ScienceDirect

Hydrometallurgy
Volume 186, June 2019, Pages 260-268

Novel hydro-electrometallurgical technology for simultaneous production of manganese metal, electrolytic manganese dioxide, and manganese sulfate monohydrate

Gigla Tsurtsumia [a], Djemal Shengelia [b], Nana Koiava [a], Tinatin Lezhava [a], David Gogoli [a], Levan Beriashvili [a], Sulkhan Suladze [b], Izolda Kakhniashvili [a]

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https://doi.org/10.1016/j.hydromet.2019.04.028
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Abstract

The main stages of a novel hydro-electrometallurgical technology for simultaneous production of electrolytic manganese metal, electrolytic γ-MnO_2, and manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$) were tested at a large laboratory scale. The unified flow sheet comprised large and small process loops. The large loop included: concentrated sulfuric acid leaching of ore obtained by high-temperature reduction of manganese oxide ore; hydrolytic and sulfide purification of $MnSO_4$ solution; production of crystalline manganese sulfate monohydrate obtained by high-temperature autoclave treatment of purified concentrated $MnSO_4$ solution; feeding of hot spent $MnSO_4$ solution from the autoclave as anolyte to an AMI-7001S anion membrane-separated electrochemical reactor where γ-MnO_2 was produced on titanium anodes. The small process loop included preparation and correction of the catholyte composition using $MnSO_4 \cdot H_2O$ crystallized in the autoclave, from which electrolytic manganese metal was deposited on titanium cathodes. A heat pump was used to maintain the necessary temperature difference between the anolyte and catholyte. The energy consumed by the heat pump was half that obtained using an electrical current heating device. Electrical power consumptions for the production of manganese metal, manganese dioxide, and manganese sulfate monohydrate were 9.67 Wh/g, 3.75 Wh/g, and 0.884 Wh/g, respectively.

Introduction

In recent years, demand for high-purity electrolytic manganese metal (EMM), electrolytic manganese dioxide (EMD), and manganese sulfate monohydrate (MSM) has substantially increased in the world market. Steel, aluminum, welding electrode, and chemical product industries are the main consumers of EMM. The

chemical industry is significantly dependent on high-purity EMD. MSM, which is used as an additive to animal food, in fungicides, and as a precursor for other manganese salts, is in increased demand.

This increased requirement for manganese-containing products promotes the development and implementation of new energy-efficient technologies that require less capital expenditure. The available literature that deals with processes and production of manganese products by hydrometallurgical technologies was thoroughly reviewed by Zhang and Cheng, 2007a, Zhang and Cheng, 2007b. Information about leaching of manganese ores using different reagents has been reported in several studies (Nayl et al., 2011; Sahoo et al., 2001; Zhang et al., 2018). The influence of various factors on electrodeposition of manganese metal have been discussed by Araujo et al. (2006), Wei et al. (2010). Lu et al. (2014) analyzed and reviewed processes of electrodeposition of manganese metal based on work of numerous authors. Important works about manganese technology considering environmental issues were conducted by Duan et al. (2010), and Duan et al. (2011).

Despite the identification of defined technical cycles for EMM and EDM production, these chemicals are produced on an industrial scale according to process schemes that differ considerably from each other. In EMM technology, electrolysis is carried out in a non-selective diaphragm electrolyzer at 30–35 °C in a $MnSO_4$ solution that includes the necessary buffer additive of 150–180 g/L$(NH_4)_2SO_4$; metal manganese (α-Mn) is deposited on the cathode at 50–60% current efficiency, while oxygen, which has no industrial application, is released at the anode. Specific electrical energy consumption for EMM production is 7000–8000 kWh/t (Agladze et al., 1975). In EMD technology, electrolysis is carried out in a diaphragm-free electrolyzer at 91–93 °C in acidified $MnSO_4$ solution; γ-$MnO_2$is deposited on the anode with 97–98% current efficiency, while hydrogen, which has no industrial application, is released at the cathode. Specific electrical energy consumption for EMD production is 2000–2500 kWh/t (Japaridze, 1987).

To deposit manganese metal on the cathode, the manganese sulfate electrolyte has to contain 150–180 g/L $(NH_4)_2SO_4$, but to obtain γ-MnO_2 on the anode, NH_4^+ ions cannot be tolerated in the electrolyte because they rapidly deteriorate the electrotechnical properties of EMD and make it unusable for chemical power sources, which is the main area of application of this product. The temperature regimes of the two electrolysis processes also differ considerably: the optimum temperature for EMM production is 30–35 °C, while EMD is obtained at 91–93 °C. These different electrolyte compositions and temperature regimes eliminate the opportunity for simultaneous production of these two products in an electrochemical reactor divided by an ordinary mechanical diaphragm.

We achieved simultaneous production of EMM and EMD in a thermostable anion-selective membrane electrochemical reactor (Tsurtsumia et al., 2015, Agladze et al., 2008). Use of the thermostable AMI-7001S anion membrane in the electrochemical reactor prevented transfer of NH_4^+ ions (which are harmful to the anodic process) from the cathodic to anodic compartment and made it possible to obtain both products in a single electrochemical reactor. The voltage on the membrane electrolyzer was approximately the same as that for EMM production in an ordinary diaphragm electrolyzer. Under conditions of preserving the same value of specific electrical energy consumption per tonne of EMM, approximately 2.6 t EMD was simultaneously obtained on the anode, taking into account the electrochemical equivalent and current efficiencies of the cathodic and anodic products. Considering that the specific electrical energy consumption for separate production of EMD is 2000–2500 kWh/t, then the electrical energy saved due to simultaneous electrolysis was 5200–6500 kWh/t. Through the synergistic implementation of anodic and cathodic processes in a single electrochemical reactor, it was possible to achieve significant reduction in electrical energy consumption.

