Electrolytic manganese metal production from manganese carbonate precipitate

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ARTICLE INFO

ABSTRACT

The recovery of manganese metal from manganese carbonate precipitate by leaching–purification–electrowinning was studied. The manganese carbonate precipitate from Baja Mining Corp.'s El Boleo project was readily leached into acidic ammonium sulfate solution. The manganese extraction reached 99.7%. The manganese leachate was purified using ammonium sulfide to remove harmful impurities (Ni, Co, Cd, Cu and etc.). Manganese electrowinning was conducted in a diaphragm cell designed to eliminate edge effects and improve manganese deposition. The addition of polyacrylamide polymer had a significant leveling effect on manganese electrodeposition. However it increased the deposit internal stress and even resulted in cracking of manganese deposits at a high dosage. With increasing polyacrylamide polymer concentration, current density, and pH, the manganese current efficiency first increased, reached a maximum value and finally decreased. The manganese current efficiency decreased with increasing deposition time as the deposit became rougher and the real current density deviated from its ideal value. A reasonable catholyte circulation rate is important to maintain the optimum manganese electrodeposition. The presence of chloride in solution has a little effect on manganese deposition in its concentration range from 0 to 2 g/L. The diaphragm selection as an important part of the cell design was analyzed.

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1. Introduction

The standard potential for Mn^{2+}/Mn is − 1.18 V vs. SHE. Manganese is the least noble metal that can be electrodeposited from aqueous solutions on a commercial scale. Manganese metal is typically produced by the electrolysis of manganese and ammonium sulfate solution. The most commonly used technology involves reductive calcining to convert higher valent manganese oxides such as MnO_2, Mn_3O_4, and Mn_2O_3 to MnO (Zhang and Cheng, 2007). The calcine is subsequently leached in spent electrolyte from manganese electrowinning to produce a neutral manganese sulfate solution.

$$MnO + H_2SO_4 \rightarrow MnSO_4 + H_2O \qquad (1)$$

This neutral solution is purified with ammonium sulfide to precipitate metal impurities contained in the solution. The purified solution is then clarified, dosed with either selenite or sulfite, and used in electrowinning. In a typical cell, catholyte flows through the diaphragm to the anode where acid and oxygen are formed; manganese is formed at the cathode. The associated electrolytic reactions are as follows:

$$Cathode : MnSO_4 + 2e^- \rightarrow Mn + SO_4{}^{2-} \qquad (2)$$

$$Anode : H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^- \qquad (3)$$

$$Overall : MnSO_4 + H_2O \rightarrow Mn + H_2SO_4 + 1/2O_2. \qquad (4)$$
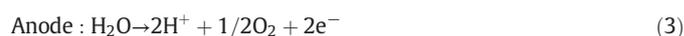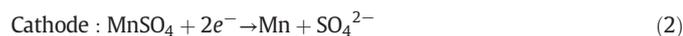
Besides the above major reactions, hydrogen evolution and the oxidation of Mn(II) to MnO_2 also take place at the cathode and anode respectively. Hydrogen evolution reduces the current efficiency of manganese electrodeposition while the oxidation of Mn(II) to MnO_2 consumes the manganese ions.

$$Cathode : 2H_2O + 2e = H_2 + 2OH^- \qquad (5)$$

$$Anode : MnSO_4 + 2H_2O = MnO_2 + H_2SO_4 + 2\ H^+ \qquad (6)$$
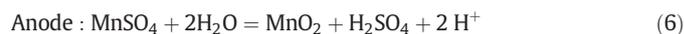
The current efficiency of manganese electrodeposition from such purified solution is low, and the quality is poor. Even without any impurity, it is difficult to produce high quality electrolytic manganese. As manganese is plated, manganese deposits become rougher, and nodules grow up and outward, forming a cauliflower-like structure or even tree-like dendrites, resulting in trapping of electrolyte, difficulty in stripping of manganese deposits, and even difficulty in removal of cathodes from cells. A short plating cycle has to be used, resulting in a low overall process efficiency. The catholyte pH is normally maintained at 7 or higher

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and Mn(II) is gradually oxidized to MnOOH by air, affecting manganese deposition and even plugging diaphragm. Some additives have to be used to counteract the harmful effects of impurities, improve manganese deposit quality and stabilize the catholyte. Without the use of additives, it is very difficult or even impossible to produce electrolytic manganese commercially.

Sulfur dioxide was first used to produce electrolytic manganese commercially with a reasonable current efficiency (60–65%). The effects of SO_2 are: (1) increasing the overpotential of hydrogen evolution and hence the manganese current efficiency; (2) promoting the formation of stable α-manganese, (3) counteracting the harmful effects of impurities, and (4) suppressing the oxidation of Mn(II) to MnOOH by air. The addition of SeO_3^{2-} is more effective to improve the manganese electrodeposition. The manganese current efficiency can reach as high as 96% in the presence of SeO_3^{2-} (Lu et al., 2014). However, the addition of SeO_3^{2-} results in the contamination of manganese metal and contributes to environmental issues at the manganese plant and the product use site. Some organic additives such as carboxylic acids (Griffith, 1950), thiourea (Hammerquist, 1951) and water-soluble polyacrylamide polymer (Jacobs, 1962; Goddard, 1979; Coleman and Griffin, 1984) were used in combination with SO_2 and SeO_3^{2-} to improve the manganese deposition. However there is very little detailed information available.

