Hydrometallurgy 110 (2011) 44–49

Contents lists available at SciVerse ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Preparation and characterization of EMD from manganese cake — A byproduct of manganese nodule processing

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ARTICLE INFO

Article history:
Received 10 March 2011
Received in revised form 20 July 2011
Accepted 12 August 2011
Available online 19 August 2011

Keywords:
Manganese nodules
Manganese cake
Electrolytic manganese dioxide
Electrolysis
Discharge capacity

ABSTRACT

Electrolytic manganese dioxide (EMD) was prepared from manganese cake, which is an oxide material and byproduct obtained during processing of manganese nodules. Manganese cake dissolution was carried out in sulfuric acid media using waste newspaper as a reductant. In the two-stage purification of leach liquor iron was initially removed by pH adjustment using lime slurry followed by sulfide precipitation using sodium sulfide. Effects of current density, Mn(II) and sulfuric acid concentrations were studied during the electrodeposition of EMD from purified solution. The EMD obtained was characterized by XRD, SEM and its discharge capacity was determined. The XRD pattern demonstrated that EMD was a mixture of γ- and ε-variety. The EMD produced from manganese cake showed a discharge capacity of 290 mAh/g, which is industrially acceptable.

1. Introduction

Electrolytic manganese dioxide (EMD) is used as a cathode mixture material for dry-cell batteries such as alkaline batteries, zinc–carbon batteries, rechargeable alkaline batteries etc. Natural manganese dioxide (NMD) can be used in Leclanche cells, but in alkaline, lithium and other "modern" batteries, synthetic manganese dioxide with improved qualities is required. Out of the different forms of manganese dioxides, γ-MnO_2 is widely used (Jantscher et al., 1999) due to its high intercalation voltage. Also, γ-MnO_2 has the ability to maintain high discharge rates, a good performance over a wide temperature range and a long storage life. Manganese dioxide can be prepared both electrochemically and chemically. However, γ-MnO_2 which is predominantly produced by electrochemical methods in the battery industry has better performance than that prepared chemically (Chou et al., 2006).

Many investigations have been carried out to develop processes for economical recovery of manganese from low grade manganese ores and other secondary sources. Various direct reductive leaching processes have been investigated for processing manganese ores using different reducing agents such as ferrous iron, sulfur dioxide, hydrogen peroxide etc. (Das et al., 1982; El Hazek et al., 2006; Naik et al., 2000). Carbohydrates are another class of non-hazardous and low cost reducing agents that have been used for manganese ore leaching either in pure form or as industrial wastes (Beolchini et al., 2001; Hariprasad et al., 2007; Ismail et al., 2004; Trifoni et al., 2000; Veglio et al., 2000, 2001). Trifoni et al. (2000) reported the leaching responses of manganiferous ores from different sources containing pyrolusite (MnO_2) and other phases like Mn-oxide hydrate ($Mn_7O_{13}\cdot 5H_2O$), groutite [MnO(OH)] etc. using 20% glucose in 3 N sulfuric acid media at 70 °C. Manganese recovery varied from 64% to 100% after 4 h of leaching depending upon the phases and iron content of the ores. In another study (Trifoni et al., 2001) technical feasibility of MnO_2 leaching in acid–alcohol mixture was carried out using glucose as the reducing agent. Apart from glucose whey, which is an environmentally hazardous waste of cheese industries containing about 40–50 g/L lactose, has also been investigated as a reducing agent (Veglio et al., 2000). In order to simulate the behavior of whey, synthetic lactose has also been used for the leaching tests because whey powder constitutes 70% lactose with varying amounts of proteins, ash, moisture etc., ligno-cellulosic waste materials such as sawdust and bagasses are also potential reducing agents in the acid leaching of manganese ore. Hariprasad et al. (2007) reported the Mn-ore leaching in sulfuric acid media using sawdust as a reductant. Effects of pulp density, amount of acid, temperature, particle size of ore and amount of sawdust were studied. Manganese extraction of ~98% was achieved under the conditions: leaching time 8 h, 5% H_2SO_4 (v/v), 10% pulp density, 90 °C and 5% sawdust (w/w), i.e. 0.5 g/g ore. Other Mn containing materials like low grade manganese ore, manganese nodule and Mn-nodule leach residues were tested and all these materials responded well, giving more than 98% Mn extraction. Hariprasad et al. (2009) further studied the Mn-ore leaching using shredded newspaper as reducing agent. The optimum conditions for >90% Mn dissolution from medium grade ore (38% Mn) was established as: 90 °C, H_2SO_4 5% (v/v), reductant: ore ratio 0.5, 10% pulp density, particle size −100 μm and time 8 h. Newspaper was also found to be equally effective for low grade (Mn 15.8%) and it was established that reductant and acid amounts are proportional to Mn content of the ore.

