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(54) Method for extracting Mn metal and manganese dioxide from divalent Mn salt solutions.

(57) The invention relates to the simultaneous obtention of elemental Mn and Mn dioxide(gamma) starting from manganese sulphate solutions by electrolysis of same in a cell split by an anionic diaphragm into an anodic and a cathodic compartment.

METHOD FOR EXTRACTING Mn METAL AND MANGANESE DIOXIDE FROM DIVALENT Mn SALT SOLUTIONS

This invention relates to a method for simultaneously extracting Mn metal and manganese dioxide in gamma form from divalent manganese salt solutions.

More particularly, the invention relates to a method for simultaneously extracting Mn metal and manganese dioxide in gamma form from manganese sulphate solutions.

The description given hereinafter refers to this second case, which is that of greatest interest.

The known art described separate methods for producing manganese dioxide or manganese metal.

Manganese dioxide is used in dry batteries in intimate mixture with graphite or acetylene black.

Preferably, manganese dioxide for batteries is in gamma form, and this can be obtained electrolytically by the following production process.

The overall electrochemical reaction on which manganese dioxide production is based is as follows:

at the anode: $2Mn^{2+} \rightarrow 2Mn^{3+} + 2e$

$2Mn^{+3} \rightleftarrows Mn^{4+} + Mn^{+2}$

$Mn^{+4} + 2H_2O \rightarrow MnO_2 + 4H^+$

at the cathode: $2H^+ + 2e \rightarrow H_2$

The production process comprises the following steps:

1) Preparing the solution to be electrolysed
2) Electrolysis
3) Recovering the crude manganese dioxide
4) Treatment to obtain the commercial product

Preparation of the solution:

The manganese salt which is dissolved in the electrolyte is the sulphate. It is obtained from various raw materials, those mostly used being the manganese minerals pyrolusite and rhodochrosite. A description of the preliminary heat treatments will be omitted for brevity. It will merely be stated that the crude manganese oxide is reacted with sulphuric acid, and the manganese sulphate solution formed is purified because minerals based on manganese dioxide generally have a certain heavy metals content. Purification with lime or limestone is followed by purification with calcium sulphide or hydrogen sulphide. The solution fed to electrolysis has an average $MnSO_4$ content of 80-150 g/l and an average H_2SO4 content of 50-100 g/l. A further component is ammonium sulphate (120-150 g/l) to act as a pH "stabiliser" during electrolysis.

Electrolysis:

Electrolysis takes place in suitable cells under the following average conditions:

-current density at the anode: 70-120 A/m^2
-voltage: 1.8-2.5 V
-electrolyte temperature: 90-95°C

To reduce the heat and evaporation losses, either closed cells are used or, more practically, the electrolyte is covered with a layer of oil or paraffin.

The electrolyte cycle can vary. In one cycle, the electrolyte is fed into the lower part of the cells in a quantity of 3% of the entire volume per minute; every one or two hours the electrolyte is cleaned by feeding 10-20% of it to treatment with $MnCO_3$ or MnO, and replacing this with fresh electrolyte. In another cycle, electrolyte is fed in such a quantity that the spent electrolyte leaves the cells containing 50 g/l of $MnSO_4$; this is mixed with an equal quantity of fresh electrolyte containing 150 g/l of $MnSO_4$ and the mixture is returned to the cycle.

Recovery of manganese dioxide from the electrodes and its treatment:

When the dioxide deposited on the electrodes has reached the scheduled thickness, the anode assembly is removed from the cell in order to recover the product. This operation, which can be carried out either manually or automatically, is the most onerous of the process.

The MnO_2 fragments obtained from the anode deposits are washed with water and ground to less than 74 microns. The powder is again washed a number of times to eliminate any remaining acidity, and is again dried at low temperature, namely 80-85°C. All the various process steps are important in terms of production economy and the quality of the commercial product. The electrolysis operating conditions are also determining with regard to product quality and electricity consumption.

Both the labour requirement and the electrode life depend on the method used for recovering the dioxide from the electrodes.

Electrolysis apparatus:

The cells are normally rectangular steel tanks clad with material which is resistant to both corrosion and temperature and is of very low conductivity, such as glass-fibre reinforced resins, rubber or acid-resistant cement or brick.

The electrodes can be flat or round bars or tubes.

The cathodes are generally of graphite, lead or stainless steel. Graphite anodes are mostly used, as they tolerate high current density without becoming passive, but their mechanical strength falls progressively due to corrosive attack.

