Sustainable Production of Electrolytic Manganese Dioxide (EMD)

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Highlights

Novel method was investigated to reduce power consumption and pollution when producing electrolytic manganese dioxide from manganese oxide ores, high or low-grade. A material balance was performed on the designed flowsheet to check the feasibility of using recycled streams.

The use of bags around the anodes makes it possible to utilize the iron in the feed as a recyclable reductant for the dissolution of manganese ores.

Electrolysis in bags of purified manganese sulfate solution at the anode and regeneration of ferrous iron at the cathode are promising to sensibly reduce the electrolytic cell voltage, hence the power consumption.

Abstract

With the rapidly growing demand for manganese products, a low-cost, environmentally friendly hydrometallurgical process needs to be developed to process high-grade, low-grade manganese ores, and secondary manganese resources. It is becoming increasingly unsustainable in many situations to use high-grade manganese ores (<40%), which are usually used for conventional pyrometallurgical processes or pyro-pre-treatment (roasting), because of the high carbon-foot print and high operational costs. In recent years, various hydrometallurgical processes have been studied and developed for the recovery of manganese from other manganese sources (Zhang and Cheng, 2007). However, no research has ever looked at the idea of regenerating ferrous iron at the electrowinning stage, instead of the hydrogen evolution reaction, recycle it with the effluent rich in sulphuric acid and be used as a reductant agent at the leaching stage.

This paper aims to develop a conceptual flowsheet of a novel low-cost and environmentally friendly hydrometallurgical process for the production of electrolytic manganese dioxide. The flowsheet includes applications of treatment strategies to minimize capital and operating costs.

1. Introduction

The use of lithium-ion batteries has accelerated rapidly for modern telephones, cars, etc. However electrolytic manganese dioxide is still required for the manufacturing of alkaline batteries and production has continued to increase, mainly from demand in China. Industry EMD usage in alkaline batteries since 2002 exceeded 230,000 tonnes per annum with an annual growth rate of over 9.6% between 1996 and 2002 (Zhang and Cheng, 2007). Future growth in the EMD market is expected to exceed current growth rates, as global demand for batteries will increase in areas such as mobile communications. A wide range of new products, such as disposable mobile telephone batteries, could see growth rates of up to 8% a year (International

Manganese Institute and RPA, 2015; Zhang and Cheng, 2007). Electrically powered consumer products, from cameras and watches to sophisticated children's games and toys are also an area of robust growth. Extra growth in the demand for EMD is also expected from the secondary or rechargeable battery market as lithium manganese ion batteries (that use EMD in their manufacture) replace cobalt-type batteries as the cheaper and more environmentally friendly alternative. Growth is also likely to come from the use of EMD in hybrid electric vehicles (HEVs). As the environmental impact of traditional cars continues to cause problems in densely populated cities, the increased usage of HEVs to minimize pollution levels seems inevitable (Research and Markets, 2019, 2015; Zhang and Cheng, 2007).

Manganese production is a large industry in South Africa as South Africa accounts for 78% of the manganese reserves in the world and roughly 31% of world trade (Edinger, 2014). The Kalahari manganese basin has an estimated reserve of 13 billion tonnes of manganese ore, which contains between 28 to 48% manganese, and thus the sustainability of this industry is important for renewing the growth of the South African economy (Chamber of Mines of South Africa, 2016). Manganese sales increased by nearly 140% and production by almost 40% between 2016 and 2017. Manganese prices accelerated by 20% over the same period. These movements are also related to the pace and technological direction of electric vehicle development (Edinger, 2014; Minerals Council South Africa, 2018).

For South Africa, EMD is generating considerable interest in terms of the country possessing the world largest reserves of manganese ores while the majority of global EMD capacity is located in China (CPM Group, 2011; International Manganese Institute and RPA, 2015). The global electrolytic manganese dioxide market size is expected to reach USD 2.06 billion by 2025, according to a new report by Grand View Research, Inc., exhibiting a 7.0% Compound Annual Growth Rate (CAGR) during the forecast period 2014 - 2025. The industry is expected to witness substantial growth over the next eight years, based on the increasing demand of EMD in various battery cathode material applications to meet the ever-rising demand from the automotive and electronics sectors (Grand View Research, 2019).

In recent years, various hydrometallurgical processes have been studied and developed for recovery of manganese from other manganese sources (Zhang and Cheng, 2007). However, no research has ever looked at the idea of regenerating ferrous iron at the electrowinning stage, instead of the hydrogen evolution reaction, recycle it with the effluent rich in sulphuric acid and be used as a reductant agent at the leaching stage. In hydrometallurgy, the problem of the presence of iron in ferrous and ferric states in liquor is well known.

The flowsheet will include applications of treatment strategies to minimize capital and operating costs. The following objectives highlight the focus of this study:

- Investigate the energy savings by use of a reductive leaching process instead of ore roasting in the conventional electrolytic manganese dioxide process. It is well established that the conventional reduction of manganese ores by roasting is characterized by high production costs and energy consumption, low productivity, and environmental pollution.
- Reduce power consumption during the electrolysis of manganese dioxide. The conventional process of electrowinning of MnO_2 from acidic manganese sulphate solution uses the anodic oxidation of Mn^{2+} to form MnO_2, and the main cathodic reaction is the reduction of protons with evolution of hydrogen at the cathode. The gas evolution at the cathode needs an overpotential. The voltage required for electrolysis is in the range 2.2 to $3.0\,V$ at $700 - 1500\,A/m^2$ for producing electrolytic manganese dioxide with

anode plates made of titanium (Bard et al., 2007; Rock and Aksenov, 2010). In order to reduce the power consumption, the regeneration of ferrous iron is suggested in the present investigation, for recycle to the leach.

