



# Electrolytic Manganese Removal from Acid Rock Drainage

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## Abstract

Manganese is a common, yet difficult to remove pollutant in acid rock drainage. Manganese is typically removed at high pH (>10) as hydroxide solids. Electrolysis promotes oxidation of manganese at low pH. Experiments were conducted using a pH 3 synthetic mine water of metal sulfates at applied voltages of 3.5 V and 5 V. Copper sheeting was the cathode and carbon cloth was the anode. Manganese was reduced from 40 mg/L to < 2 mg/L in 12 h batch tests and to 2.5 mg/L at steady-state for 11 h flow tests. Electrolysis is a viable option to remove manganese at low pH without reagent addition.

**Keywords:** Electrochemical, electrolysis, manganese, mine drainage, treatment

## Introduction

Acid rock drainage (ARD) is the most common cause of negative effects to surface waters from mining. Sulfide-containing minerals are exposed to atmospheric conditions during mining, leading to oxidation of the sulfides. Sulfide oxidation generates acidity, causing mineral dissolution and release of metals. Metals common in ARD include iron, copper, cadmium, zinc, and manganese, with the metal composition depending on site-specific mineralogy. High manganese concentrations may occur in ARD from weathering of manganese-containing minerals such as oxides, carbonates, or iron minerals in which manganese substituted for iron (Neculita and Rosa 2019). ARD manganese concentrations are frequently in the range of 1 to 50 mg/L, but can be over 100 mg/L, as in Gilson Gulch drainage, located within a historic mining area in Idaho Springs, Colorado (Holm and Crouse 2009).

Effluent discharge limits set for manganese removal systems, are typically in the range of 1 to 4 mg/L. The U.S. Environmental Protection Agency set the total manganese effluent limit for coal mines at 4 mg/L (one-day limit) and 2 mg/L (30-day average) (CFR 2008). Surface water quality standards for manganese fall within a similar range. For example, the state of Colorado set hardness-based standards for dissolved manganese, with limits ranging from near 1 mg/L

(chronic aquatic life standard for water with a low hardness of 25 mg/L as CaCO<sub>3</sub>) to 4.7 mg/L (acute aquatic life standard for water with a high hardness of 400 mg/L as CaCO<sub>3</sub>) [Colorado Department of Public Health and Environment 2020]. These manganese limits are up to two orders of magnitude lower than concentrations found in ARD.

The most common method to treat ARD is the addition of an alkaline reagent, such as lime or sodium hydroxide, to precipitate metal hydroxides and oxyhydroxides in a sludge. Metals are precipitated from solution as the pH increases, with most metals removed at circumneutral pH or below. At neutral pH, oxidation of aqueous manganese (Mn<sup>2+</sup>) and precipitation of MnOOH and MnO<sub>2</sub> is thermodynamically favored in oxidized waters, as shown in the mineral stability diagram (Fig. 1). However, kinetics of oxidation by oxygen are slow and manganese may remain dissolved for long periods of time (i.e. weeks) in pH-neutral aerated waters (Hallberg and Johnson 2005; Handa 1969). Therefore, active treatment of manganese-rich mine water is typically accomplished by raising the pH to 10 to precipitate manganese hydroxides, followed by neutralization prior to discharge.

Manganese oxidation reaction rates can increase by creating strong oxidizing conditions, typically accomplished by use of

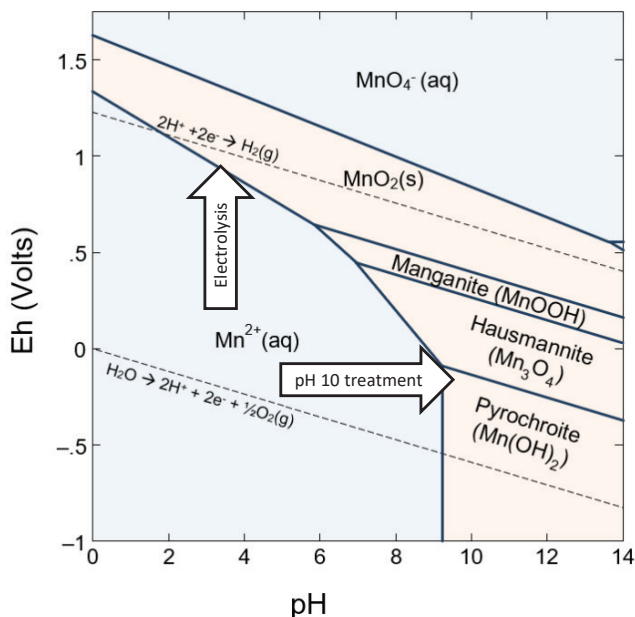
a chemical oxidant such as permanganate. (Van Benschoten et al. 1992). Freitas et al. (2013) demonstrated that permanganate addition can remove manganese to less than 0.1 mg/L in 10 minutes for pH 7 water with an initial manganese concentration of 100 mg/L. However, permanganate dosing requires close monitoring because coloration of discharge occurs if excess reagent is used. Electrolysis creates strong oxidizing conditions at the anode, without the need for chemical oxidants. Also, electrolysis allows for manganese removal by precipitation of manganese oxides at low pHs, as conceptually shown in Fig. 1. Treatment at low pH can reduce costs associated with pH adjustments required by pH-10 precipitation as manganese hydroxides.

