved oxygen and the concentration of Mn^{+2} in the system. It is observed that the experiments with lime show an inverse dependence between these two parameters: the higher the rate of manganese removal, the smaller the concentration of dissolved oxygen. This can be explained by the fact that stable forms of solid manganese in alkaline solutions are constituted of oxides (Mn_3O_4 (Hausmannite), Mn_2O_3

(Manganite or Feitknechtite), MnO_2 (Pyrolusite) and Mn_7O_{13} (Birnessite)) and for their formation the dissolved oxygen is consumed.

Another possible explanation for the low concentration of dissolved oxygen in the experiments with lime is the formation of a highly viscous sludge, which hinders the exchange of gases between the air and the solution. As the experiment was conducted without aeration, this could have been responsible for the diminution in the concentration of dissolved oxygen in the solution.

On the other hand, the experiments with limestone show no clear correlation between manganese removal and the concentration of dissolved oxygen in the system. In such case, it can be considered that the formation of stable Mn solid forms consume carbonate and not dissolved oxygen. This statement is supported by the fact that the values of dissolved oxygen observed during the experiments are similar to the solubility of oxygen in aerated water (e.g. 7-8mg/L). The values of dissolved oxygen in the system are close to 8mg/L even in high percentages of Mn removal. This result differs from the one obtained with lime and suggests that the dissolved oxygen do not participate in the formation of stable Mn solid forms in the systems with limestone. An example of manganese carbonate is Rhodochrosite (MnCO_3) that forms in systems with low concentrations of O_2 and high concentrations of CO_2 [11], despite the fact that the system under study does not present low concentrations of O_2 .

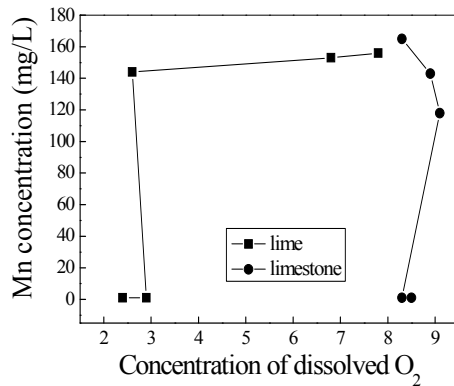


Figure 2: Influence of dissolved oxygen on manganese removal. Experiments carried out without aeration, $T=25^\circ\text{C}$.

3.3 The influence of MnO_2

The removal of manganese may be catalyzed by solids, including manganese oxides (autocatalysis) [6]. Moreover, the presence of small amounts of solids through the recycling of the precipitates or due to turbidity may enhance the rate of oxidation from Mn^{+2} to Mn^{+4} . The oxidation accelerates the precipitation process as the latter is favoured by the presence of the oxidized form of manganese. Figure 3 shows the data for manganese precipitation with lime at pH between 6.8 and 7.2 by adding different amounts of the MnO_2 residue. It is

observed that the larger the quantity of the MnO_2 added to the system, the more effective the manganese removal is. Furthermore, for amounts greater than 2.25g and reaction time of 6 hours, the final solution reaches the maximum admissible concentration of manganese in liquid effluents. By comparing these results with the ones from figure 1, one can conclude that at the pH range 6.8-7.2 and without the addition of MnO_2 , the removal of Mn was lesser than 10% and the final concentration of manganese was extremely high (above 140mg/L) whether at the same pH range and with the addition of 2.25g of MnO_2 the removal was very effective and the Mn final concentration was smaller than 1mg/L.

Figure 4 shows the influence of the use of MnO_2 residue in Mn removal by using limestone to set the pH in a range of 6.8-7.2. Similar to the experiment

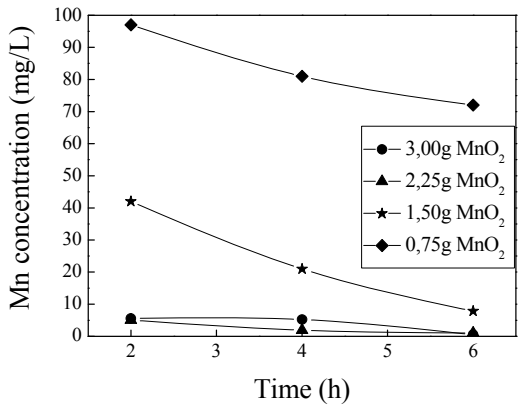


Figure 3: Influence of MnO_2 in the removal of Mn, pH adjusted with lime (6.8-7.2), aeration and $T=25^{\circ}C$.