- The process can be tested using any manganese resource ores, i.e. the dust generated in manganese electric arc furnaces (EAFD) which is environmentally friendly. EAFD is generated in ferromanganese production units as off-gas from manganese alloys smelters. EAFD contains some Mn in an unstable oxidation state, and storage of EAFD presents a long-term environmental concern (Ghafarizadeh et al., 2011). Hence, efforts have been made to develop a hydrometallurgical process to recover manganese from these low-grade manganese materials.

2. Material and methods

The manganese ores used as feed to the electrolytic manganese dioxide (EMD) plant are generally classified into two types:

- High-grade ore, containing more than 40% Mn by mass.
- Low grade ore, mainly sludges from ferromanganese furnace, containing between 20 and 35% Mn.

There is an important point to make before the development of a sustainable flowsheet for the extraction of manganese dioxide by electrolysis is discussed. Since only the divalent manganese (Mn (II)) is readily leachable in dilute sulphuric acid, high-grade ores as well as low-grade ores require a reducing stage before leaching. This thesis proposes the development of manganese dioxide extractive metallurgy for low- or high-grade resources in sulfuric acid media, using ferrous ion as a reducing agent, which is regenerated as a co-product by electrolysis.

3. Theoretical background

For a better understanding of the proposed conceptual flowsheet, we provide an overview of flowsheets for manganese treatment, including pyrometallurgy and hydrometallurgy processes.

3.1 Pyrometallurgy

Manganese metal or alloys are refined and/or produced at elevated temperature using oxidation or reduction. A blast furnace is used for heating and refining of high-grade ore using only coke as reductant and an energy source. Electric smelting furnace can be used to provide the heating, to reduce the amount of coke and associated impurities.

Depending on the ore quality, efficient electric furnaces consume about 2100 - 2800 kWh electric power per tonne of ferromanganese alloy (Elvers et al., 1994; Elvers and Ullmann, 1990; Kroschwitz, 2004). Manganese is combined with oxygen in its ores, and carbon is the most economical reducing agent for oxides. Therefore, the essential characteristics of manganese metallurgy are evident from an examination of the interactions between manganese oxides and carbon. The highest oxide, MnO_2, decomposes to Mn_2O_3 at 507.8°C, Mn_2O_3 decomposes to Mn_3O_4 at 1240.8°C. These oxides can be reduced exothermically by CO in the shaft of a furnace. Because of the relative instability of FeO, the reduction to metallic Fe occurs at a much lower temperature and appreciable CO_2 is present in the product gas.

Reduction with carbon (coal) or silicon is the method to produce ferromanganese (FeMn) with high carbon (HC), medium carbon (MC) or low carbon (LC) content or silicomanganese (SiMn) intermediates for the steel industry. The temperature required for complete reduction of manganese in Eq. (2) is high (1267°C) owing to the stability of the MnO compound (Elvers et al., 1994; Elvers and Ullmann, 1990; Kroschwitz, 2004).

$$FeO + C \xrightarrow{air} Fe + CO \uparrow \quad (1)$$

$$7\,MnO + 10\,C \xrightarrow{air} Mn_7C_3 + 7CO \uparrow \quad (2)$$

The particle size of manganese ores is also an important factor for a smelting furnace. In general, the ore size for the furnace charge is -75 mm with a limit to the amount of fines (-6 mm) allowed (Kroschwitz, 2004). Neither electric furnaces nor blast furnaces operate satisfactorily when excessive amounts of fines are in the charge. Large amounts of fines in the ores and other raw materials promote agglomeration or caking of the charge in the furnace. This is detrimental to efficient smelting because it inhibits the downward movement of the charge and the uniform distribution of reaction gases through the burden. Thus many of the ferromanganese-smelting operations around the world, which use electric furnaces, limit the amount of -6 mm ore fines in the charge to a maximum of 15%. Fines produced by mining are removed on site and may be available from the mine at reduced price.

Pyrometallurgical methods can be applied only for high-grade ore with low content of certain impurities. Phosphorus and arsenic content are very critical, and their mass content in the feed to smelting should not exceed 0.5%. Other compounds that are critical to the quality of the metal product are Al_2O_3, SiO_2, CaO, MgO and S (Elvers et al., 1994).

The drawback of a pyrometallurgical processes, from the perspective of the environmental lobbyists, is the large production of greenhouse gases CO and CO_2 and dust containing potentially soluble metals. An environmentally friendly process needs to be developed to sustain manganese production.

3.2 Hydrometallurgy

3.2.1 Overview of hydrometallurgical processes

Hydrometallurgy is concerned with methods of producing metals, and some compounds from certain types of ores, concentrates and waste products, by reactions which take place in by aqueous solutions containing different chemical reagents Burkin (2001). Firstly, in comparison to the pyrometallurgical methods, which employ reagents and refining metals with fire and fluxes, hydrometallurgical processes employed reagents in water or organic solvents.