The effects of the catholyte composition, current density, temperature and pH on the manganese electrodeposition from sulfate media have been discussed by Jacobs et al. (1946); Louis and Martin (1976) and Araujo et al. (2006). The optimum catholyte manganese concentration is 12 g/L. A lower manganese concentration resulted in a lower current efficiency. A higher manganese concentration (above 15 g/L) resulted in precipitation of manganese hydroxide and then a lower current efficiency. An optimum ammonium sulfate concentration is around 125 g/L (Araujo et al., 2006). In the industry, the ammonium sulfate concentration ranges from 130 to 150 g/L. Due to diffusion and migration of ions, the ammonium sulfate concentration is 20 to 30 g/L higher in the catholyte than that in the anolyte or in the feed. This phenomenon was also observed in this study. The optimum temperature reported varies from 30 to 40 °C for different authors (Jacobs et al., 1946; Louis and Martin, 1976) since it is related to the current density, catholyte cooling efficiency and energy consumption. At a temperature below 35 °C, the manganese deposit is light gray, smooth and fined-grained while at a temperature above 35 °C, the manganese deposit becomes more nodular and dendritic with increasing temperature (Jacobs et al., 1946). At a temperature above 45 °C, dendrites form readily and manganese re-dissolution takes places at the base of trees. However a temperature slightly higher than 40 °C is used in some industrial plants for a higher production efficiency and a lower energy consumption. The optimum current density ranges from 450 to 600 A/m² (Jacobs et al., 1946; Louis and Martin, 1976), which is in turn related to the other operation parameters. A detailed review about the current state of the art in manganese electrodeposition technology was provided by Lu et al. (2014).

The El Boleo project (originally developed by Baja Mining Corp, Vancouver, Canada) has the option to recover manganese carbonate from solvent extraction raffinate solution as a solid precipitate. This may be done by adding sodium carbonate to an impure manganese sulfate solution (Dreisinger et al., 2008) to selectively precipitate manganese away from calcium and magnesium. It is possible to produce manganese metal from this manganese carbonate product. The chemical reaction involved in leaching of manganese carbonate is:

$$MnCO_3 + H_2SO_4 \rightarrow MnSO_4 + H_2O + CO_2. \tag{7}$$

The objective of this study was to test the feasibility of production of high purity manganese metal from chemically precipitated manganese carbonate in ammonium sulfate solutions with the use of alternative electroplating additives.

2. Experimental

2.1. Leaching

Manganese leaching was conducted in a 2-L baffled glass reactor. The temperature was controlled at 50 ± 0.5 °C using a heating mantle and temperature controller. The reactor was sealed with a lid with several openings. These openings allowed the insertion of an impeller, temperature sensor, and pH and redox potential probes. Agitation was provided by a 45° pitched-blade titanium impeller with a 5.7 cm diameter. The impeller was driven via an overhead motor and was suspended around 1.5 cm from the bottom of the leach vessels. The rotational speed was controlled at 900 rpm. The feed solution with 12 g/L Mn(II), 36 g/L H_2SO_4 and 130 g/L $(NH_4)_2SO_4$ was prepared using reagent grade manganese sulfate, sulfuric acid and ammonium sulfate.

2.2. Purification

The leachate purification was conducted in a 2-L water-jacked, baffled reactor using ammonium sulfide. The temperature was controlled at 45 ± 0.2 °C using a water bath. The reactor was sealed with a glass lid with several openings for different purposes. Nitrogen gas was used to prevent manganese(II) oxidation. Agitation was provided by a 45° pitched-blade titanium impeller with a 5.7 cm diameter. The impeller was driven via an overhead motor and was suspended around 1.5 cm from the bottom of the reactors. The rotational speed was controlled at 900 rpm. The purified leachate was pressure-transferred to a 9-L thickener and the sulfide precipitates settled under a nitrogen atmosphere for 4 days. The mostly clear solution was filtered using a 0.2 μm membrane filter under a nitrogen atmosphere.

2.3. Manganese electrowinning

Manganese electrowinning was conducted in a diaphragm cell with one 316 stainless steel cathode and one lead anode with 1% silver. The electrolytic cell was placed in a water bath to maintain the catholyte temperature at 42 ± 0.5 °C. The catholyte was circulated from the bottom to the top using a peristaltic pump to maintain a uniform catholyte in the cell. The feed solution was added to the cell at the top using a peristaltic pump and circulated to the bottom. The cathode with a plating area of 13.2 × 5.8 cm was polished using 1200 grit sandpaper, washed with soap, and dried. The cathode was weighed prior to and after electrowinning to determine the amount of manganese deposited. When a cathode was pulled out of the cell, it was dipped in 2% potassium dichromate solution to passivate the deposit surface, washed with water, dried, and stripped. The stripped cathode was pickled in anolyte to dissolve the residue manganese. The anode was sandblasted to achieve an average roughness of 30 μm to reduce the lead dissolution. The active area of the anode was 1/2.5 of the cathode plating area to maintain a higher current density at the anode and suppress the formation of MnO_2. The non-active area was blanketed using CPVC plastic.

The cathode and anode were placed 5.5 cm apart. A high precision DC power supply was used to maintain a constant current. The cell voltage and current were measured using a data acquisition module and DC Ammeter shunt. The pH measurements were taken during a run at varying time intervals.

The initial catholyte was prepared using purified feed, and reagent grade ammonium sulfate and ammonium hydroxide, and sodium sulfite. The initial catholyte composition was: 12 g/L Mn(II), 150 g/L $(NH_4)_2SO_4$, 0.3 g/L SO_2 and pH 8.3. The typical purified feed composition was: 32 g/L Mn(II), 130 g/L $(NH_4)_2SO_4$, 0.3 g/L SO_2 and pH 6.7 to 7.0. The anolyte initial composition was the same as the catholyte. The catholyte pH was measured at room temperature.