

Oxidative Precipitation of Manganese from Dilute Waters

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Abstract Various metals may be removed from mine water by precipitation of their hydroxides. However, over the pH range of 7–9, it is more efficient to oxidize Mn II to Mn IV than to precipitate Mn II as its hydroxide. Chlorine (or hypochlorite) can be used to do this, but its use may not be appropriate for mine waters that will be recycled as process solutions or discharged into a receiving body. Consequently, there has been interest in reducing chlorine use or its total replacement by non-chlorinated oxidants, such as oxygen and peroxygens, for treatment of mine water. In this work, we report the results of a comparative investigation of the following oxidants: NaClO (as reference), O₂; H₂O₂; Caro's acid (H₂SO₅), and the combination of H₂O₂ with NaClO, with initial [Mn] = 10 mg/L, at 25 °C, with 100 and 300 % excess oxidant above the stoichiometric requirement. It was found that the reaction pH has to be greater than 8 to obtain effective precipitation. It is possible to reach a final [Mn] below 1.0 mg/L in 60 min of batch reaction time, using either NaClO, Caro's Acid, or a combination of NaClO + H₂O₂. Using only O₂ or H₂O₂ was ineffective.

Keywords Treatment of mine water · Oxidation in mine waters · Precipitation in mine waters · Hypochlorite · Non-chlorinated oxidants · Caro's acid

Introduction

Manganese is a common contaminant in mine waters around the world (Chamberlain et al. 1995; Wolkersdorfer and Howell 2005). And although hydroxide precipitation is usually an efficient way to remove cations from aqueous solutions (it works for iron, copper, zinc, nickel, and cobalt), it is not effective for lowering the concentrations of Mn to less than 1 mg/L. The Pourbaix diagram derived for the present study (Supplemental Figure 1) for a concentration of 1.8×10^{-5} mol/L (1 mg/L) of aqueous Mn species in equilibrium with its precipitated compounds indicates that the aqueous species MnO (a water-soluble neutral oxy-complex) is dominant over the corresponding solid species Mn(OH)₂ above a pH of 8.2. This indicates that precipitation of Mn(OH)₂ is not a feasible way to lower Mn concentrations to less than 1 mg/L.

The alternative to Mn(OH)₂ precipitation is the precipitation of MnO₂ (or MnO·OH). This is convenient, as MnO₂ is stable over a wide pH range and can form after oxidation of the soluble Mn²⁺ ion. To effectively precipitate MnO₂ or MnO·OH from a dilute Mn²⁺ solution, a suitable oxidant has to be used. Also, as demonstrated by Hedin et al. (1994), no dissolved Fe²⁺ should remain in the treated water, as it will cause reductive redissolution of the precipitated MnO₂. Early investigations (Aziz and Smith 1996) found that Mn removal requires the use of powerful oxidants such as permanganate, chlorine, hypochlorite, chlorine dioxide, or ozone, as oxidation of Mn(II) to Mn(IV) by aeration alone is slow unless the pH is well into the alkaline range. Sikora et al. (2000) reported that MnO₂

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precipitation does not occur readily without highly oxidizing or pH > 9 conditions. Once it starts, Mn oxidation is autocatalytic, and is a two-step process: first, Mn^{2+} is adsorbed onto the MnO_2 or $\text{MnO}\cdot\text{OH}$ surface, with simultaneous oxidation of Mn^{2+} to Mn^{3+} ; then, disproportionation of Mn^{3+} to Mn^{4+} occurs (Morgan and Stumm 1964).

