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Electrorefining of high purity manganese

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ABSTRACT

The recovery of manganese metal from manganese chloride medium by purification–electrorefining was studied. The ammonium chloride – manganese chloride electrolyte was selected as the most promising for refining. The physical properties of the electrolyte were first studied as a function of solution composition and temperature. The electrorefining process introduces impurities into the anolyte from the dissolving anode. It is necessary to purify the anolyte before passing the solution to catholyte. The purification of the electrolyte by ion exchange was investigated. This paper reports the uptake of copper, nickel, cobalt, cadmium, zinc and manganese from manganese chloride solution onto the chelating resin Lewatit® MDS TP220 in batch and column experiments. The results demonstrate the ability for Lewatit® MDS TP220 to remove contaminants to an extent satisfying the quality criteria required for the utilization of the manganese chloride solution for electrorefining. In the electrorefining process, the synergistic effects of selected impurities on manganese deposit quality were first investigated. The parameters of current density, deposition time, and cathode usage frequency on the electrorefining process were investigated. With increasing the current density, the cathodic current efficiency first increased, reached a maximum value and then decreased. With increasing deposition time from 24 h to 48 h, the manganese current efficiency decreased and the deposit became more dendritic. The more times the cathode was used, the lower the current efficiency.

1. Introduction

Either pyrometallurgical or hydrometallurgical processes can produce manganese. The typical manganese material produced via pyrometallurgical routes is ferromanganese and silicomanganese. These products are not pure due to the presence of iron or silicon. Elemental manganese metal is conventionally produced by hydrometallurgical processes (leaching, purification and electrowinning). Manganese electrodeposition from ammonium sulfate and chloride media has been well studied. Electrolytic manganese is conventionally produced from ammonium sulfate media due to some limitations of chloride media such as the removal of chlorine from the anolyte and consumption of ammonia (Lu et al., 2014). However, sulfate media is not suitable for the production of high-purity manganese. The electrowinning process in the sulfate system requires sulfur dioxide gas (SO_2) or selenium compound addition to control the structure and morphology of manganese, increase the manganese quality, and stabilize the catholyte (Petroseviciute et al., 1985). Accordingly, manganese produced from sulfate media contains sulfur (0.002–0.1%) and selenium at levels that disqualify the product from use in high purity applications.

It is reported that manganese can be electrorefined in halide media (Kozin et al., 1998). As manganese is a very active metal and its self-dissolution may be too fast, it may not be suitable for conventional electrorefining like copper electrorefining. In such a situation, less pure manganese should be first dissolved in chloride solution, and then manganese is electrodeposited from the catholyte in a diaphragm cell. The anode solution in such a process will contain impurity elements and must be purified for small amounts of nickel, cobalt, copper, zinc, etc. before cathode deposition. These impurities have to be removed before the anolyte is circulated to the cathode compartment. There are many purification methods such as hydrolytic precipitation, sulfide precipitation, electrochemical methods, and ion exchange. The precipitation of metals in solutions as metal hydroxides is the most common way to remove metals from solutions in hydrometallurgical processes. But hydrolytic precipitation cannot be used for the level of purification required to achieve the high purity Mn (Huisman et al., 2006). The precipitation and separation of metal sulfides from manganese is based on different sulfide solubilities of metals at a certain pH and temperature. Sulfide precipitation can effectively remove heavy metal impurities (Ni, Co, Cu…) (Lewis, 2010). However, sulfur from sulfides may be introduced to the manganese deposit if residual sulfide ion remains in the purified solution. This eliminates the use of sulfide

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precipitation for purification when producing high purity manganese metal. Accordingly, in this work the focus has been on ion exchange purification. Ion-exchange methods have been extensively used to remove heavy metals from the solution due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics (Kang et al., 2004). We have screened several commercial resins for their suitability for this separation, in an acidic manganese chloride solution; the chelating resin Lewatit® MDS TP220 appears to be very promising (Wołowicz and Hubicki, 2012). Lewatit® MDS TP220 is a macroporous weakly basic resin with chelating bis-picolylamine functional groups attached to a styrene/divinylbenzene co-polymer (Littlejohn and Vaughan, 2012). Bis-picolylamine resin is highly selective for transition metals such as nickel, cobalt and copper even at low pH, making it appropriate for removal of these elements from solutions with containing large excesses of unwanted metals (Diniz et al., 2005). Thus, this paper deals with the application of separation using chelating resins Lewatit® MDS TP220 to the purification of Mn in a chloride medium, which is used as an electrolyte after separation.

In this work, the physical properties of $MnCl_2$-NH_4Cl solutions were measured to characterize the electrorefining medium and the purification of $MnCl_2$ with TP220 resins in NH_4Cl media was investigated and optimized. Physical properties of electrolytes such as electrical conductivity, density and viscosity all have considerable economic importance in refining. Conductivity is related to electrical energy consumption while density and viscosity may influence heat transfer and the carryover of impurity from the anode into the final cathode product (Price and Davenport, 1980; Priestner and Steel, 1976). The electrorefining process for production of high purity manganese from chloride medium was investigated. The variables of interest in the electrorefining process were impurity levels in solution, current density, cathode use frequency and electrorefining time.