The hydrometallurgical processes are characterised mainly by heterogeneous reactions, for example, in leaching the solid phase interacts with the liquid or also gas phase, and the solid phase is partially or completely dissolved. In another type of reaction, a gas reacts with the solution, and the overall rate of reaction may be controlled by the rate of dissolution of the gas in the liquid phase (Havlík, 2014). Second, contrary to pyrometallurgical processes which require only some form of carbon as the principal reagent and energy source, hydrometallurgical processes use acids, alkalis and other inorganic and organic compounds.

Thirdly, particle reduction, mixing, and handling of large volumes of solids and liquids are a challenge in hydrometallurgical processes. The rate of reaction is substantially lower, relative to pyrometallurgical processes, and hence significantly longer residence times are required. Nowadays, the improvements made in process equipment, primarily in design and operation, has increased the efficiency of hydrometallurgical processes.

Several factors need to be taken into account in order to choose hydrometallurgy in metal production. The growing constraints within which metallurgical plants must operate due to environmental protection laws make roasting and smelting, increasingly unattractive. Also, elimination of these steps by the widespread adoption of hydrometallurgical routes, for the processing of certain sulphide ores, can produce elemental sulphur. The increasing demands for metals, which can only be met in many instances by processing ores of greater complexity and lower grade via hydrometallurgical routes.

4. Application to a conventional EMD circuit

4.1 Material balance of the proposed process for the production of electrolytic manganese dioxide

Figure 2 shows a simplified flow sheet of the studies of this work. This route includes one leaching stage, followed by a solid-liquid separation circuit for the solid residues and a purification path for a portion of the pregnant leaching solution (PLS). The solution from the first leaching stage is conventionally purified (Nattrass and Te Riele, 1985; Te Riele, 1983; Zhang and Cheng, 2007), by adding lime to precipitate impurities, particularly iron. The unique aspect of the process is to surround the anodes with bags, so that impure leach solution can be pumped into the electrolysis tank(s), where the cathodes will reduce the ferric ions in solution, to regenerate ferrous ions for recycle to the leaching stages. Acid is also regenerated at the anode and flows through the bag (together with residual manganese, to become part of the recycle stream. It is envisaged that the enhanced acid concentration will prevent the accumulation of precipitate in/on the bags. Firstly, this process eliminates the need for a reducing roast before leaching. Secondly, the natural hydrogen evolution reaction (HER) is suppressed by favouring the recovery of the ferrous iron which is needed at the leaching stage. This results in a significant reduction in potential. Thirdly, there is no need of purifying the entire electrolytic stream feed. Only the anode feed stream is purified.

