Study of Manganese Removal from Mining Effluent

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Abstract This study investigated the removal of Mn^{+2} from an acid mine water through batch and continuous column experiments by using limestone, lime and MnO_2. The pH of the acid effluent was around 2.7 and the manganese concentration varied from 140 to 180mg/L. The Brazilian Standard Limits for discharging is 1 mg L^{-1} and pH within 5 to 9. Batch experiments showed no difference between lime and limestone in manganese precipitation at pH range 2.7 to 10.5 and an effective removal was achieved at pH > 10. Columns experiments were run with fixed beds packed with limestone, MnO_2 or with a mixture of limestone/MnO_2 and fed with the mine effluent. For columns packed with limestone and fed with mine water at pH 2.7, five (5) hours of residence time was not sufficient to reach the limit of 1 mgL^{-1}. For experiments containing a mixture of limestone/MnO_2 the results were slightly better, although the low pH (< 5) in the out coming effluent was the main cause for the unsatisfactory performance. Best results were obtained for columns packed with only MnO_2, fed with mine water neutralized with limestone at pH 7.0 and a residence time of 3.3 hours. The main advantage of using MnO_2 is that it makes the removal of soluble manganese possible at pH near neutrality preventing the generation of large volumes of precipitate.

Key Words manganese, acid mine water, manganese oxide,

Introduction

The occurrence of manganese in industrial effluents has increased significantly and, especially in acid mine drainage, manganese has been found in concentrations much higher than the recommended discharge values. Generally, manganese in solution is in the form of the divalent ion (Mn^{2+}) under normal environmental conditions. In acid mine drainage the divalent species are predominant up to pH around 10. Increase in pH as well as oxygenation of the system lead to the formation of different forms of solid manganese (Lovett, 1997). However, the necessity of raising the pH above 10, in order to meet the standard limits, is a problem for discharging.

Manganese oxides are the most important scavengers for aqueous trace metals in soils, sediments and rocks due to their sorption properties As MnO_2 is added to a solution containing Mn^{2+} a sharp removal of the metal is observed. This can be explained by the oxidizing capacity of MnO_2 as well as the negative charge of surface. However, different types of MnO_2 have different sorption/removal properties. Therefore, the selection of appropriate material is necessary. (ZOU *et al.*, 2006).

The effluent used in the present study is a sample of acid water from one uranium mine under decommissioning. Currently, this water is treated for discharge with the addition of lime. This procedure has been widely questioned because of high operational and environmental costs. Mn represents the main cause of the high cost of this treatment, given that its presence requires an extremely large amount of lime, in order to raise the

pH above 10, necessary to achieve the concentration level of 1mgL^{-1}, as established for discharge. The optimization of the removal process will result in a lower volume of precipitate, which would reduce the costs and environmental risks.

Methodology

Liquid Sample was supplied by INB (Brazil Nuclear Industry) and consists of acid mine effluent generated at waste rock piles in a deactivated uranium mine in the southeast of Brazil. The effluent was analyzed for Mn, Zn, Al and Fe through Atomic Absorption Spectroscopy (model AA240FS, Varian). Uranium was determined by the neutron activation technique using Triga Marki IPR-R1 reactor (100 KW; neutron flow of 6.6 × 10^{11} n.cm^{-2}.S^{-1}). Potentiometric determination, by ion selective electrode method, was used for fluoride analyses. Sulfate was determined using barium sulfate turbidimetric method (UV Visible Varian Spectrophotometer - model Cary 50). The experimental errors for all assays were within ± 5%.

Solid Sample: The manganese oxide (MnO_2) was a residue from the zinc eletrowinning process supplied by the zinc industry. Cement (5%) was mixed with the residue to produce a particle size within 1.4 mm and 1 mm. MnO_2 content in the residue was around 60% and was determined through Energy Dispersive X-ray (SHIMADZU-model EXD -720). The limestone was sieved within 1.4 mm and 1 mm as well.

Batch experiments were carried out with 200mL of acid effluent whose pH was set to different values with lime or limestone. The pH range

was from 2.8 to 10.5. The suspension was agitated for 30 minutes or up to pH stabilization at 25ºC. Afterwards it was filtered through a 0.45 µm membrane and acidified to pH lower than 1. Mn analyses were performed with AA Spectrometer (model AA240FS, Varian).