Electrolytic removal of manganese consists of oxidizing  $Mn^{2+}$  at the anode to form manganese dioxide ( $MnO_2$ ),  $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$ . Electrolytic removal of manganese from acidic and circumneutral mining influenced water has been accomplished in a few previous laboratory studies,

however, results demonstrate the need for additional research before methods can be applied efficiently at full scale. Luptakova et al. (2012) and Ulbaldini et al. (2013) pre-treated synthetic ARD to pH 4 to remove both iron and aluminum, followed by electrolysis to remove manganese as  $MnO_2$  on the anode. Manganese recovery was over 93% after 2 h, however, electrolytic cells required heating and electrodes were platinum, which would be cost prohibitive at full scale. Our work aims to improve upon previous research by reducing material and energy costs through use of low-cost carbon anodes and conducting treatment at room temperature. Consistent with previous studies, our work assumes that iron is removed before electrolytic treatment to avoid a decrease in efficiency from iron redox cycling between ferric and ferrous states in the electrochemical cell.

## Methods

Batch and flow-through laboratory experiments were conducted using an iron-free synthetic mine water generated from metal



**Figure 1** Conceptual approach for electrolytic manganese removal; Arrows show changes in Eh and pH for electrolytic removal of manganese and alkaline treatment, respectively. Dashed lines show limits of water stability. Tan shading indicates solid phases. Figure created using GWB Community (Bethke et al. 2021) and ThermoChimie database (ThermoChimie Partners 2018). Conditions modeled: 40 mg/L Mn at 25 °C at 1 atm.

**Table 1** Initial concentrations (mg/L) in batch and flow-through tests

Test	Cd	Cu	Mn	Pb	Zn	pH
Batch	0.31	11	44	0.11	33	2.8
Flow	0.29	11	43	0.11	31	3.4

sulfates and deionized water. Samples of the mine water were filtered ( $< 0.45 \mu\text{m}$ ), acidified, and analyzed by ICP-AES. Pre-treatment concentrations are presented in Table 1.

Batch tests were conducted using two different applied voltages (3.5 V and 5 V) for the purpose of selecting an applied voltage for use in the flow-through experiments. Tests were conducted in single-compartment reactors constructed of clear PVC (5.5 cm length, 7.7 cm diameter), positioned horizontally with acrylic end plates, having a total capacity of approximately 250 mL. Copper sheeting (5 × 5 cm of 24-gauge, unpolished copper sheeting) was used as the cathode and carbon cloth (5 × 5 cm, purchased from Fuel Cell Earth) was used as the anode. Electrodes were positioned adjacent to the acrylic end plates, at opposite ends of the reactor. The distance between the anode and cathode was maintained at approximately 5 cm. Titanium wire (24 gauge) was used to connect the electrodes to electrical leads of a direct current power supply (Extech, model #382202). Batch tests were run for a total of 72 h at applied voltages of 5 V and 3.5 V. Electrical current in the cell was measured with a handheld multimeter (Fluke, model #289). Reactors were open to the atmosphere and stirred using a stir-plate and magnetic stir bar throughout testing. Samples of the treated water were collected periodically throughout treatment and at the end of testing. A disposable polypropylene syringe was used to pull a sample from the center of the reactor through tubing (1/4-inch diameter low-density polyethylene tubing). Water samples were filtered (0.45  $\mu\text{m}$  disposal filter), diluted, and acidified prior to analysis by ICP-AES.

Flow-through experiments were conducted in 500 mL beakers with 300 mL of synthetic mine water (Table 1). Electrodes were suspended in solution at opposite sides of the beaker (approximately 6 cm apart).