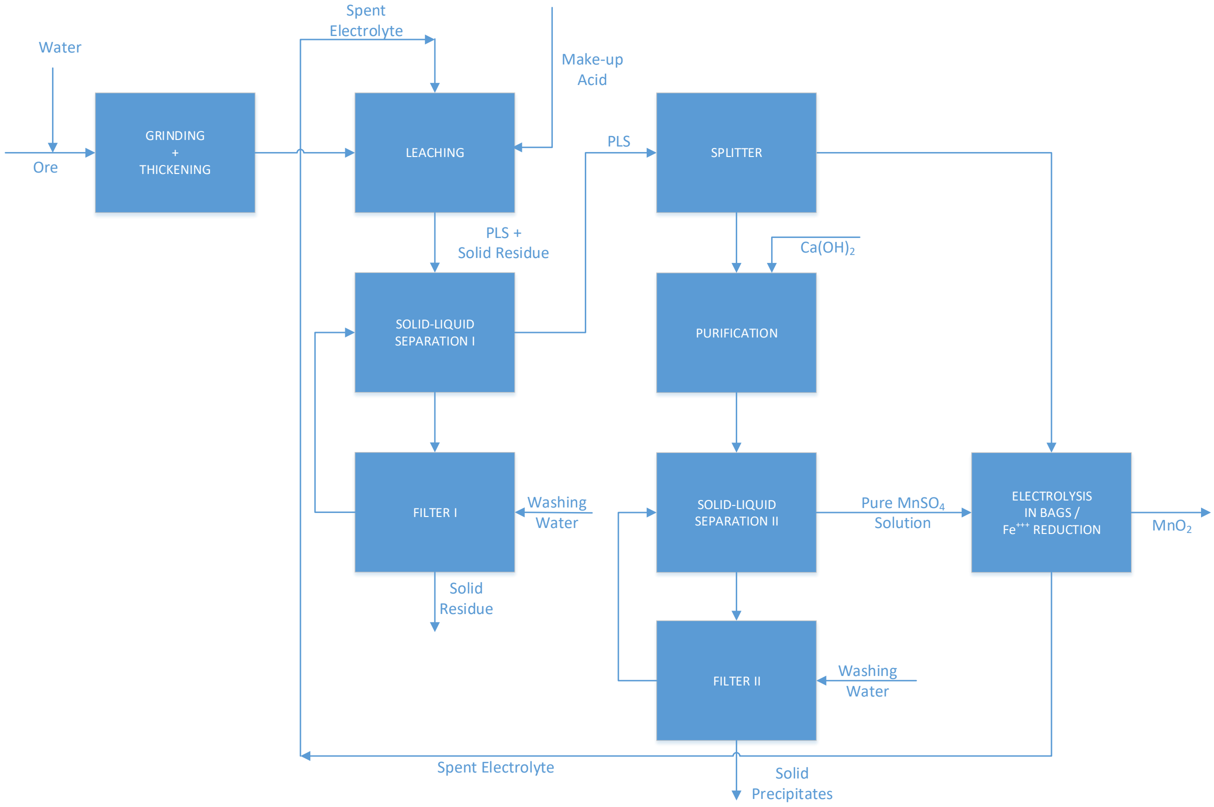

Figure 2. Proposed block diagram of electrolytic manganese dioxide production

The mass balance follows the main steps in the block flow diagram, as shown in Figure 2. The concentration of metals in leach liquor, in a typical a hydrometallurgical plant, are limited by solubility, and hence the flowrate of liquor determines the size of leaching vessels, thickeners, etc. The proposed process requires sufficient solution to be recycled, to provide a reductant for the ore. Hence the practical implementation of the method may require the use of stirred leaching vessels in which coarse particles are allowed to segregate to some extent, to accommodate the large flow of solution. The method used to calculate the mass balance, subject to various constraints, such a solubility, is summarized in discussion section.

The main processes of the conceptual flowsheet involve:

Grinding of the ore, followed by thickening, to reduce the quantity of water entering the circuit with the ore.

Leaching is conducted under acidic conditions, to improve the final recovery of manganese. It should be noted that in order to achieve an iron balance, the iron which was dissolved from the ore must exit the system as a precipitate, either during the purification stage or in the final residue. Hence, the final pH in the leach is constrained, to allow for some iron precipitation, but not too much, as the ferric ion is required for reaction with the cathodes. The concentration of ferrous ions in the leach solution must also be adequate for leaching the manganese in the ore. Hence, the control of ferrous and ferric concentration in various parts of the circuit is key to the success of the process.

4.1.1 Milling circuit

High-grade samples of South African manganese ore are readily available for preliminary laboratory tests. In view of the high density and component nature of the ore, the grinding circuit could consist of a SAG primary mill, followed by a pebble mill, in closed circuit with cyclones. However, for laboratory purposes, fine crushing and rod-milling may be used. It is good to note that the ore is harder than quartz and hence fine grinding would be a significant cost.

A sample of low-grade resource material (dust) might be collect from local ferromanganese smelters and as it is very fine and does not need any grinding treatment.

4.1.2 Leaching circuit

The ground material is leached with the recycled spent electrolyte in a row of stirred tanks. The leachate contains Fe^{2+} ions produced at the cathodes in the electrolysis stage, together with sulfuric acid produced at the anodes and the residual manganese sulphate. The primary purpose of the leaching stage is to dissolve manganese, but iron and other impurities also go into solution. A two-stage, counter-current leach could be envisaged, as used for leaching zinc calcine, to reduce acid consumption. However, initial experimental findings, which are reported elsewhere, showed that the leaching of manganese and the subsequent solid/liquid separation are adversely affected at low acid concentration, by the precipitation of iron compounds. Hence the conceptual flowsheet shown in Figure 1 has a single leaching stage, which requires sufficient acid to keep iron from precipitating. The iron is allowed to recycle, as it has an important role to play in reacting with the cathode. The iron dissolved in the leach (plus other impurities), must be removed in the purification stage, where lime is added, together with air at elevated temperature, as practiced in conventional EMD circuits (Zhang and Cheng, 2007) as illustrated in Figure 3.

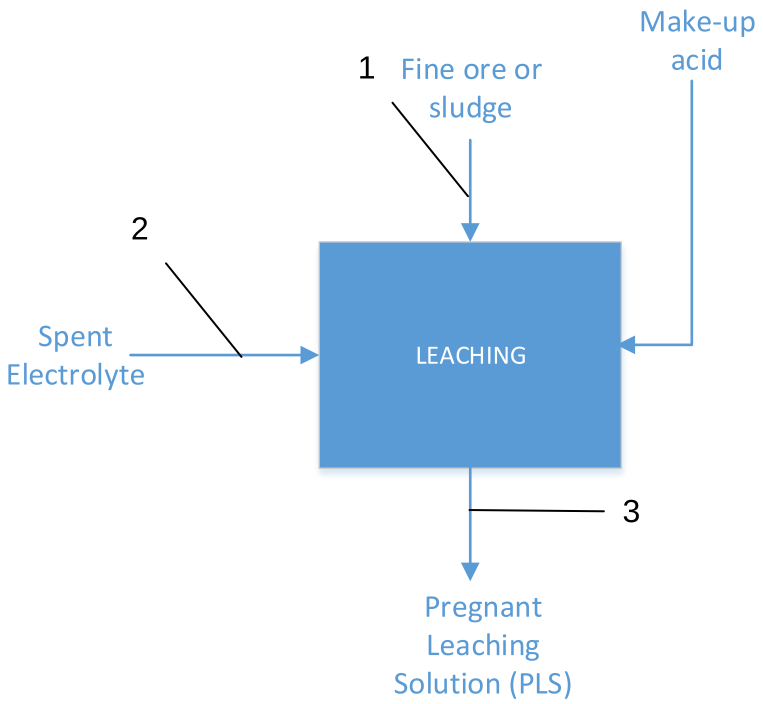

Figure 3 Diagram of the leach stage. 1, 2, and 3 represent the stream number

Assuming that the main mineral in the ore is manganese (III) oxide, Mn_2O_3, the primary leaching reaction of manganese oxide ore with ferrous sulphate and acid is represented the following reaction:

$$Mn_2O_3 + 2FeSO_4 + 3H_2SO_4 \rightarrow 2MnSO_4 + Fe_2(SO_4)_3 + 3H_2O \tag{4}$$

4.1.2.1 Manganese balance

The amount of manganese dissolved is easily calculated as following:

$$Mn\ Dissolve = Dry\ Ore\ (kg/h) \times Mn\ content\ \times Efficiency\ \times\ 54.938/157.874 \tag{5}$$

With 54.938 and 157.874 being the atomic mass of manganese and molecular mass of Mn_2O_3 in kg/kmol respectively.