The opportunity for simultaneous production of EMM and EMD in the anion-selective membrane electrochemical reactor enabled us to develop a new unified hydro-electrometallurgical technological

scheme that also envisages the production of MSM. The process flow sheet consists of large and small interconnected loops (Fig. 1).

The large loop includes: (i) preparation of solutions with a high content of manganese sulfate via concentrated sulfuric acid leaching of MnO-containing raw material obtained from high-temperature reduction of manganese oxide ores; (ii) hydrolytic and sulfide purification of the resulting $MnSO_4$ solution to remove cations of Fe^{3+}, Ni^{2+}, Co^{2+}, and other metals; (iii) obtaining crystalline $MnSO_4{\cdot}H_2O$ through high-temperature autoclave treatment of a concentrated solution of purified $MnSO_4$; (iv) delivery of hot spent $MnSO_4$ solution from the autoclave to the anode compartment of the electrochemical reactor divided by an AMI-7001S anion membrane, where γ-MnO_2 is obtained on the anode at 91–92 °C with 98–99% current efficiency. The small loop comprises use of crystalline $MnSO_4{\cdot}H_2O$ obtained in the autoclave for correction of the catholyte composition, purification of solutions prepared from technical $(NH_4)_2SO_4$ by $(NH_4)_2S$, and delivery of pure manganese-ammonium sulfate solution to the cathode compartment of the same reactor, where EMM is obtained on the cathode at 30–35 °C with 60% current efficiency.

The novelty of the proposed unified hydro-electrometallurgical process lies in the fact that, after the stages of ore leaching and purification, a concentrated manganese sulfate-containing solution passes to autoclave treatment. A portion of crystalline MSM, obtained from autoclave crystallization, is delivered to the catholyte circulation process loop with the aim of providing Mn^{2+} ions to the EMM feed; the remaining portion of MSM is an end product. Hot mother solution of manganese sulfate exiting the autoclave is used as anolyte for EMD production. The spent manganese sulfate solution from the anolyte compartment, which contains an increased quantity of sulfuric acid as a result of the electrolysis reactions, is mainly returned to leaching of the reduced ore. Small portions are used for acidifying the purified manganese sulfate solution that is delivered to the autoclave (with the aim of avoiding hydrolysis) and for adjustment of catholyte pH.

An important novelty of this technology is the use of a heat pump for maintaining two quite different temperature regimes in the cathodic and anodic compartments of the membrane electrochemical reactor in the process of coproduction of EMM and EMD. An ecologically acceptable cooling agent, R-600a (isobutane), was used as the refrigerant.

This paper presents: a) results of large-scale laboratory tests of the most important stages of this hydro-electrometallurgical process scheme; b) assessment of the thermal efficiency of the heat pump used for maintaining the different temperature regimes in the membrane electrochemical reactor at a load of 20A; c) results of integrated large-scale laboratory tests.

Section snippets

Materials, analysis, and procedures

Reduced manganese oxide ore produced by Rustavi Manganese Chemical Georgia LLC was used as the source raw material. Its composition is given in Table 1.

The reduced ore was ground and sieved to <0.1 mm. Leaching was conducted using concentrated sulfuric acid at stirring speeds of 350, 550, 750, 950, 1200, and 1400 rpm at solid:liquid ratios of 1:20 and 1:5 (mass:volume). The results showed that no further increase in manganese leaching rate occurred once the agitation speed of the impeller was…

Leaching of reduced manganese oxide by concentrated sulfuric acid

The process envisages production of purified concentrated manganese sulfate solution, because MSM required for the catholyte is crystallized out through autoclave treatment of such solution and the hot spent mother solution exiting the autoclave provides the anolyte for the electrochemical reactor.

The reaction of reduced ore with concentrated sulfuric acid is highly exothermic and proceeds rapidly in the case of vigorous stirring. During the initial stage of research, it was established that…

Testing of integrated technology on large laboratory scale

The results of testing this hydro-electrometallurgical technology on a large laboratory scale are given in Fig. 5. Results for separate stages were recalculated according to hourly outputs.

The specific electrical energy consumptions for the targeted products were 9.67 Wh/g for manganese metal (α-Mn), 3.75 Wh/g for γ-MnO_2, and 0.884 Wh/g $MnSO_4 \cdot H_2O$, of which 735.1 g/h was produced, consuming 650 W of electric energy.…

Conclusions

1. A new hydro-electrometallurgical technology for manganese oxide ore treatment, which envisages simultaneous production of EMM, EMD, and MSM was tested on a large laboratory scale.…
2. The unified process comprised large and small process loops connected to each other. The large loop includes:
   a) Preparation of solutions with a high content of manganese sulfate via leaching of MnO-containing raw material obtained from high-temperature reduction of manganese oxide ores by concentrated sulfuric acid.…

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Acknowledgments

This work was supported by Shota Rustaveli National Science Foundation of the Republic of Georgia (Grant No. 216704).…

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