United States Patent [19]

Kosaka

[11] **3,855,088**

[45] **Dec. 17, 1974**

[54] **PROCESS FOR REMOVING CLUSTER ADHERING TO CATHODE DURING ELECTROLYSIS OF MANGANOUS SULFATE**

[75] Inventor: **Tetsuji Kosaka,** Takehara, Japan

[73] Assignee: **Mitsui Mining & Smelting, Co., Ltd.,** Tokyo, Japan

[22] Filed: **Aug. 27, 1973**

[21] Appl. No.: **391,804**

[52] **U.S. Cl.** **204/96,** 204/10, 204/57, 204/281

[51] **Int. Cl.** **C01b 13/14**

[58] **Field of Search** 204/57, 96, 10, 281

[56] **References Cited**

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Primary Examiner—John H. Mack
Assistant Examiner—R. L. Andrews
Attorney, Agent, or Firm—Armstrong, Nikaido & Wegner

[57] **ABSTRACT**

Cluster formed on and adhering to a cathode during electrolysis of manganous sulfate solution containing calcium sulfate and magnesium sulfate in the production of electrolytic manganese dioxide is easily removed without injury to the cathode by newly effecting electrolysis but using the cathode as an anode to deposit manganese dioxide thereon and giving an impact to the depositied manganese dioxide to peel off the cluster together therewith.

5 Claims, No Drawings

PROCESS FOR REMOVING CLUSTER ADHERING TO CATHODE DURING ELECTROLYSIS OF MANGANOUS SULFATE

This invention relates to removal of cluster formed during electrolysis on the surface of a cathode in the production of electrolytic manganese dioxide by electrolysis using as an electrolyte an aqueous sulfuric acid manganous sulfate solution by the use of electrodes insoluble in the electrolyte.

In electrolytically producing manganese dioxide, materials insoluble in an electrolyte are used as electrodes. Generally speaking, there are usually employed lead, lead alloys or graphite for cathode, and lead or lead alloys, carbon or titanium for anode. In the production of electrolytic manganese dioxide, particularly in the process step of electrolysis, there are adopted, for example, such conditions that an anode current density is 0.6–1.2 A/dm^2, an electrolyte temperature is 85°–95°C, amounts of manganese and sulfuric acid are 10–60 g/l and 20–100 g/l, respectively. An anode is pulled up from the electrolyser every 10 to 40 days, and the manganese dioxide block deposited electrolytically on the anode is peeled off by means of a suitable procedure, for example, by giving a slight impact to the block. The anode is then cleaned by washing and returned again back to the electrolysis process step. On the other hand, a cathode is used continuously while being immersed and maintained in the electrolyte. However, when concentrations of sulfates of the alkali earth metals dissolved in the electrolyte, such as calcium or magnesium, exceed their solubilities in said electrolyte with the progress of electrolysis, the sulfates come to adhere to the surface of cathode to form a so-called cluster rigidly adhered thereto.

The alkaline earth metals such as calcium and magnesium are originally contained as impurities in the starting manganese ore, and extracted in the form of sulfates therefrom with an aqueous sulfuric acid solution or spent electrolyte in the preparation of a replenishing neutral aqueous manganous sulfate solution for consumed manganese in electrolyte. Further, the replenishing manganous sulfate solution comes to be contaminated with calcium sulfate when the extract of the manganese ore is neutralized with calcium salts such as calcium carbonate and calcium hydroxide. If the electrolysis is continued while using a cathode having cluster adhering thereto, as it is, ununiform current is caused and, as the result, invites the increase of electrolyte voltage and lowering of current efficiency, which results in remarkable increase of overall power required. Further, the ununiform current influences an anode and shortens its life. Accordingly, the continued operation of electrolysis is usually suspended every 5 to 6 months. After suspension of the operation, there is need for such labor that the cathode is pulled up from the electrolyser, the electrode system is disintegrated, the cluster adhering to the cathode is permitted by giving a compact thereto for example, with a hammer to fall down therefrom, and the surface of the cathode is then subjected to smoothening operation by means of sand brushing or the like. Furthermore, not only the cluster adheres closely to the cathode and is difficult to remove but also the cathode is damaged in many cases during the removal operation of the cluster when the material of the electrode is selected from such one as graphite which is mechanically fragile, and this causes