If the efficiency of the leaching reaction is known or assumed, the amount of manganese dissolved can easily be calculated by using Eq. (5).

The manganese balance of a boundary system defined around the block diagram shown in Figure 3 is:

$$Q_1C_{Mn^{2+},1} + Q_2C_{Mn^{2+},2} + Mn\ Dissolved\ in\ Leaching = Q_3C_{Mn^{2+},3} \tag{6}$$

Knowing that stream 1 does not contain any Mn^{2+} ions, the exit concentration of Mn^{2+} is found to be:

$$C_{Mn^{2+},3} = (Q_2C_{Mn^{2+},2} + Mn\ Dissolve\ in\ Leaching)/Q_3 \tag{7}$$

With Q_2 and Q_3 respectively the water flow in m^3/h in stream 2 and 3.

4.1.2.2 Water flow balance

It is easy to determine the water flowrate in stream 3 if the slurry density in that stream is known. Typically, a slurry stream of 70% solid by volume is generally acceptable in order to facilitate subsequent solid-liquid separation with a thickener. The amount of water exiting this process is found to be:

$$Q_3 = Q_1 + Q_2 \tag{8}$$

To account for evaporation during the neutral leaching, a reasonable percentage can be assumed and the water flowrate Q_3 can be corrected. The make-up water for the neutral leaching can come from the water used washing the filtrate. About 5% of evaporation can be assumed.

4.1.2.3 Ferric iron balance

Looking at the reductive leaching reaction represented by Eq. (4), the amount of ferric iron (Fe^{3+}) formed is equivalent to the amount of manganese dissolved in the leach process. The stoichiometric amount of ferric iron produced during the leaching reaction can simply be obtained using the following iron (III) balance:

$$\begin{aligned} &Q_1 C_{Fe^{3+},1} + Q_2 C_{Fe^{3+},2} + Fe^{3+} from\ leaching \\ &+ Mn\ Dissolved\ in\ Leaching \times 55.847/157.874 = Q_3 C_{Fe^{3+},3} \end{aligned} \tag{9}$$

As there is no Fe^{3+} ion in the ore stream and the ore content in iron has been oxidised to Fe^{3+}, the concentration of ferric iron in the stream exiting the leaching stage can be expressed as:

$$\begin{aligned} C_{Fe^{3+},3} = (&Q_2 C_{Fe^{3+},2} + Fe^{3+} from\ leaching \\ &+ Mn\ Dissolved\ in\ Leaching. \times 55.847/157.874)/Q_3 \end{aligned} \tag{10}$$

4.1.2.4 Ferrous iron balance

The amount of ferrous iron (Fe^{2+}) contained in stream 2 recycled must be completely consumed during the neutral leaching process. It is vitally important for this process to get rid of Fe^{3+}/Fe^{2+} couple before the electrolysis of a purified solution of $MnSO_4$ in bags. Assuming under the operating conditions (increasing the pH, a temperature above 65°C and the presence of air), it may be assumed that there is no ferrous iron in stream 3 and all iron has been brought to the ferric state.

4.1.3 Solid-liquid separation circuit I

The slurry leaving the leaching stage is acidic and has little or no precipitated solids. Thickening and filtration is used to separate the pregnant leach solution (PLS) from the solid residues. Adequate settling is achieved by operating at a higher temperature with a % solid by mass in the slurry of about 45%. The overflow (OF) is sent a clarifier, (not shown in Figure 3.1) to remove fine suspended particles. The underflow is filtered and the filter cake is washed, to recover entrained pregnant solution. The water recovered from washing the filter, containing some Mn^{2+}, is recycled to the same thickener to account for evaporation. The Mn concentration in this stream is maintained at an adequate level to allow for electrolysis inside the bags.