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doi:10.1016/j.hydromet.2011.08.003

Manganese nodules, abundantly available on the ocean floor are a potential source for manganese. At present, primary interests in deep-sea nodules are nickel, copper and cobalt values. CSIR-IMMT has developed and pilot-tested a hydrometallurgical process to recover Cu, Ni and Co from manganese nodules (Das and Anand, 1997; Mittal and Sen, 2003). Manganese cake – a precipitated oxide of manganese – is produced during the demanganization step, i.e. removal of residual Mn(II) from ammoniacal leach liquor by oxidizing under oxygen overpressure. Since Mn-cake contains high amounts of manganese, recovery of Mn from this byproduct will improve the overall economics of nodule processing technology.

In the present study an attempt has been made to develop a simple, effective and viable process for converting a process by-product into a useful product. No systematic work has been reported so far on the production of EMD from Mn-bearing by-product through a hydrometallurgical route. Novelty of the process lies in that one of the reagents (waste newspaper) used during leaching is also a waste product. In this investigation results on leaching, leach liquor purification and electrolytic deposition of MnO_2 have been demonstrated along with the discharge behavior of the EMD produced.

2. Experimental

2.1. Material

Manganese cake contains manganese as the major element along with other minor elements as impurities such as Cu, Ni, Co, Zn, and Fe etc. The composition of Mn cake (air dried sample) is Mn 57.15%, Fe 0.58%, Ni 0.12%, Cu 0.18%, Co 0.044% and Zn 0.21%.

Waste newspaper cuttings were used as a reducing agent during leaching. The ultimate analysis of waste newspaper, done in TrueSpec CHN Analyser (LECO Corporation, USA) was determined as: 37.1% fixed carbon, 12.7% moisture, 7.4% ash and 42.8% volatile matter.

All other reagents used for the experimental work were of analytical reagent grade.

2.2. Leaching studies and purification of leach liquor

Leaching experiments were carried out at the 100 g scale in a 2 L capacity Parr autoclave. Initially, the required amount of concentrated H_2SO_4 was mixed with the weighed amount of shredded newspaper and mixed thoroughly, followed by addition of manganese cake and thorough mixing. The whole mass was then transferred to the reactor vessel and a measured volume of distilled water was added to make a 10% (w/v) slurry. From the previous studies carried out with similar materials in our laboratory (Ghosh et al., 2008; Hariprasad et al., 2009) a standard leaching condition was chosen: pulp density 10%, temperature : 90 °C, reductant amount : 0.65 g/g Mn cake, H_2SO_4: 7.25% (v/v) and time: 2 h. The slurry was heated to 90 °C and agitated under fixed agitation for 2 h. After 2 h, the slurry was cooled, filtered and the filtrate was analyzed for metal ions using atomic adsorption spectrophotometer (Perkin Elmer AA 200). Mn analysis was done volumetrically by EDTA titration using thymolphthelexone as indicator.

First stage purification of leach liquor for iron removal was carried out by adding 20% lime slurry with constant stirring and simultaneous monitoring of pH. After attaining the target pH value the solution was filtered and was analyzed for metal content. For the second stage purification the pH adjusted solution was further treated with 2.5 times stoichiometric (of Cu, Ni, Co and Zn content) amount of Na_2S to obtain $MnSO_4$ solution free from other impurities.

