



# Manganese consumption during zinc electrowinning using a dynamic process simulation



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## ABSTRACT

The consumption of manganese in a zinc electrowinning cell house is examined using a process simulation coupled with industrial cell house data. A cell house of a major industrial producer of zinc was simulated using process simulation software. Process data was input in to the simulation on a simulated hourly basis to provide a simulation which appropriately represented the dynamic process. A small amount of dissolved manganese is desired in a zinc electrowinning electrolyte in order to reduce corrosion of the anodes by the formation of a thin layer of manganese dioxide. The manganese consumption was followed through a major change in the Mn concentration. The consumption rate of manganese ions from solution was found to vary between  $8 \times 10^{-7}$  and  $4 \times 10^{-7}$  mol s<sup>-1</sup> m<sup>-2</sup> on PbAg anodes. During shut downs, aqueous manganese concentration was not reduced. Larger rates of manganese consumption were found to be associated with lower concentration ratios of manganese ions to chloride ions in the electrolyte.

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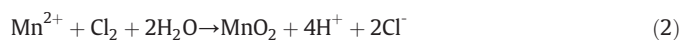
## 1. Introduction

### 1.1. Manganese in zinc electrowinning

Manganese in zinc electrowinning is an essential component for optimal cell house operation. Mn contributes to mud generated in zinc electrowinning which has both adverse and beneficial contributions to the performance of the cell. Over the course of operation, a cell will generate mud consisting largely of manganese dioxide, lead sulfate, and gypsum. The mud will accumulate in two general areas; first as a scale adhering to the anodes and second as a precipitate mud product residing on the bottom of the cell. The composition of these two muds (further referred to as anode and cell mud) is typically dissimilar, with the anode mud usually being largely  $\gamma$ -MnO<sub>2</sub>, a solid solution of MnO<sub>2</sub> and lower oxidation state manganese containing hydroxyl ions (MnO<sub>n</sub> · (2-n)H<sub>2</sub>O) (Kelsall et al., 2000). The cell mud is usually a mixture of gypsum, MnO<sub>2</sub> which has sloughed off of the anode coating, and Pb (as PbO<sub>2</sub> or PbSO<sub>4</sub>) which flakes off along with the MnO<sub>2</sub> scale from the anode or precipitated from solution using strontium carbonate. The muds accumulate over the course of operation, and periodically the anodes and cells are cleaned, with the solids being collected for sale or operational use in other sections. Mud accumulation presents several problems for operation. MnO<sub>2</sub> scale built up on the anodes presents an increased risk for electrical shorts where a physical connection between the cathode and the anode is formed. As well, particulate MnO<sub>2</sub> formed (often associated with new anodes) can diminish cathode Zn morphology

(Rodrigues and Meyer, 1996). Accumulation of mud at the bottom of the cell will reduce the available liquid volume of the cell and in extreme cases may prevent electrodes from fully submerging and connecting with busbars. Cell muds will accumulate at a rate dependent on many conditions, such as concentrations, additive additions, and the type of anode used.

Manganese has benefits as well for the cell. The MnO<sub>2</sub> scale on the anode provides valuable corrosion protection and lowers the oxidation overpotential of the water electrolysis reaction (Cachet et al., 1999; Tunnickliffe et al., 2012; Yu and O'Keefe, 2002). The corrosion protection reduces lead from dissolving and entering solution which will reduce contamination of the cathode product as well as reduce the volume of Pb precipitated contributing to the cell mud. Further, the presence of manganese ions has been reported to reduce the evolution of chlorine gas through proposed scavenging reactions (Eqs. (1) and (2)) (Hierzyk et al., 1969; Kelsall et al., 2000; Pakhomova and Marenkova, 1966). This limits the dissolved chlorine in the electrolyte and consequently reduces chlorine gas venting out of the cells. Chlorine is a hazard for operators and can corrode equipment, particularly at the solution level of the electrodes. The surface of MnO<sub>2</sub> has been noted to inhibit the evolution of Cl<sub>2</sub> gas as well as in comparison with bare Pb electrodes (Kelsall et al., 2000; Pakhomova and Marenkova, 1966).



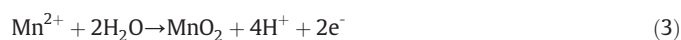
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Typically a target concentration of  $\text{Mn}^{2+}$  of 3–4 g L<sup>-1</sup> in order to promote the protective anodic scale (Sinclair, 2005) however concentrations can be higher for example 18 g L<sup>-1</sup> (Rodrigues and Meyer, 1996). The produced  $\text{MnO}_2$  rich mud can be a valuable process reagent, and often added during leaching prior to electrowinning in order to boost the concentration of  $\text{Mn}^{2+}$  if the purified zinc solution entering the cell house is deficient. In solvent extraction circuits where Mn is removed entirely from the leach solution the addition of  $\text{MnO}_2$  after purification is particularly important (Sinclair, 2005).

These beneficial and detrimental effects of the generation of cell mud and anode scale require a balance which is a complex task. With competing factors affecting the consumption of  $\text{Mn}^{2+}$  in a cell house, controlling a constant concentration of  $\text{Mn}^{2+}$  in order to maintain the  $\text{MnO}_2$  coating is difficult. The concentration of Mn in the purified feed must be kept at such a level that the concentration of Mn in the highly recirculated cell house electrolyte remains at the desired target. The rate of Mn consumption is complex to calculate for a cell house as the conditions are difficult to replicate in a laboratory in order to conduct conventional rate tests. Conversely, calculating the rate direct from cell house data will also carry errors because there is a variable input of new feed electrolyte with changing Mn concentration which is then recirculated through the cell house. This makes determining a consistent basis to do the calculation difficult. A process simulation can be a method of predicting the consumption of Mn in a cell house as it can be used to replicate the conditions in the cell house and apply mathematical algorithms in order to determine appropriate Mn consumption rates. A well validated simulation is capable of corroborating measurements taken from the facility and predicting the amount of Mn consumed in the process. For this reason the following work focuses on developing a simulation capable of providing a prediction of the consumption of  $\text{Mn}^{2+}$  during zinc electrowinning using process simulation.