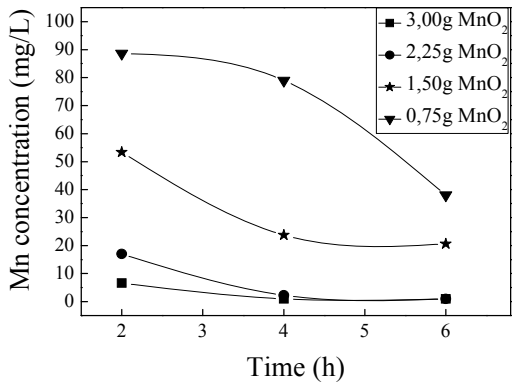


Figure 4: Influence of MnO_2 in the removal of Mn, pH adjusted with limestone (6.8-7.2), aeration and $T=25^{\circ}C$.

with lime, the addition of MnO_2 increased the rate of Mn removal. Amounts greater than 2.25g of MnO_2 and 6 hours of reaction time imply that the final solution complies with the legal requirement for Mn concentration in liquid effluents. It was demonstrated that the Mn removal at pH near the neutrality is only possible, in the systems under investigation, with the addition of MnO_2 .

It is also observed from figure 3 and 4 that the metal removal increases over time. In the experiments with limestone, the effluent reached the maximum admissible concentration for Mn after a reaction time of 6 hours. The only exception is observed with the trial with 3.00g of MnO_2 , which reached the maximum permitted concentration within a reaction time of 4 hours. The results obtained with lime are similar to the ones obtained with limestone, however by using lime, the rates of Mn removal are initially higher and Mn concentrations lower than 10mg/L are more easily obtained.

3.4 Adsorption isotherms

Figure 5 shows the adsorption isotherms for the laboratory solution and the acid mine effluent using the MnO_2 residue as adsorbent/catalyst. The pH was adjusted with lime or limestone to 6.8-7.2 [11]. The solid lines represent the adjustment of

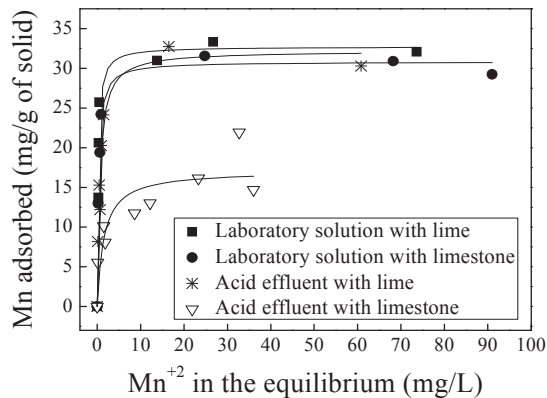


Figure 5: Equilibrium isotherms for Mn adsorption with MnO_2 . The solid lines represent the adjustment of the experimental data to Langmuir's equation. $T=25^\circ\text{C}$.

the experimental data to the Langmuir's equation. The clear definition of the plateaus, observed in figure 5, suggests that the manganese removal occurs by adsorption on the solid surface and not by precipitation. Langmuir's equation is well accepted to describe the adsorption phenomenon and is presented below:

$$Q = \frac{Q_{\max} \times k \times C_e}{1 + k \times C_e} \quad (1)$$

where,

Q = the amount of manganese adsorbed by the solid MnO_2 (mg/g of solid);
 Q_{max} = maximum adsorption capacity (mg/g); C_e = equilibrium concentration of Mn in the solution (mg/L); k = constant of affinity between the metal and the adsorbent.

Maximum adsorption capacities (Q_{max}) were determined by data extrapolation using Langmuir's equation. The Q_{max} for each experimental condition is shown in table 1. The results were very similar, except for the experiment with acid effluent and pH adjusted with limestone, in which the adsorption plateau was not clearly formed.

Table 1: Values for K and Q_{max} (mg/g) determined by fitting Langmuir's equation.

Sample	Q_{max} (mg/g)	k
Laboratory solution with lime	32,73	4,405
Laboratory solution with limestone	30,83	3,252
Acid effluent with lime	32,21	1,678
Acid effluent with limestone	17,13	0,643

The values of Q_{max} were between 17mg/g and 32mg/g. Literature reports Q_{max} values around 110mg/g for Mn adsorption on the mineral scolecite [12]. However, the initial concentration of the solutions used in the aforementioned study was up to 5000mg/L. The use of more concentrated solutions implies in higher loading capacity of the adsorbent. Moreover different experimental conditions make the comparison of the results difficult.