Lead anodes normally containing 3-8% of antimony have the drawback that at high current density they are subject to chemical attack and contaminate the dioxide produced. They have the advantage that when they are no longer usable the lead can be recovered by smelting. Titanium anodes would perhaps be the ideal, but certainly very costly; they have excellent mechanical stability and a useful life of some years; they tend to become passive, but this drawback can be obviated by careful monitoring of the current density and the H_2SO_4 concentration in the electrolyte.

The useful anode:cathode surface area ratio is about 2:1. The distance between anodes and cathode is about 25-50 mm. A production cell can contain as many as 220 graphite anodes (flat bars of 1100 x 175 x 25 mm) arranged in 44 rows of 5 anodes each.

The manganese dioxide obtained by known methods has an average chemical composition of 62% Mn by weight, of which 92% is in the form of MnO_2, 1.6% is in the form of soluble Mn and the remainder is in the form of oxides other than MnO_2, together with traces of As, about 0.0004% of copper by weight, traces of Ni and Co, 0.0001-0.05% of Pb by weight, about 0.02% of Fe, about 1.2% of SO_4 by weight, and about 0.01% of SiO_2 by weight, the remainder to 100% being oxygen.

Having described the conventional system for producing electrolytic MnO_2, the known processes for producing Mn metal will now be described, as the process according to the present invention relates to the simultaneous electrolytic production of MnO_2 and Mn.

Electrolytic production of manganese

The solution to be electrolysed generally consists of manganous sulphate and ammonium sulphate, and is practically neutral.

Cathodic electrodeposition in accordance with the overall reaction:

$Mn^{2+} + H_2O \rightarrow Mn + 2H^+ + \frac{1}{2}O_2$

takes place under the following conditions.

Conditions:

Catholyte:	Mn as $MnSO_4$	30-40 g/l
	$(NH_4)_2SO_4$	125-150 g/l
	SO_2	0.3-0.5 g/l
	pH	6-7.2
Anolyte:	Mn as $MnSO_4$	10-20 g/l
	H_2SO_4	25-40 g/l
	$(NH_4)_2SO_4$	125-150 g/l
Current density:		430-650 A/m^2
Anode composition:		Pb + 1% Ag
Cathode composition:		Hastelloy or AISI 316 or Titanium
Cell voltage:		5.2 V
Diaphragm:		acrylic, cotton
Current yield:		65-75%

The following table shows the impurities usually contained.

ELEMENT	CONTENT
Fe	15 mg/l
Cu	10 g/l
As	5 g/l
Co	25 g/l
Ni	25 g/l
Pb	25 g/l
Mo	10 g/l

A method has been surprisingly found, and constitutes the subject of the present invention, for simultaneously obtaining Mn metal and manganese dioxide, ie for combining the separate processes heretofore described, by electrolysing a manganese sulphate solution in an electrolytic cell provided with an anionic membrane.

The present invention provides a method for simultaneously obtaining Mn metal and manganese dioxide in gamma form by electrolysis of a manganese sulphate solution, comprising feeding a manganese salt solution into the two parts into which an electrolytic cell provided with a separating membrane is divided; said method being characterised in that the membrane is anionic and is a membrane consisting of a hydrocarbon or fluorocarbon polymer containing quaternary ammonium groups, and the anode compartment of the electrolytic cell divided by said membrane is fed with an aqueous sulphuric solution of manganese sulphate, whereas the cathode compartment of said cell is fed with an aqueous solution of manganese sulphate, ammonium sulphate and SO_2.

The reaction which takes place at the anode is as follows:

$2Mn^{2+} \rightarrow 2\ Mn^{3+} + 2e$

The reaction which takes place at the cathode is as follows:

$Mn^{2+} + 2e \rightarrow Mn$

The following hydrolysis reaction also takes place:

$2Mn^{3+} + 2H_2O \rightarrow MnO_2 + Mn_2^{+} + 4H^{+}$

The electrolysis proceeds with the passage of SO_4^{2-} ions from the cathode compartment to the anode compartment of the cell divided by the anionic membrane.

The overall reaction which takes place during the electrolysis can be represented by the following equation:

$2Mn^{2} + 2H_2O \rightarrow MnO_2 + Mn + 4H^{+}$

In a preferred embodiment of the method according to the present invention, the electrolysis is implemented with a cell which is shown diagrammatically on the accompanying figure.