Column experiments were carried out in a glass column with a 1.9 cm inner diameter, fed with acid water at pH 2.7 and also with different pHs adjusted with lime or limestone at temperature 25 ± 0.5°C. Different volumes of MnO_2, limestone or a mixture of both were packed into distinct glass columns. The operation was performed by a downstream flow rate varying from 0.2 to 0.4 mL.mim^{-1} using a peristaltic pump Master Flex L/S model 7519—20. Liquid samples were collected periodically, by means of Spectra/Chrome Fraction Collector (model CF-1), from the column output, acidified and analyzed to determine manganese by AAS.

Results and Discussion
Acid Mine Effluent
The main elements present in the acid effluent are Mn = 140 to 155mg.L^{-1}, U = 10 to 12 mg.L^{-1}, Al = 180 mg.L^{-1}, Zn = 21 mg.L^{-1}, Fe = 1.5 mg.L^{-1}, SO_4^{2-} = 1440 mg.L^{-1}, F^{-} = 52 mg.L^{-1} and pH = 2.8. Generally, the acid mine drainage may contain manganese from 5 to 10mg.L^{-1}, but values higher than 50 mg.L^{-1} are not uncommon (Johnson & Hallberg, 2005). According to chemical analysis, the manganese is present in concentrations much higher than the levels usually found in mining effluents. That is most worrying since the permitted limit for manganese discharging in Brazil is 1.0 mg.L^{-1}.

Influence of the pH on Mn removal
Figure 1 was obtained by using the software HSC Chemistry 4.1 and depicts the formation of solid species of manganese depending on the pH and Eh of the system.
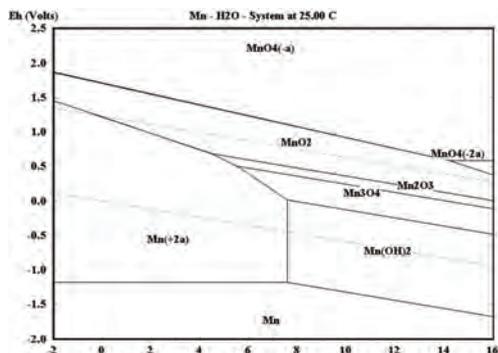
A large area of stability for Mn^{+2} is observed up to pH around 8. For acid system which is the case of the majority of mine waters, the formation of the oxides is verified only at significantly high Eh. Lovett, 1997 reported that the formation of stable manganese oxides is obtained only at pH higher than 7.0 and Eh above 500mV.

Figure 2 shows the influence of the pH on Mn removal. As can be notice the manganese removal is very low at pH range from 3.0 to 8.0. For pH values above 8.5, the removal increases significantly and reaches the value required by the protection standards; 1.0mg.L^{-1}, at pH 9.1 for limestone and at pH 10.0 for lime. Figure 2 also shows that the curves are very similar and the performance presented by both reagents could be considered comparable. However, for the same removal, the amount of limestone necessary to produce a final effluent that meets the Mn recommended value for discharge is greater than the amount of lime. This results in the generation of an additional volume of residue when the pH of the acid water is set with limestone, which incurs an extra expense, namely for disposal and/or storage. The viability of the use of limestone industrially depends on the form it is used, which could be in drains, tanks or fixed bed.

Column experiments with limestone
Column experiments were carried out in order to simulate limestone drains. Cravotta e Traha (1997) investigated oxic limestone drains to raise the pH and also remove dissolved metals from an acid mine water. Those authors determined that 3 hours was sufficient to increase the pH from 3.5 to 6.2—7.0 and remove Fe and Al to less than 5% of the influent concentration. Gazea *et al.* (1996) demonstrated that oxic limestone drains could be effective when used as a pre-treatment option for waters at pH as low as 2.6 containing Fe^{2+}, Zn^{2+} Mn^{2+}. It could partially remove the metals as solid
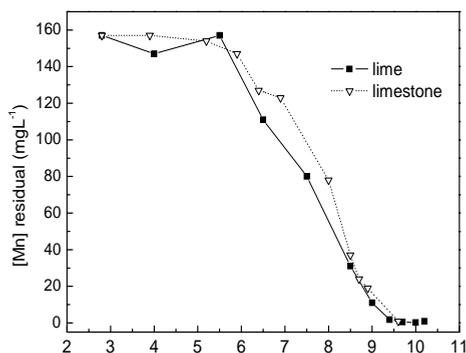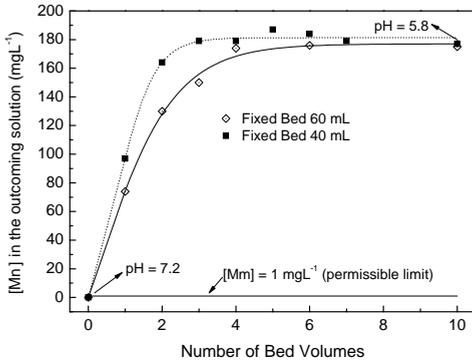