The acid effluent is an acid mine water with pH around 2.7 and an initial concentration of sulphate of 2.4g/L. In the presence of sulphate, the maximum adsorption capacity of the MnO_2 residue was expected to be smaller, due to the possibility of precipitation of calcium sulphate on the surface of the solid. However, the maximum capacity obtained for the acid effluent having its pH adjusted with lime is close to the maximum capacity obtained for the laboratory solutions. On the other hand, the Q_{max} for the acid effluent having its pH adjusted with limestone (17mg/g) is inferior to that obtained for the other solutions, indicating some sort of interference of other ions of the effluent. This statement is supported by the decrease in the affinity constant (K). So far, there is no explanation for this lower capacity.

4 Conclusion

The present study highlights the importance of the pH in the achievement of an effective Mn precipitation which means a final effluent within the recommended values for discharging. The necessity of alkaline pH in the formation of solid stable forms of the metal is then confirmed.



By using a non-conventional adsorbent/catalyst (MnO_2 residue) it was possible to attain the recommended value for manganese discharge, i.e. 1.0mg/L, at pH range of 6.8-7.2, whereas when this non-conventional adsorbent/catalyst was not used, a pH next to 10 was required. Mn removal at pH next to neutrality reduces the volume of precipitate up to 50%, which means a smaller volume of residue for disposal.

The maximum adsorption capacities (Q_{max}) of the MnO_2 residue were calculated by fitting the Langmuir's equation and were between 17mg/g and 32mg/g.

Acknowledgements

The authors would like to thank FAPEMIG and CNPq for financial support.

References

- [1] Johnson, D.B. & Hallberg, K.B., Acid mine remediation options: a review. *Sci. Total Environ*, **338**, pp. 3-14, 2005.
- [2] Mariner, R., Johnson, D.B. & Hallberg, K.B., Characterisation of an attenuation for the remediation of Mn (II) contaminated waters. *Hydrometallurgy*, **94**, pp. 100-104, 2008.
- [3] Bamforth, S.M., Manning, D.A.C., Singleton, I., Younger, P.L. & Johnson K.L., Manganese removal from mine waters – investigating the occurrence and importance of manganese carbonates. *Applied geochemistry*, **21**, pp. 1274-1287, 2006.
- [4] Fernandes, H.M., Franklin, M.R. & Veiga, L.H., Acid rock drainage and radiological environmental impacts - A study case of the Uranium mining and milling facilities at Poços de Caldas. *Waste Management*, **18**, pp. 169-181, 1998.
- [5] Nascimento, M.R.L., Fatibello, O.F.O. & Teixeira, L.A., Recovery of uranium from acid mine drainage waters by ion exchange. *Mineral Processing & Extractive Metall. Re*, pp. 129-142, 2004.
- [6] Lovett, R.J. Removal of manganese from acid mine drainage. *J. Environ. Quality*, **26(4)**, pp. 1017-1024, 1997.
- [7] Aklil, A., Mouflih, M. & Sebti, S. Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent. *J. Hazardous Materials* **A112**, pp. 183-190, 2004.
- [8] Dias, A., Sá, R.G., Spitale, M.C., Athayde, M. & Ciminelli, V.S.T., Microwave-hydrothermal synthesis of nanostructured Na-birnessites and phase transformation by arsenic (III) oxidation. *Materials Research Bulletin*, **43**, pp. 1528-1538, 2008.
- [9] Goncalves, C.R. & Ladeira, A.C.Q. Remoção de manganês e recuperação de urânio de águas ácidas de mina. *Anais do XXI Encontro Nacional de tratamento de minérios e metalurgia extrativa*, v.2, eds. I.A.S. de Brum & C.H. Sampaio, pp. 57-63, Natal, Brasil, 2005.



- [10] Ladeira, A.C.Q. & Goncalves, C.R. Uranium recovery and manganese removal from acid mine drainage. *Proceedings of the 9th International Conference on Water Pollution: modeling, monitoring and management*, v.1. eds. D.P. Rico, C.A. Brebbia & Y.V. Esteve, WIT press, Southampton, pp. 465-474, Alicante, Spain, 2008.
- [11] Sikora, F.J., Behrebds, L.L., Brodie, G.A. & Taylor, H.N. Design criteria and required chemistry for removing manganese in acid mine drainage using subsurface flow wetlands. *Water Environment Research*, **5**, pp. 536-544, 2006.
- [12] Dal Bosco, S.M., Jimenez, R.S. & Carvalho, W.A., Removal of toxic metals from wastewater by Brazilian natural scolecite. *Journal of Colloid and Interface Science*, **281**, pp. 424-431, 2005.