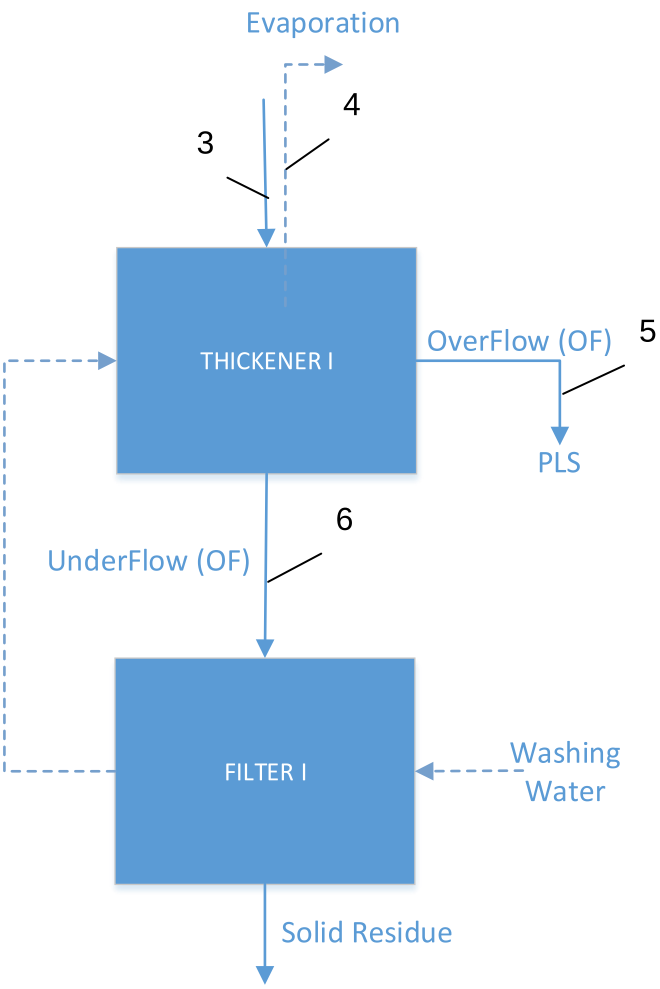

Figure 4 Block diagram of solid-liquid separation I. Dotted line on the diagram represents washing water flow, and solid lines are the main process streams containing manganese or solid residue

As it can be seen on the block diagram of Figure 4, there is evaporation in the thickener and fresh water is used to wash the filter. The used water can be recycled to the thickener to compensate for evaporation. Furthermore, some Fe^{2+} ions present in Thickener I will oxidize to Fe^{3+} due to the presence of oxygen and the higher temperature.

4.2.3.1 Water flow balance

As the % of solids in the underflow from the thickener can be anticipated to be around 45% by mass, the amount of solids leaving the thickener can also be determined:

$$Q_6 = [Solids[kg/h] \times (100 - \%\, Solid)/\%\, Solid]/1000 \qquad (11)$$

The rate of evaporation will depend upon weather and operating conditions, and a mass balance will determine the exit concentration of manganese.

4.2.3.2 Manganese balance

The thickener and the filter in the solid-liquid separation circuit I being mostly equipment of physical separation, there is no generation neither consumption of Mn^{2+} species. The concentration of manganese in stream 5 should be the same as the concentration of manganese in stream 3 and 6. This allows the concentration of manganese in stream 5 to be calculated.

$$C_{Mn^{2+},5} = Q_3 C_{Mn^{2+},3}/(Q_5 + Q_6) \tag{13}$$

4.1.4 Splitter and purification

The manganese concentration $C_{Mn^{2+},5}$ leaving the separation circuit depends on the evaporation in the thickener. The solution in stream 5 is expected to be more acidic because of evaporation. A pH control by liming of the stream is necessary to achieve before electrolysis.

Stream 5 is split into two streams namely stream 7 and stream 8. Stream 7 feeds the cathodic compartment of the electrowinning circuit. It contains Mn^{2+} and Fe^{3+} to be reduced at the cathode. This stream does not need any purification.

On the other hand, stream 8 containing manganese sulphate solution must be purified to remove impurities which affect the efficiency of the process or the quality of the EMD, such as iron, aluminium, arsenic, iron, silica and zinc. The aluminium, arsenic and silica are precipitated by adding lime to raise the solution pH to about 6 in a stirred tank. Sparging of air in the tank will promote the precipitation of iron. Any soluble ferrous iron present at this stage is oxidized to less soluble ferric iron and removed from the solution.

A strict control of the split is vital for the new process. The split determines the amount of solution to be purified before the electrolysis. This amount will always be less than the purification needed in a conventional process of depositing EMD in undivided cell. This is an advantage. The split also ensures that sufficient Fe^{3+} is available to be reduced at the anode.3.2.5 Solid-liquid separation circuit II.

Stream 8, which leaves the purification stage, contains the precipitated impurities, to be removed in a thickener and washed in a filter. A clarifier (not shown in Figure 3.4 below), is required for the thickener overflow, Stream 9, to remove fine, entrained precipitates, as they would re-dissolve in the acid generated by the anodes. A 45 % solid by mass is desirable in the thickener underflow, but in view of the lower density and fine particles, a lower concentration is anticipated. The underflow (UF) is sent to a filter for washing, to recover manganese solution. The water recovered from washing the filter cake will contain some Mn^{2+} and it is recycled to the same thickener. The flow of wash water is assumed to be equivalent to water lost by evaporation. Figure 5 illustrates a typical solid-liquid separation circuit II.