Figure 1 Eh-pH diagram with the main species of manganese, [Mn] = 1 Molar, 1atm; software HSC Chemistry 4.1.

Figure 2 The influence of the pH on Mn^{2+} removal, by using lime and limestone, aerated system, T = 25ºC, [Mn] $_{initial}$ = 155mgL^{-1}.

Figure 3 Manganese removal using columns filled with 40 mL and 60 mL of limestone; residence time 3.3h and 5h; $pH_{initial}$ = 2.8; T = 25ºC, $[Mn]_{initial}$ = 140mgL^{-1}, flow rate = 0.2mLmin^{-1}.

carbonates and increase the pH up to the neutral range.

Figure 3 shows the profiles for manganese removal for two columns packed with different amounts of limestone where the final concentration of the contaminant (mg L^{-1}) is plotted against cumulative bed volume (BV). Bed volume refers to the volume of solution equivalent to the limestone volume in place. It can be seen that, for Bed Volume (BV) number 1, there was a rapid decrease in the initial Mn concentration from 140 mgL^{-1} to 70 mgL^{-1} when using 60ml of limestone. On the other hand, the use of 40mL of limestone promoted the decrease of manganese concentration

from 140 mgL^{-1} to close to 100 mgL^{-1}. It is also verified that, from BV numbers 3 to 4, manganese removal ceased in both experiments. The results showed that the use of fixed bed consisting of limestone in the removal manganese from this kind of acid mine water was not satisfactory. The required standard limit for discharge of 1 mgL^{-1} and also the desired pH of around 7.0 for the out coming effluent was not achieved under any condition. The maximum pH of the out coming solution was 5.8. This could be explained by the low solubility of limestone; around 50mgL^{-1} in aerated systems. The residence time for the fixed beds of 40 and 60 ml were 3.3h and 5h, respectively. Residence time higher than 5 hours was not assessed as it could be operationally not feasible due to great flows generally found in acid mine drainages.

Besides the low dissolution of limestone which delays the process, the ferric, manganese and/or aluminum hydroxide formation is also deleterious; as the solids can cause "armouring" to the limestone surface leading to a decrease in solubility. In the present work, the "armouring" effect could be one reason for the low performance observed due to the presence of ferric (around 1.5mgL^{-1}) and also aluminum and sulfate besides manganese; all of them could precipitate on the surface of the limestone. In addition, the pH of the out coming solution decreased from 7.2 to 5.8 over time which is unfavorable in the case of Mn oxidation. The authors concluded that the low pH of this acid water as well as the high concentration of Mn render the use of limestone not feasible.
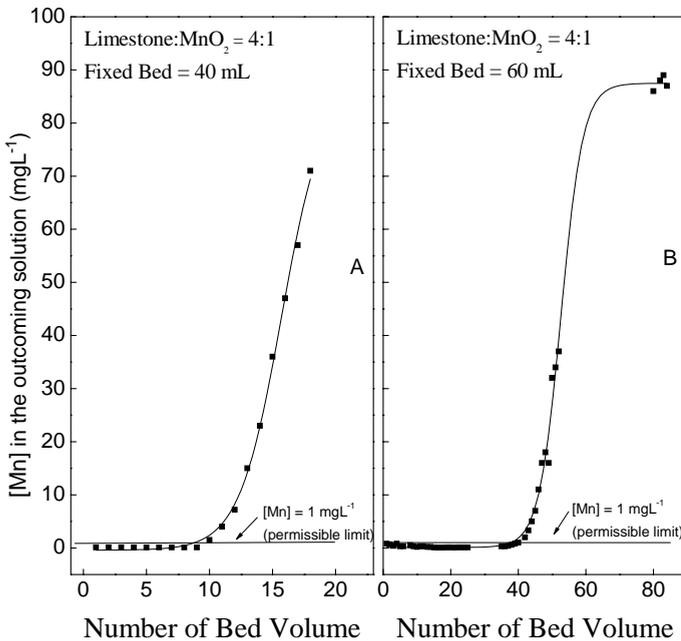
Figure 4 Manganese removal by columns with a mixture limestone and MnO$_2$; bed volumes of 40 and 60 mL; residence time of 3.3 and 5 h; initial pH = 2.8; T = 25ºC, $[Mn]_{initial}$ = 140mgL^{-1}, flow rate = 0.2mLmin^{-1}.
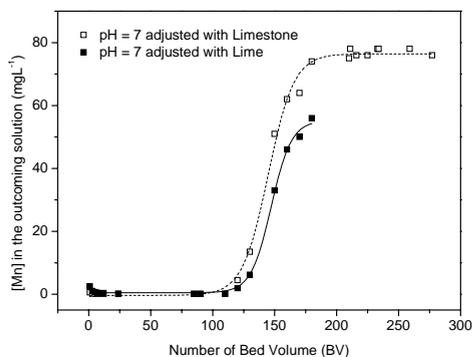
Figure 5 *Manganese removal by columns with MnO2 and fed with mine water at pH*$_{initial}$ *= 7.0 adjusted with lime or limestone; bed volume of 40mL; residence time of 3.3h; T = 25ºC; [Mn]*$_{initial}$ *= 100mgL*$^{-1}$*, flow rate = 0.2mLmin*$^{-1}$*.*