wear of the electrode to a large extent. There has also been proposed a process of chemically removing cluster from cathode, for example, by treating the cluster with hydrochloric acid to allow said cluster to dissolve in the acid, thereby removing the cluster from the cathode. In this process, however, it takes a long period of time to dissolve the cluster in the acid and, in addition, electrodes may suffer from corrosion with the acid when they are made of metallic materials.

An object of the present invention is to provide a process for removing cluster from cathode in which a labor for removal of the cluster may be decreased and the electrodes may be freed from damage and corrosion.

The present inventors conducted extensive studies and have found that when an electrolysis of the electrolyte is conducted anew by use of the cathode to which the cluster has adhered as an anode, that is, when the electrolysis is conducted exchanging the electrodes each other, the deposition of manganese dioxide occurs on the cluter which can be readily removed together with the manganese dioxide having been deposited from the anode which has been used formerly as a cathode.

That is, the present invention is to provide a process for removing from a cathode a cluster formed on and adhered to the surface of the cathode during electrolysis of an aqueous sulfuric acid-manganous sulfate solution containing alkali earth metal sulfates for the production of electrolytic manganese dioxide, said cluster being composed mainly of the alkaline earth metal salts, which process is characterized by carrying out said electrolysis using the cathode having said cluster firmly adhered to the surface thereof as an anode, electrolytically depositing manganese dioxide on said cluster, and peeling off said cluster together with the electrolytically deposited manganese dioxide by giving a compact to said deposited manganese dioxide.

Formation of the cluster on a cathode during the production of electrolytic manganese dioxide is considered ascribable to the fact that the aforesaid neutral aqueous manganous sulfate solution is replenished at 50° to 60°C, and the electrolyte is maintained at a high temperature such as 85° to 95°C as mentioned previously, and, on the other hand, solubilities of the sulfates such as $CaSO_4$ and $MgSO_4$ contained in the electrolyte decrease with the increase of temperature, thus the solubilities are inversely relative to the temperature, and hence the sulfates deposit on the cathode when the concentrations of calcium and magnesium become 0.10–0.50 g/l and 20–60 g/e, respectively. When an aqueous sulfuric acid-manganous sulfate solution is electrolyzed under common electrolysis conditions as mentioned previously using a cathode having a cluster deposited thereon as an anode, while using a cathode made of the same or different material, manganese dioxide deposits on the anode having the cluster deposited thereon. In this case, it is considered that the deposited manganese dioxide permeates into crystal lattices of $CaSO_4$ and the like, which constitute the cluster, thereby deteriorating the adhesion of crystals of $CaSO_4$ and the like to the electrode, and hence the cluster comes to peel off more readily therefrom. The electrolysis time employed in the above case is, in short, a minimum time required for attaining a state where the cluster comes to readily peel off together with the manganese dioxide deposited thereon, and such electrolysis time may be experimentally decided.

For example, under the electrolysis conditions referred to previously, the electrolysis time is usually 3 to 10 hours, preferably about 5 hours. By conducting such an electrolysis as in changing electrodes formerly used in accordance with the present invention, a cluster adhered to the surface of a graphite or carbon cathode can be removed together with the manganese dioxide formerly deposited thereon without injury to the cathode by giving such a slight impact as may be usually given to manganese dioxide deposited on an anode in a conventional manner.

The electrolyte used in the practice of the invention may be any aqueous solution for electrolysis so long as it contains sulfuric acid and manganous sulfate. When, however, an electrolyte which has been already used in the preceding electrolysis and which contains calcium and magnesium salts is used, the object of the invention may be conveniently accomplished by merely changing the electrodes or shunting the negative and positive currents employed in the preceding electrolysis operation.