The cell consists of a cylindrical container 1, particularly of PVC, in which a lead alloy anode 2 and a stainless steel cathode 3 are disposed.

The anode region 4 is separated from the cathode region 5 by an anionic membrane 6 having a funnel-shaped base.

The membrane 6 is of the aforesaid type, its purpose being to allow the SO_4^{2-} ions to pass from the cathode region to the anode region.

The feed to the anode region is represented by the reference numeral 7; the feed to the cathode region is represented by the reference numeral 8. The discharge from the cathode region is indicated by the reference numeral 9 and the discharge from the anode region is indicated by the reference numeral 10. The reference numeral 11 indicates the anode recycling, and 12 the feed and discharge pipes for the cooling water of the anode 2.

It should be noted that the height of the anode discharge offtake is adjustable so as to obtain a level difference between the free surface of the anolyte and that of the catholyte.

The conditions additional to the aforesaid under which the method according to the present invention is operated are as follows:

-anode current density between 3000 A/m^2 and 5500 A/m^2
-cathode current density between 250 A/m^2 and 400 A/m^2
-anolyte consisting of a solution containing 20-40 g/l of Mn and 100-300 g/l of H_2SO_4
-catholyte consisting of a solution containing 30-50 g/l of manganese and 150-200 g/l of ammonium sulphate, at a pH of between 6 and 7
-anolyte temperature between 15 and 30°C
-catholyte temperature between 20 and 35°C

Some examples are given hereinafter in order to better illustrate the invention, which however is not limited by them or to them. The described apparatus shown on the figure and comprising an anionic membrane is used in the examples.

EXAMPLE 1

Overall feed solution	Mn	40 g/l
	$(NH_4)_2SO_4$	170 g/l
	SO_2	0.1 g/l
	pH	6.3
Cathode current density		350 A/m^2
Temperature of cathode region		30°C
Anode current density		4500 A/m^2
Temperature of anode region		30°C
Cathode current yield (Mn)		56%
Anode current yield (MnO_2)		83%

EXAMPLE 2

Overall feed solution	Mn	38 g/l
	$(NH_4)_2SO_4$	200 g/l
	SO_2	0.2g/l
	pH	6.5
Cathode current density		300 A/m^2
Temperature of cathode region		28°C
Anode current density		3850 A/m^2
Temperature of anode region		30°C
Cathode current yield (Mn)		60%
Anode current yield (MnO_2)		95%

EXAMPLE 3

Overall feed solution	Mn	42 g/l
	$(NH_4)_2SO_4$	150 g/l
	SO_2	0.1g/l
	pH	6.1
Cathode current density		400 A/m²
Temperature of cathode region		35°C
Anode current density		5100 A/m²
Temperature of anode region		30°C
Cathode current yield (Mn)		55%
Anode current yield (MnO_2)		93%

EXAMPLE 4

Overall feed solution	Mn	35 g/l
	$(NH_4)_2SO_4$	180 g/l
	SO_2	0.2g/l
	pH	6.8
Cathode current density		250 A/m²
Temperature of cathode region		22°C
Anode current density		3100 A/m²
Temperature of anode region		25°C
Cathode current yield (Mn)		58%
Anode current yield (MnO_2)		89%

Claims

1. A method for simultaneously obtaining manganese metal and manganese dioxide in gamma form by electrolysis of a manganese sulphate solution, comprising feeding a manganese salt solution into two parts into which an electrolytic cell provided with a separating membrane is divided, characterised in that the membrane is anionic and that the anode compartment of said electrolytic cell divided by said anionic

membrane is fed with an aqueous sulphuric solution of manganese sulphate, whereas the cathode compartment of said electrolytic cell is fed with an aqueous sulphuric solution of manganese sulphate, ammonium sulphate and SO_2, the electrolysis taking place by the passage of SO_4^{2-} ions from the cathode compartment to the anode compartment.

2. A method as claimed in claim 1, characterised in that the anionic membrane is a membrane consisting of a hydrocarbon or fluorocarbon polymer containing quaternary ammonium groups.

3. A method as claimed in claim 1, characterised in that the anode is of lead or lead alloy and the cathode is of stainless steel.