2. Evaluation factors

The purpose of the electrorefining process is to produce a high purity cathode product with high current efficiency and good deposit quality and low energy consumption. To determine the cathodic current efficiency related to the manganese deposit, Eq. (1) was used, and Eq. (2) for the specific energy consumption (unit manganese quantity on the cathode) calculation was also necessary (Wei et al., 2010).

$$CCE = \frac{p}{E_{Mn} I_c A_c}\left(\frac{\Delta M_c}{\Delta t}\right) \tag{1}$$

$$SEC = \frac{CV \times 1000}{E_{Mn} \times CCE} \tag{2}$$

In Eq. (1) and (2), CCE is the cathodic current efficiency is expressed as a percentage, and $\frac{\Delta M_c}{\Delta t}$ (g/h) is the weight gain of the cathode mass over the time interval Δt. A_c is the effective cathode area (m^2), and I_c is the applied apparent current density (A/m^2). p is the purity of the deposited manganese. E_{Mn} is the electrochemical equivalent and its value is 1.025 g/(A·h). SEC is the specific energy consumption as kWh/t for the metallic manganese, and CV is the cell voltage (V).

Deposit morphology is also a key factor to evaluate the quality of deposited manganese. The micro-morphology of the manganese deposit was observed by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD).

3. Experimental

3.1. Materials

The raw manganese plates (> 99.9% pure), which were used as anodes, were obtained from Manganese Metal Company in South Africa. In the physical properties study, the electrolyte solutions used throughout the work were prepared from analytical reagent grade manganese (II) chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$) and ammonium chloride (NH_4Cl) with deionized water. In the purification study, the manganese chloride solutions were prepared by dissolving manganese metal with a 12 mol/L HCl solution and Milli-Q water. The anion exchange membrane was AMI-7001S, bought from Membranes International INC. in USA. In the electrorefining study, the 316 stainless steel plates, which were used as cathodes, were bought from McMaster-Carr. The additives for the electrorefining process were available in the UBC hydrometallurgical laboratory. The synthetic electrolyte feed solutions for electrorefining were synthesized from manganese chloride and ammonium chloride solutions after purification.

3.2. Physical properties of manganese electrorefining electrolytes

Densities were measured with a standard 25 mL pycnometer with three measurements taken for each reported value. The measurements were converted from specific gravities to density values. Electrical conductivities were measured with a Jenway conductivity meter type 4320 with three measurements taken for each reported value in conjunction with a high conductivity cell. Test solutions of about 50 mL were freshly prepared in a volumetric flask before each experiment. The solution was placed in test tubes and inserted into the water bath to establish the target temperature. Viscosities were determined by means of a Brookfield viscometer, Model LVDV-III with LV2 spindle. Test solutions of about 500 mL were freshly prepared in a volumetric flask before each experiment. The solution was placed into the container and inserted them into the water bath to maintain the temperature. The solution, together with the spindle had to be immersed in the bath for a minimum half hour if the temperature was below 10 °C in order to obtain a stable reading. When the solution was at the test temperature (± 0.1 °C of the specific temperature), the viscosity was measured and recorded.

3.3. Purification

The sorption of metals was studied by the batch technique. Adsorption tests were carried out at room temperature in a 250-mL baffle reactor by mixing the solution with resins under sufficient agitation for 20 h to ensure that equilibrium loading was established. For each experiment, 150 mL of feed solution was added to the test vessel equipped with overhead stirrer impeller. To provide good suspension of the resin in the test solution, 250-RPM speed of overhead stirrer (Cole Parmer) was provided throughout the test. After equilibrium was reached, the resin was separated from the solution by vacuum filtration and washed with de-ionized water. For column studies, resin was placed in a Plexiglas column, 400 mm long, and 8 mm in diameter, with a bed height of 150 mm. The resin was rinsed with 2 mol/L HCl solution and deionized water before separation tests in order to remove organic and inorganic contamination during the manufacturing process. Two flow rates, namely 13.8 and 41.4 BV/h, were tested because chelating reactions generally take a long time so the separation efficiency will be affected by the flow rates. The treated solution was collected from the outlet of the column at different time intervals.

3.4. Electrorefining of manganese

Manganese electrorefining was conducted in a diaphragm cell with one 316 stainless steel cathode and one raw manganese anode. The electrolytic anion membrane reactor was made out of PVDF. PVDF is a specialty plastic used in applications requiring the highest purity, as well as resistance to solvents, acids and bases. 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 distance between the cathode and anode was kept constant (30 ± 1 mm) through fixing the electrode position with the polypropylene holder. The anode was made of manganese flakes with