Synthetic mine water was pumped into the bottom of the beaker and pumped out from within 0.5 cm from the water surface at average rates of 28 mL/min (hydraulic residence time of 10.7). The water was mixed using a stir plate and magnetic stir bar throughout testing. Two tests were conducted using an applied voltage of 3.5 V for 36 h. Sample analyses, current measurement, electrode material, and electrode size were the same as for batch testing. During the flow-through experiments, cathode potential was also measured using silver/silver chloride (Ag/AgCl) reference electrode (Hanna Instruments, model #HI5311).

After testing, electrodes were analyzed using scanning electron microscopy (SEM), coupled with energy dispersive spectroscopy (EDS) to provide a qualitative analysis of elements present. Solids that had formed on the cathode were scraped off the electrode surface and placed on carbon tape. For the anode, a piece of carbon cloth was cut and placed on carbon tape.

## Results

Manganese concentrations over time are shown in Fig. 2 for the batch tests. Over 72 h, manganese concentrations decreased from 44 mg/L to 0.30 mg/L for the 3.5 V batch test (over 99 percent removal) and to 1.1 mg/L for the 5 V batch test (98 percent removal). Manganese concentrations in the batch tests reached levels typical of effluent discharge limits ( $< 2 \text{ mg/L}$ ) after approximately 12 h. Steady state concentrations for the flow-through tests are similar, with an average manganese concentration of 2.5 mg/L for tests having a hydraulic residence time of 10.7 h. Data from the 3.5 V and 5 V tests were fit using first-order reaction rate constants of  $0.24 \text{ h}^{-1}$  and  $0.39 \text{ h}^{-1}$ , respectively, with fits shown in Fig. 2. For the flow-through test, the first-order rate constant was calculated to be  $1.5 \text{ h}^{-1}$ .

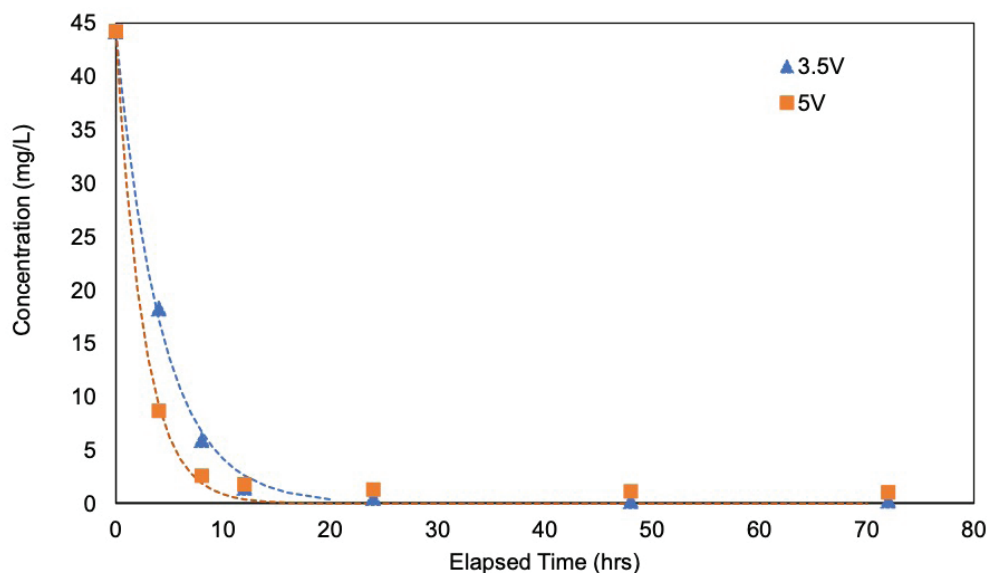


Figure 2 Manganese concentrations overtime for batch tests at 3.5 V and 5 V. Dashed lines show fit for first-order reaction rates.

After testing, SEM-EDS analysis of the carbon cloth anode showed that a coating had formed on the fibers. EDS indicated that the coating consists of manganese and oxygen, with no other elements present at detectable contents (above approximately 1% by mass). Solids removed from the cathode were also analyzed by SEM-EDS and were found to include zinc, copper, and lead, but no manganese was detected in solids scraped from the cathode.

## Discussion

Electrolytic methods are effective for removal of manganese from acidic mine water. Manganese in pH 3 mine water was reduced from approximately 40 mg/L to levels near typical discharge limits (2 mg/L) after 12 h of treatment in batch or with continuous flow stirred tank reactor (CSTR). This finding is relevant because manganese removal from ARD is typically accomplished by alkaline adjustment to pH 10. The high pH is required specifically for manganese removal, as other metals in ARD can be removed at lower, circumneutral pH ranges (Wei *et al.* 2005; Park *et al.* 2015). Electrolytic removal of manganese at pH 3 could therefore reduce

the use of pH-adjusting reagents because electrolytically-treated water would only need to be neutralized prior to discharge.