Eckenfelder (1989) investigated improving Mn precipitation using oxygen, but this only worked at a pH > 9.4. At lower pH ranges, high precipitation efficiency requires stronger oxidants. Sincero and Sincero (2002) also reported the need for strong oxidation of manganese to achieve efficient precipitation at lower pH ranges. Pavlovic et al. (2007) studied the precipitation of Mn as a hydroxide with various other metals and found that the concentration of Mn reached a minimum at a pH value of 11.0. Johnson and Younger (2005) observed that the removal of Mn from natural waters in an aerated reactor required 8 h to precipitate 95 % of the metal from an influent with an initial $[\text{Mn}] = 20 \text{ mg/L}$. Zhang et al. (2010) investigated the oxidative system SO_2/air (O_2) and found that Mn precipitated efficiently at a pH range of 6–7 from solutions with an initial $[\text{Mn}] = 2000 \text{ mg/L}$ that also contained Ca and Mg. In another study using the same SO_2/air (O_2) oxidation system, Bello-Teodoro et al. (2001) treated a solution with an initial $[\text{Mn}]$ of approximately 4000 mg/L in a pH range of 4–6; oxidation was slow (30 % maximum precipitation achieved in 60 min at room temperature). More recently, Akhbarizadeh et al. (2014) employed adsorption on iron oxide nanoparticles for efficient removal of Mn and other metals from acid mine drainage; best removal efficiency was obtained at pH 8.5. Adsorption on biomaterials has also been shown to be a viable method for Mn removal from acidic mine waters (Karathanasis et al. 2010).

A recent review by Patil et al. (2016) listed various techniques for Mn removal from wastewaters of different sources and compositions. They confirmed the difficulty of precipitating $\text{Mn}(\text{OH})_2$ to levels below 5 mg/L and the need to operate at pH 8.5 and above (citing Zhang et al. (2010)). They also cited efficient precipitation of MnO_2 from groundwater after oxidation with NaClO or KMnO_4 (Phatai et al. 2014; Roccaro et al. 2007; Salema et al. 2012).

Of all the above-mentioned powerful oxidants, active chlorine (hypochlorite) appears to be the most cost-effective for Mn precipitation. However, active chlorine may be detrimental for treatment of mine water that will be recycled as a solution in a process, reused as agricultural irrigation water, or discharged into a receiving body. There is thus interest in reducing the requisite chlorine used for mine water treatment, or totally replacing it with non-chlorinated oxidants, such as oxygen and peroxygens.

Teixeira et al. (2010) carried out a preliminary study comparing the effectiveness of oxygen, hydrogen peroxide plus carbonate, and Caro's Acid, to treat high Mn concentrations (1200 mg/L). In that study, the most efficient precipitation was obtained using Caro's Acid, and hydrogen peroxide + carbonate in 1 h of batch reaction time. Nonetheless, attempts by the present authors to treat more dilute mine water with an initial $[\text{Mn}] < 10 \text{ mg/L}$ (in the absence of complexing agents), proved that reaching $[\text{Mn}] < 1 \text{ mg/L}$ was difficult. The aim of the present work was to compare Mn removal from already dilute solutions to achieve $[\text{Mn}] < 1 \text{ mg/L}$ with known oxidants such as NaClO, O_2 , H_2O_2 , and Caro's acid (H_2SO_5). Singlet oxygen $^1\text{O}_2$ species, generated by combining $\text{H}_2\text{O}_2 + \text{NaClO}$, which had previously been used to detoxify a cyanide-containing mine effluent (Teixeira et al. 2013), was also tested. The equilibrium constants calculated (not reported here) indicated that all oxidative precipitation reactions considered were thermodynamically feasible. This investigation did not include Mn complex ions that, if present in the solution to be treated, would inhibit precipitation. Although oxidative Mn oxides precipitation is autocatalytic, with a first step involving homogeneous and heterogeneous nucleation, no seeding was used in these experiments. Precipitation conditions in the present work involved only homogeneous nucleation from clear solutions. No other species apart from sulphate were included in the tests to understand the effect of oxidant dose and pH on Mn removal.