2.3. Electrolytic preparation of EMD

The electrolysis was carried out at 90 °C in an electrolytic cell containing an aqueous electrolyte comprised of manganese sulfate and sulfuric acid. Generally, EMD produced at low temperature shows inferior capacity in comparison with EMDs produced at elevated temperature (96–98 °C) (Ghaemi, 1995; Ghaemi et al., 2001). The anode and the cathode used were 5 cm × 8 cm sheets made out of lead metal and stainless steel respectively. The current was supplied from a constant current D.C. source. Then the deposited EMD from the anode was removed mechanically, ground and washed repeatedly with distilled water. It was dried at 60 °C and then subjected to particle size analysis using a Malvern laser particle size analyzer (Model: AWM 2000). In addition the samples were also characterized using XRD and SEM.

2.4. Discharge/charge experiments

For the discharge/charge study cathode made out of a mixture of 1 g powdered EMD and 0.25 g pure graphite was used. Graphite was added to increase the conductivity. During mixing, a few drops of 5% poly vinyl alcohol (PVA) was added which served as a binder. The mixture was transferred to a die of 20 mm diameter containing a stainless steel mesh. The cathode mixture compressed under a load of 5 t for 5 min which resulted in a pellet of 20 mm diameter and 2 mm thickness. For discharging the cells and to determine their discharge capacity, a floated test cell arrangement was made. For this purpose a beaker containing 9 M KOH solution was taken. The pellet was soaked in KOH solution for 30 min. A zinc plate was used both as counter electrode and reference electrode. The cell with such arrangements was discharged using BITRODE battery tester (LCN1-25-24). Discharging was done at 20mAh with a cutoff voltage of 0.9 V.

3. Results and discussions

3.1. Leaching of Mn cake and purification

The major structural components of waste paper are cellulose, hemicellulose and lignin which make it a good source of sugar (Shleser, 1994). Cellulose is a linear polysaccharide of β-1,4 glycosidic linkage and is susceptible to acid catalyzed hydrolysis that releases soluble sugars such as glucose which is an established reducing agent for MnO_2. Concentrated H_2SO_4 disrupts the hydrogen bonding of cellulose making it amorphous and gelatinous mass which hydrolyses under dilution. Considering the total manganese in the cake to be present as MnO_2 the overall reaction can be written as follows

$$12nMnO_2 + (C_6H_{10}O_5)n + 12nH_2SO_4 \rightarrow 12nMnSO_4 + 6nCO_2 + 17nH_2O \quad (1)$$

The main purpose of the leaching step was to generate a feed solution for the electrochemical deposition. Hence, attempts were not made in the present study to optimize the leaching conditions, but instead the standard leaching conditions mentioned in Section 2.2 were chosen based on our prior experience with similar materials (Ghosh et al., 2008; Hariprasad et al., 2009). Under the standard conditions of leaching, the leach liquor obtained had the following composition: Mn 54.94 g/L, Cu 96.8 mg/L, Co 52.6 mg/L, Ni 69.0 mg/L, Zn 277 mg/L and Fe 586 mg/L and a pH of 0.68. In the first stage of purification the leach liquor pH was increased stepwise to 5.5 from initial pH of 0.68 and concentrations of the metal ions at different pH are given in Table 1.

It is observed from Table 1 that the optimum pH to remove most of the iron without affecting the manganese concentration is 4.0. It is evident that by pH adjustment alone other impurities cannot be removed effectively. In order to prepare pure $MnSO_4$ solution for EMD preparation, the first stage purified solution (iron free) was treated with Na_2S (2.5 times stoichiometric). The final purified solution contained Mn 54.9 g/L, Cu 0.1 mg/L, Co 0.6 mg/L, Ni 0.7 mg/L, Fe 0.2 mg/L and Zn 0.4 mg/L. The final pH of the solution was 5.86.