## 1.2. Manganese reactions during zinc electrowinning

The overall chemical equation for the deposition of  $\text{MnO}_2$  is seen in Eq. (3). However it is unlikely that this reaction occurs in a single step given the change in oxidation state of the Mn and exchange of multiple electrons (Pajunon et al., 2003).

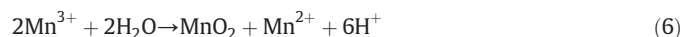
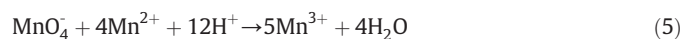
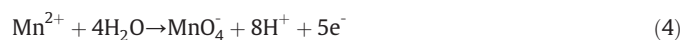


Many pathways have been suggested for manganese reactions and the formation of  $\text{MnO}_2$  in typical zinc electrowinning conditions due to the complex nature of Mn oxidation. Four valences of manganese are typical in zinc electrowinning conditions:  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ , and  $\text{Mn}^{7+}$ , with  $\text{Mn}^{4+}$  and  $\text{Mn}^{7+}$  typically present exclusively as  $\text{MnO}_2$  and  $\text{MnO}_4^-$  respectively. Manganese is thermodynamically stable as  $\text{Mn}^{2+}$  in the acidities common with electrowinning.  $\text{Mn}^{3+}$  formed in the zinc electrolyte is known to persist for long periods of time due to the high acidity of the electrolyte and gives the zinc electrolyte a characteristic pink color (Clarke et al., 2006; Selim and Lingane, 1959). In reported laboratory tests, the purple color characteristic of permanganate ions has been observed close to the anode. While the potential of the anode during zinc electrowinning is large enough to generate permanganate ions, it is thought it reacts quickly near the anode and thus is not observed in the bulk solution (Ipinza et al., 2007; Yu and O'Keefe, 2002).

When a new anode is placed into a cell, a large amount of  $\text{MnO}_2$  mud is generated. After a time period of approximately a month, the amount of mud generated is greatly reduced and a mature, coherent coating of  $\text{MnO}_2$  is established (Rodrigues et al. 2001). Anodes are cleaned periodically (1 to 3 months depending on operational preferences) using pressurized water or mechanical brushes (Sinclair, 2005). The cleaning is done to remove the surface layer of deposited  $\text{MnO}_2$  to prevent the layer from reaching the cathode and causing a short. A thin layer of dense  $\text{MnO}_2$  is left on the anode in order to prevent the excessive

$\text{MnO}_2$  formation which is observed with new anodes. This suggests that  $\text{MnO}_2$  formation in a cell house, and associated Mn ion consumption, is typically done on an established layer of  $\text{MnO}_2$ .

Clarke et al. (2006) conducted an investigation of the electrodeposition of  $\text{MnO}_2$  on a  $\text{MnO}_2$  substrate with a ring disk electrode over a range of temperatures, pHs, and concentrations. At concentrations greater than 1 M  $\text{H}_2\text{SO}_4$  and 40 °C,  $\gamma\text{-MnO}_2$  was observed to form under activation controlled conditions. Kelsall et al. (2000) proposed a mechanism relying on the mechanism as described in Eqs. (4)–(6), with Eq. (6) being the rate limiting, activation controlled step.



A diffusion controlled mechanism was proposed (Eqs. (7)–(9)) where  $\text{Mn}^{3+}$  present in solution deposits initially as a hydroxide with a further electrochemical oxidation to form the  $\text{MnO}_2$ . This mechanism was reported to be favored for conditions of low acid concentration (<1.0 M) (Clarke et al., 2006).



Along with deposition on the anode,  $\text{MnO}_2$  has also been reported to precipitate from solution rather than forming on the anode.  $\text{MnOOH}$  is thought to be a precursor to  $\varepsilon\text{-MnO}_2$  which will precipitate in the cell mud, while the disproportionation of  $\text{Mn}^{3+}$  results in the creation of the  $\gamma\text{-MnO}_2$  found on the scale on the anodes for the case of PbCaSn anodes (Ipinza et al., 2003, 2007).

## 2. Materials and setup

### 2.1. Simulation setup

The framework of the simulation used a time transient process simulation developed by the authors (Mahon et al., 2012). The simulation was set up in the process simulation software CADSIM Plus published by Aurel Systems. As outlined in Fig. 1, the simulated cell house used a conventional circulating electrolyte flow. Two cell houses (referred to as A and B) were set up identically and examined. A solution with a high concentration of zinc (Purified Electrolyte) from the previous purification steps flowed into the circuit. Purified electrolyte entered a cooled electrolyte tank and was mixed with electrolyte coming from cooling towers. The electrolytes were assumed to perfectly mix in this tank along with the resident volume, and electrolyte exited this tank as cooled electrolyte where it entered the cell house. The cell house consisted of blocks of cells which were fed cooled electrolyte from headers which were assumed to distribute the cooled electrolyte evenly among cells. Each block of cells had a dedicated rectifier. Cells were assumed to remove solid zinc immediately, gasses were vented to atmosphere, and no impurity or additive effects were simulated. The cells were assumed to be well mixed tanks with the kinetics of zinc deposition, hydrogen evolution, and oxygen evolution predicted by Butler–Volmer equations. Greater detail on the process simulation of the electrowinning cells can be found elsewhere (Mahon et al., 2012). The spent electrolyte exited the cell house, entered

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