## Reaction Pathways

Oxidized manganese solids were found to have formed on the carbon cloth anode during electrolytic tests. The exact form of manganese oxide could not be identified by X-ray diffraction because the solids did not have a crystalline structure. However, anodic formation of manganese oxide has been demonstrated in other applications, including commercial production of manganese dioxide for use in batteries, and formation during copper and zinc electrowinning operations (Zhang and Cheng 2007a, 2007b), and numerous studies provide insight into the potential reaction pathways and types of solids formed (Vereecken and Winand 1972; Yu and O'Keefe 2002).

$Mn^{2+}$  may be oxidized to form  $Mn^{3+}$ , an aqueous intermediate phase ( $Mn^{2+} \rightarrow Mn^{3+} + e^-$ ).  $Mn^{3+}$  may then hydrolyze to form  $MnOOH$ , which is then oxidized to  $MnO_2$  ( $Mn^{3+} + 2H_2O \rightarrow MnOOH + 3H^+$  and  $MnOOH \rightarrow MnO_2 + H^+ + e^-$ ) (Yu and O'Keefe 2002; Kao and Weibel 1992). Another

potential mechanism is by disproportionation of  $Mn^{3+}$  to  $MnO_2$  and  $Mn^{2+}$  ( $2Mn^{3+} + 2H_2O \rightarrow MnO_2 + Mn^{2+} + 4H^+$ ) (Yu and O'Keefe 2002).

### Reaction Rates

Batch test results fit first-order reaction kinetics, with an overall rate constant of  $0.29\text{ h}^{-1}$  for aggregate data from the 3.5 V and 5 V tests. For the conditions of the flow-through test (initial concentration of 43 mg/L, volume of 300 mL, and flow rate of 28 mL/min), the expected effluent concentration for a continuous-stirred tank reactor is approximately 10 mg/L based on the batch test derived first order rate constant. However, the steady-state effluent concentrations from the flow-through test were lower (2.3 mg/L and 2.7 mg/L). Higher than expected removal of manganese in the flow-through test is attributed primarily to more effective stirring in the beaker used for the flow-through test, than in the horizontal PVC pipe used to construct the batch reactor. Mixing can increase manganese removal by both replenishing dissolved  $Mn^{2+}$  from the bulk solution to the reactive anode surface and moving newly oxidized permanganate away from the anode surface and into the bulk electrolyte. Differences in electrode placement in the cells may have also contributed to higher reaction rates in the flow-through test. In batch tests, electrodes were affixed to endplates on opposite sides of the cell, thereby limiting reactions to the side of the electrode facing the bulk solution. In contrast, electrodes in the flow-through cell were submerged, but not affixed to the sides of the beaker, thereby increasing the reactive surface area of the electrodes.

### Implications

Work presented here demonstrates the use of materials and methods that are more cost-effective than used in previous studies. Work was done at room temperature rather than heated as in previous studies by Luptakova *et al.* (2012a; 2012b) in which the electrolyte was heated to 35 °C and 95 °C, respectively. For cost-effective scale-up, manganese solids ideally would form either as a precipitate or

on the surface of a low-cost, easily replaceable anode. Carbon cloth was specifically tested as anode material because of its low costs relative to platinum, which was used in previous studies (Luptakova *et al.* (2012a, 2012b) and Ulbaldini *et al.* (2013).

Additional work is needed to optimize the electrolytic cell design, which is critical to improve efficiencies and economic feasibility of this treatment method. Efficient mixing is likely an important parameter in manganese oxidation and should be evaluated further, in addition to standard cell design considerations, such as electrode area and spacing. Anode potentials should also continue to be evaluated. Although a higher anode potential may lead to permanganate formation, there may be tradeoffs, such as an increase in undesirable oxygen evolution at the anode.

### Conclusions

This study demonstrates that manganese can be removed from mining influenced water using electrolytic methods at room temperature, low pH, and using low-cost materials. Manganese concentrations in pH 3 mine water were reduced from approximately 40 mg/L to less than 2 mg/L in batch tests with applied voltages of 3.5 V and 5 V after 12 h of treatment. Steady state concentrations for the flow-through tests are similar, with an average manganese concentration of 2.5 mg/L for tests having a hydraulic residence time of 10.7 h. SEM-EDS analysis of the carbon cloth anodes show that manganese oxides coated the carbon cloth fibers.

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