4. A method as claimed in claim 1, characterised in that the anode current density is between 3000 A/m^2 and 5500 A/m^2.

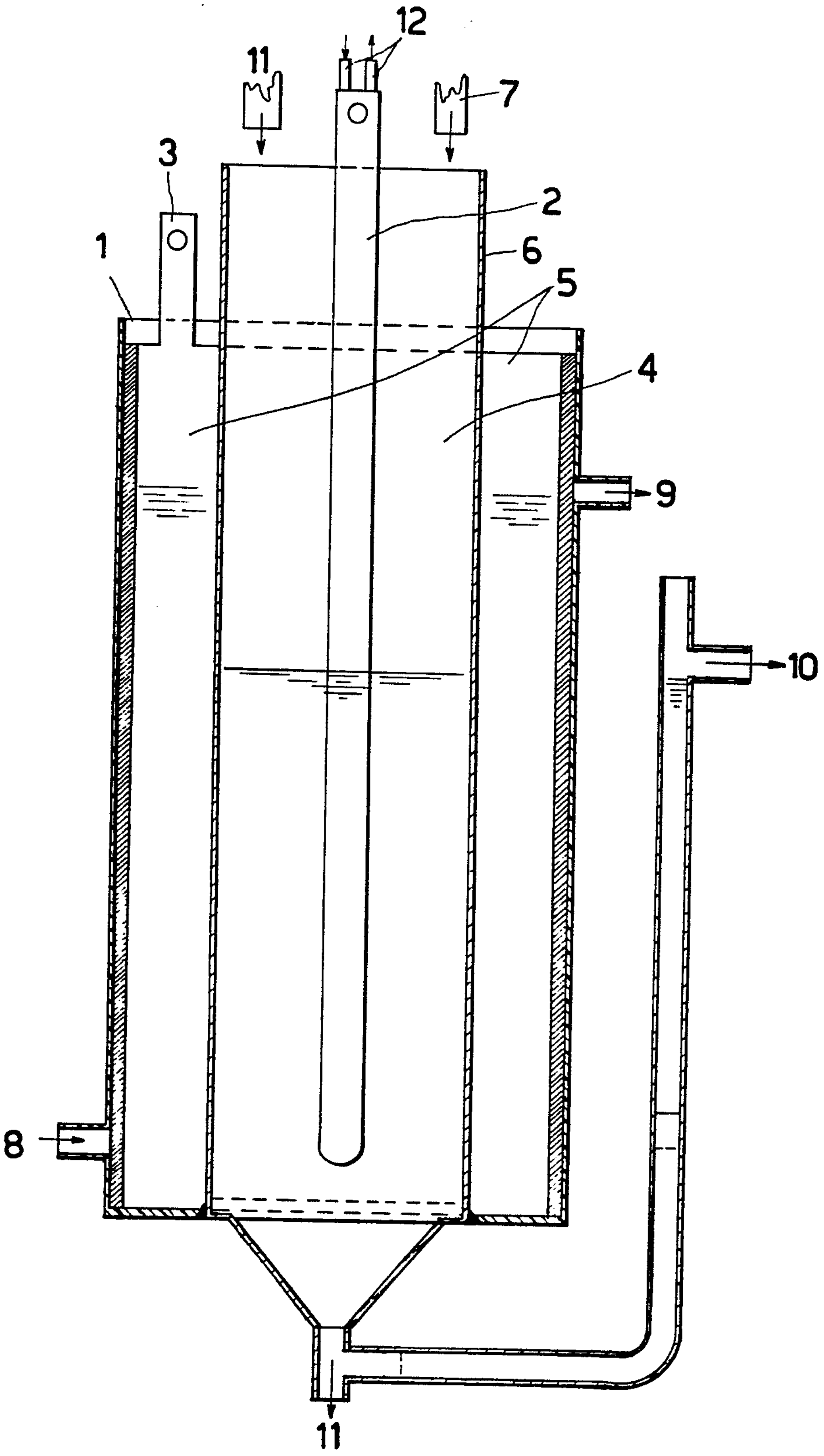
5. A method as claimed in claim 1, characterised in that the cathode current density is between 250 A/m^2 and 400 A/m^2.

6. A method as claimed in claim 1, characterised in that the anolyte contains 20-40 g/l of Mn and 100-300 g/l of H_2SO_4.

7. A method as claimed in claim 1, characterised in that the catholyte contains 30-50 g/l of manganese and 150-200 g/l of ammonium sulphate, and has a pH of between 6 and 7.

8. A method as claimed in claims 1 and 6, characterised in that the anolyte temperature is between 15 and 30°C.

9. A method as claimed in claims 1 and 7, characterised in that the catholyte temperature is between 20 and 35°C.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