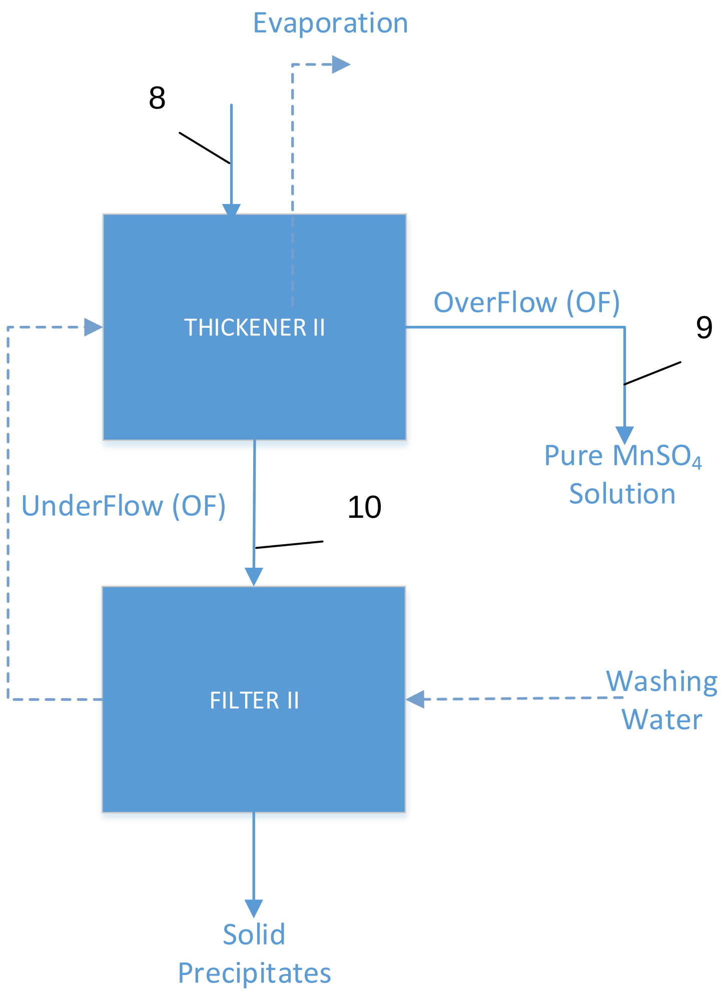

Figure 5 Block diagram of solid-liquid separation II. The dotted line on the diagram represents washing water flow and solid lines are the main process streams containing manganese

As it can be seen on the block diagram of Figure 5, there is evaporation in the thickener and fresh water is used to wash the filter. The used water can be recycled to the thickener to compensate for evaporation.

4.1.4.1 Water flow balance

As the % of solids in the underflow from the thickener II is also assumed to be about 45% by mass, the amount of solids leaving the thickener can also be determined:

$$Q_{10} = [Remained\ Solids[kg/h] \times (100 - \%\,Solid)/\%\,Solid]/1000 \qquad (14)$$

If the water flowrate of evaporation can be assumed, the flowrate of water leaving the solid-liquid separation circuit II in stream 9 can also be easily deduced:

$$Q_9 = Q_8 - Q_{10} \qquad (15)$$

4.1.4.2 Manganese balance

As said in section 4.1.3, the thickener and the filter in the solid-liquid separation circuit I being essentially equipment of physical separation, there is no generation/consumption of Mn^{2+} species. The concentration on manganese in stream 9 is the same as the concentration of manganese in stream 8 and 10:

$$C_{Mn^{2+},9} = (Q_8 - Q_{10})C_{Mn^{2+},7}/Q_9 \tag{16}$$

There is no need for further purifying stream 9. Under acidic conditions, the Fe^{3+} ions in stream 11 will co-exist Mn^{2+}.

4.1.5 Electrolysis circuit

The electrolysis circuit for producing MnO_2 in this developed conceptual flowsheet has been designed to operate in bags with pure manganese sulphate inside the bags at the anode and Mn^{2+} containing Fe^{3+} at the cathode. This is achieved by operating the plant in closed circuit with recycles. Instead of hydrogen evolution reaction at the cathode, Fe^{3+} is reduced as Fe^{2+}. The acid produced at the anode permeate through the membrane bags and mixes with the catholyte solution. Operating in this manner, power consumption during electrolysis can be reduced significantly and by-products Fe^{2+} and H_2SO_4 are used as leaching reagents.

The purified solution is introduced into the bag, which constitutes the anode compartment. The spent anolyte will permeate through the membrane and mixed with the spent catholyte and will be recycled back to dissolve MnO_2 at the leaching stages.

The main electrochemical reactions are as follows:

Main anode reaction:

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \tag{17}$$

Main cathode reaction:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{18}$$

As the electrolysis of MnO_2 proceeds only at about 90% current efficiency for modern plants (Rock and Aksenov, 2010), the following side cathodic reaction can occur:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{19}$$

The production of OH^- generated by the cathodic side reaction introduces a risk of an increase of pH in the cathode compartment. An increase in pH would cause Mn precipitation on the cathode surface as $Mn(OH)_2$. The catholyte comes from the leaching stage, where most of the free acid has been consumed. However, acid is generated on the anode and is transferred through the membrane. Hence precipitation of $Mn(OH)_2$ is unlikely. The presence of acid near the cathodes increases hydrogen generation, as a side reaction, and the efficiency of Fe^{2+} production and cell voltage need to be determined by experimentation.