Materials and Methods

The experiments were carried out as batch runs in 1 L beakers, with good mechanical stirring, at room temperature ($25 \pm 1^\circ\text{C}$). The pH was adjusted using a Hanna pH meter (model pH21), and the addition of either 0.1 mol/L of H_2SO_4 or NaOH solution, as required. The Mn solution employed was a 10 mg/L solution made from MnSO_4 . All reagents were analytical grade supplied by Vetec (Brazil). Hydrogen peroxide was supplied by Peróxidos do Brasil (Solvay group) and sodium hypochlorite by Panamericana Brazil.

Caro's acid was prepared following Solvay's published procedure (Solvay 1982), by controlled mixing of concentrated grades of H_2O_2 (50 % technical grade) and H_2SO_4 (98 % analytical grade), starting from a molar ratio of H_2SO_4 to H_2O_2 of 3:1, which yielded a solution with 26 % w/w H_2SO_5 . That was further diluted with water to a 10 % w/w working concentration.

Each run started by adjusting the initial pH of 1 L of the test solution to the desired value, followed by the addition

of the oxidant in a single shot (taken to be time zero) and immediate compensation of either acidity or alkalinity to compensate for the effect of the injected oxidant. The exception was when O_2 was the oxidant; then air was injected continuously during the length of the run at a rate of 8 L/min (for a 0.5 L volume of solution) using an aquarium pump (Sarlo S520) to ensure O_2 saturation during the run. During each run, a set of aliquots were taken, filtered through a 0.22 μm membrane, and immediately analyzed for [Mn] by colorimetry using a Merck's kit for Mn determination in water, number 1.14770.0001, and a Merck's Nova 60 spectrophotometer. This is the routine colorimetric determination of Mn described in the Standard Methods of Analysis of Waters and Wastewaters (USEPA 1983). For all runs, the oxidant dose employed corresponded to excesses of 100 and 300 % above the reaction stoichiometry (Eqs. 1–5 below).

Results and Discussion

Oxidative Precipitation Using NaClO

The proposed process reaction for Mn precipitation is:



The kinetic run results (Supplemental Figure 2) showed that for a pH of 7, Mn oxidative precipitation was limited to a maximum of 70 % for the first 60 min. At pH 8 and 9, quantitative precipitation was obtained in 20 min or less. Overall, hypochlorite oxidation was confirmed as an efficient way to precipitate Mn to low levels in less than 60 min. More efficient precipitation was observed at higher pH, which is consistent with reaction (1), which includes OH^- as a reactant.

Oxidative Precipitation Using O_2 (air) or Hydrogen Peroxide

The proposed process reaction for Mn precipitation using O_2 (air) as the oxidant is:



and for precipitation using H_2O_2 as oxidant is:

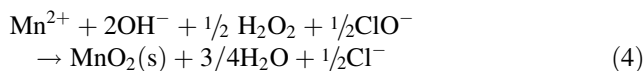


Less than 5 % of the Mn was removed using either saturated O_2 or H_2O_2 , at 100 and 300 % excess, over a pH range of 7–9, in 60 min of reaction time. Nevertheless, slow Mn precipitation (over several hours) does occur in solutions exposed to air (Johnson and Younger 2005). H_2O_2 is capable of oxidizing and precipitating Mn in less than 60 min from much higher initial Mn concentrations at

correspondingly higher peroxide doses (Teixeira et al. 2010).

Oxidative Precipitation Using Singlet Oxygen Produced by $\text{H}_2\text{O}_2 + \text{NaClO}$

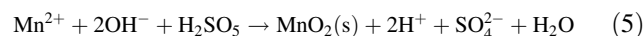
Previous studies have shown that singlet oxygen ($^1\text{O}_2$) generated by the reaction of H_2O_2 and ClO^- separately added to the solution is capable of oxidizing compounds such as cyanide and surfactants (Teixeira et al. 2012, 2013). The proposed process reaction for Mn oxidation and precipitation is:



The results of the kinetic runs (Supplemental Figure 3) show that at pH 7, Mn oxidative precipitation practically does not occur for the first 60 min. At pH 9, 90 % efficiency is obtained with 100 % of excess oxidant. Quantitative precipitation was obtained in 10 min with 300 % excess. The fact that more efficient precipitation was observed at higher pH is consistent with reaction (4), which includes OH^- as a reactant. Compared to hypochlorite oxidation, singlet oxidation is either less efficient or significantly slower, but may offer the benefit of achieving Mn precipitation using less NaClO.