Column experiments with limestone and MnO2

Manganese oxide is supposed to act as catalyst in the oxidation process necessary to convert Mn^{2+} into Mn^{+4}. As the conversion of Mn^{2+} into solid oxide forms in water is a slow process, the treatment of large flows, as currently found in mining activities, is time consuming. Therefore, the presence of some kind of catalyst may be very useful. According to Lovett, 1997 the presence of small amounts of solid can also catalyze the rate of the oxidation reaction. Therefore, in order to improve Mn removal the columns were filled with a mixture of limestone and MnO_2. The experimental conditions i.e. bed volume and residence time, were kept the same as in the experiments using only limestone. Figure 4 shows that the best experiment, which corresponds to 5 h of contact, shows that the permitted limit of $1mgL^{-1}$ was attained up to BV 40, from this point the Mn concentration starts increasing and the saturation of the column was completed at BV 80. The loading capacity of the column, depicted in Figure 1A, is $0.45mgg^{-1}$ whereas for Figure 1B it is 3.21 mgg^{-1}. It was demonstrated that the process was favored by the presence of MnO_2 and that it is effective in producing a treated water with Mn concentration lower than $1mgL^{-1}$.

Column experiments with MnO2

According to Figure 5, columns filled with only MnO_2 and fed with the effluent at pH 7.0 showed that up to BV 110 Mn removal was very efficient, i.e., Mn final concentration was lower than 1 mgL^{-1}, for both columns. Compared to Figure 4A, which consist in a mixture of limestone and

MnO_2, the discharging limit was achieved only up to 10BV. In addition, the results where the MnO_2 was not used, as presented in Figure 3, were significantly inferior to the former ones. The loading capacity of the columns from Figure 5, calculated by integrating the area above each curve, is 12.7 mgg^{-1} for pH adjusted with lime and 13.9 mgg^{-1} for pH adjusted with limestone. It is observed that when the pH was set to 7.0 by using limestone, the loading capacity was slightly better, 13.9 mgg^{-1}, however, so far the authors have no explanation for that. Raman analyses on the MnO_2, after being used in the columns, are being carried out to identify the solid species formed on the surface of the Mn oxide.

Conclusion

The removal of soluble Mn^{+2} from acid mine drainage was greatly improved with the use of MnO_2. The acid mine pH has to be adjusted around 7.0 and the residence time in the column should be around 3hours. The main advantage of using MnO_2 is to make the removal of soluble manganese possible at pH near neutrality and avoid the generation of large volumes of precipitate. The maximum loading capacity of the columns filled with MnO_2 varied from 12.7 mgg^{-1} to 13.9 mgg^{-1}.

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