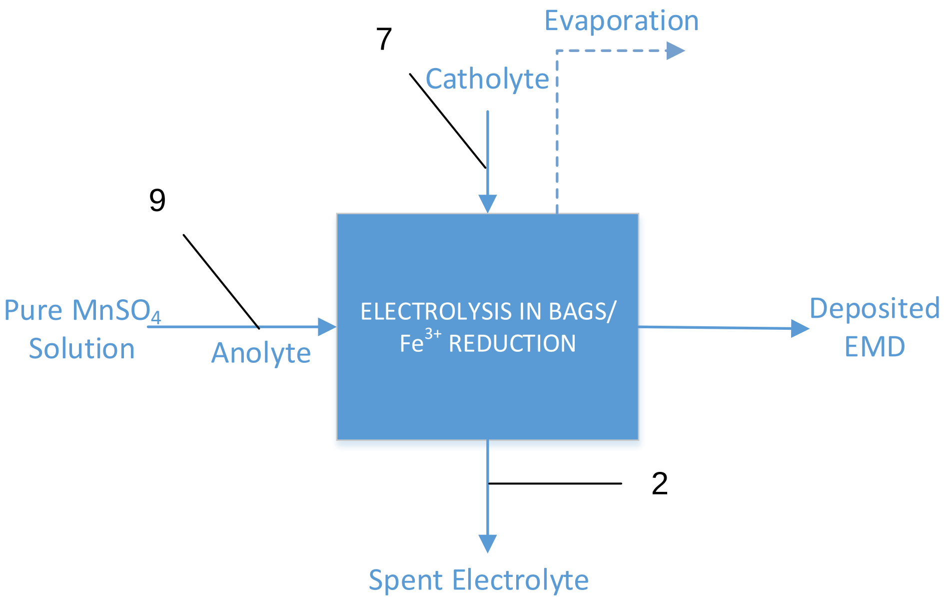

Figure 6 Block diagram of electrolysis of MnO_2 circuit

The temperature is kept at around 90°C. As it can be seen on the block diagram of Figure 6, there is evaporation at the electrolysis compartments.

4.2.5.1 Water flow balance

The water flowrate in stream 2 leaving the electrolysis circuit can also be calculated by a mass balance around a boundary system around the electrolysis cell:

$$Q_2 = Q_7 + Q_9 \tag{20}$$

4.2.5.2 Manganese balance

The plating of MnO_2 happens in bags. Catholyte and anolyte solutions are separated from each other with a membrane and ideally the platting is operated in a way of allowing a stoichiometric variation of Mn^{2+} and Fe^{2+} i.e. if 0.5 moles of EMD are platted at the anode, it will correspond to 0.5 equivalent moles of Fe^{2+} formed at the cathode assuming a 100% current efficiency.

Table 1 summarizes the results of model on a spreadsheet.

Table 1 Spreadsheet model of the electrolytic manganese dioxide circuit

Stream No.		**1**	**2**	**3**	**5**	**6**	**7**	**8**	**9**	**10**	**9a**	**12a=2**
Stream Name	**Units**	**Ore Feed**	**To Leach**	**Feed Thickener 1**	**O/F Thickener 1**	**U/F Thickener 1**	**To Electrowinning (outside bags)**	**Feed Thickener 2**	**O/F Thickener 2**	**U/F Thickener 2**	**Inside Bag**	**Combined Stream After Electrolysis**
Solid Flow Rate	**kg/h**	100		11,85		11,85		30,46		30,46		
Water Stream Flow	**m^3/h**	0,0429	2,0000	2,0429	2,0284	0,0145	1,5213	0,5071	0,4787	0,0203	0,4787	2,0000
Mn Flowrate	**kmol/h**		1,9224	2,8252	2,8252	0,0202	2,1189	0,7063	0,7063	0,0300	0,7063	1,9224
Stream Flow Mn^{2+}	**kmol/m^3**		0,9612	1,3830	1,3929	1,3929	1,3929	1,3929	1,4754	1,4754	1,4754	0,9612
Fe^{2+} Flowrate	**kmol/h**		0,9032	0,0004	0,0004	0,0000						0,9031
Stream Flow Fe^{2+}	**kmol/m^3**		0,4516	0,0002	0,0002	0,0002	0,0002	0,0002				0,4516
Fe^{3+} Flowrate	**kmol/h**		0,0903	1,1400	1,1400	0,0081	0,8550	0,0000	0,0000	0,0000	0,0000	0,0903
Stream Flow Fe^{3+}	**kmol/m^3**		0,0452	0,5580	0,5620	0,5620	0,5620	2,7900E-15	2,7900E-15	2,7900E-15	0,0000	0,0452
H_2SO_4 Flowrate	**kmol/h**		3,1599	1,8057	1,8057	0,0129	1,3543				1,8057	3,1599
Stream Flow H_2SO_4	**kmol/m^3**		1,5800	0,884	0,890	0,890	0,890	0,0000	0,0000	0,0000	3,7719	1,5800

5. Discussion

The entire process flowsheet was modelled by combining unit models. The unit models are interconnected by the process flow streams and key assumptions about the process were made in the spreadsheet. The method used to obtain mass balances was to assume reasonable flow and concentrations at selected nodes and then observe if the other streams converge to values which satisfy constraints. At the end of calculations, a goal seek routine is automatically adjusted and a new stream value is found.

6. Conclusions

The paper proposes a conceptual flowsheet for the process production of the electrolytic manganese dioxide without calcination and less iron purification after the leaching stage. Iron (II) is regenerated in the electrolytic cell and reuse in the ore leaching. A solution to the mass balance was found using a simple Excel spreadsheet.

It is concluded that the flow of ‘Spent Electrolyte’ was not excessive. The leach vessels can be stirred tanks, in which some thickening takes place in the upper parts of the vessel, to accommodate the relatively dilute overall conditions which are required by the mass balance for leaching.

The evidence from the conceptual flowsheet design suggests five main circuit blocks. Two circuits, namely milling, leaching, purification, solid/liquid separation, and electrowinning. Laboratory leaching and electro-winning tests have been conducted on a selected ore, which demonstrated that a significant reduction in operating voltage was achievable. However, in view of the effect of solution recycle and electro-winning current density, further laboratory and pilot-plant tests are required to test the process on a suitable ore.

7. References

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