Oxidative Precipitation Using H_2SO_5 (Carós Acid)

The use of Carós Acid has been previously reported for Mn oxidative precipitation (Burkin and Chouzadjian 1983; Teixeira et al. 2010) for the treatment of solutions with initial [Mn] = 1200 mg/L. The process reaction for Mn oxidation and precipitation is:



The results of the kinetic runs (Supplemental Figure 4) show that Mn oxidative precipitation does not occur at pH 7. At a pH of 8, about 30 % of the Mn was removed in 60 min. At pH 9, quantitative precipitation was obtained in 20 min. No significant kinetic or efficiency advantage was observed when the oxidant excess was increased from 100 to 300 %. The dependence of the reaction rate on pH was compatible with the stoichiometry of reaction (5).

Overall Process Comparison

Supplemental Table 1 contains the calculated average precipitation rates for the period $t = 0\text{--}20$ min [mg/(L min)] for runs with 100 % of excess oxidant. At pH 7, precipitation does not occur or is too slow, with the NaClO process being the fastest; even in this case, precipitation

efficiency was limited to 70 %. At pH 8, NaClO was fastest and more efficient. Quantitative precipitation occurred in 20 min for 100 % excess oxidant or in 10 min for 300 % excess. With Caro's Acid, the reaction started, but did not go beyond 30 % efficiency.

At pH 9, Caro's Acid and NaClO were equally fast and very efficient oxidants. The combination of H_2O_2 + - NaClO also appears to be a fast option, with the potential benefit of working with a lower hypochlorite dose than the standard NaClO reaction.

The need for high pH (8 and above) was common for all of the tested oxidants. At sites where use of an active-chlorine oxidant is inappropriate, Caro's Acid would be the best option, compared to oxygen or hydrogen peroxide. Precipitation will be fast and very efficient, but the reaction will have to be conducted at a pH of at least 9.

Both a simulated effluent with 1200 mg/L of Mn (Teixeira et al. 2010), and the dilute Mn solution tested (10 mg/L) in the present work were less difficult to treat than real diluted mine water previously used in past attempts of Mn oxidative precipitation by the same authors. This indicates that the low [Mn] was not the only factor hindering the precipitation reaction kinetics. The presence of other dissolved substances, including metals such as Fe, organics, and possibly complexing species, are obstacles to the feasibility and kinetics of Mn precipitation in most mine waters. The results of this study will only be useful for mine waters that naturally contain low Fe concentrations or that have already been partially treated to remove Fe.

Conclusions

Based on this work, and given the requirements to economically produce an aqueous solution with less than 1.0 mg/L of Mn from process or mine waters with low initial Mn concentrations, some points need to be considered:

1. The need to adjust the pH of the water to be treated to a range of 8–9 (as close to 9 as possible).
2. The fastest oxidant at pH 8 was hypochlorite; at pH 9, hypochlorite and Caro's Acid (H_2SO_5) were equally fast and efficient; neither oxygen nor hydrogen peroxide were effective.
3. The actual nature of the mine water to be treated can pose obstacles to the feasibility and kinetics of Mn precipitation.
4. The possibility of restrictions on species derived from oxidants containing chloride or sulphate, for either treated effluent discharges or reuse as process or irrigation water, will help determine the choice of oxidant.

5. The cost of reagents to adjust the pH to provide the conditions required for precipitation and the dose of oxidant will also help determine the system to be used.

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