In accordance with the present invention, there are brought about such marked effects that labor in treating a cathode for removing cluster in the conventional process can be sharply reduced and the wearing-out of the cathode in use is markedly reduced. The present process may also be applicable to the case where manganese dioxide is produced by electrolysis using metallic materials such as lead and/or lead alloys are used for an anode and a cathode, respectively, or for both. However, the process is most preferably applied to the case where a graphite or carbon cathode is used, whereby particularly marked results can be obtained.

As a secondary effect of the process of the present invention when a fresh graphite material is used as an anode, there may be brought about such advantage as mentioned below. That is, the fresh graphite material has a conductivity better than the graphite material once used as an anode, and hence the manganese dioxide deposited thereon becomes difficult to be removed therefrom because the dioxide compactly deposits on the surface of said fresh graphite anode, thus removal of the deposited manganese dioxide from the fresh graphite anode frequently tends to do damage to the anode. In the above case, therefore, when the fresh graphite anode is first used as a cathode and a cluster is allowed to deposit on the cathode and, thereafter, the cluster is removed together with the manganese dioxide deposited thereon according to the present process as mentioned previously, and the cathode from the surface of which the cluster has been removed is then used anew as an anode, the wearing-out of the anode after the treatment as mentioned above is thus reduced from an overall point of view because the deposited manganese dioxide easily comes off therefrom.

The present invention is illustrated below in further detail with reference to an example, but the example is merely given as illustrative and the invention is not limited only thereto.

EXAMPLE

Electrolysis of an aqueous sulfuric acid-manganous sulfate solution containing calcium and magnesium sulfates was carried out for 5 hours using as an anode a carbon round bar of 33 mm in diameter and 1,100 mm in length which has been already used as a cathode in the preceding electrolysis for six months and, as a result, which has on its surface a cluster layer of 2.16 mm in thickness, and as a cathode a carbon round bar having the same dimention as in said anode but free from cluster.

The electrolysis conditions were same as in the preceeding electrolysis and such that an electrolyte containing 25 g/l of Mn^{++}, 75 g/l of H_2SO_4, 36 g/l of Mg^{++} and 0.15 g/l of calcium^{++} was used, the temperature of the electrolyte was maintained at 90°C., and the anode current density was 0.8 A/dm^2.

When a normal impact was given to the manganese dioxide electrolytically deposited on the surface of the cluster adhering to the anode, the cluster was readily removed together with the deposited manganese dioxide from said anode. The results of assay of the cluster before and after the electrolysis are given in the following table.

(%)	Total Mn	Soluble Mn	MnO_2	Ca	Mg	SiO_2	SO_4	H_2O	Peeling property
Cluster before electrolysis	6.0	6.0	9.2	17.8	2.4	0.11	61.4	1.0	Difficult
Cluster after electrolysis	22.5	2.9	21.6	11.6	3.6	0.02	37.2	4.7	Good

The anode, from the surface of which the deposited manganese dioxide and adhered cluster had been removed in the manner as mentioned above was used, as it was, as a cathode in the subsequent electrolysis operation without any difficulty. And, the cluster thus removed was mixed with a starting manganese ore and used in the step of preparing a fresh electrolyte.

What is claimed is:

1. A process for removing cluster comprising alkaline earth metal sulfates, which cluster is deposited on a cathode during electrolysis of an aqueous sulfuric acid-manganous sulfate solution containing the alkali earth metal salts in the production of electrolytic manganese dioxide, which process comprises effecting the electrolysis of an aqueous sulfuric acid-manganous sulfate solution by use of the cathode having the cluster deposited on its surface as an anode to deposit the electrolytic manganese dioxide on the cluster, and giving an impact to the deposited manganese dioxide so that the cluster is peeled off together with the manganese dioxide.

2. A process according to claim **1**, wherein the cathode having the cluster deposited thereon is made of graphite or carbon.

3. A process according to claim **1**, wherein the electrolysis is effected at a temperature of 85° to 95°C under a current density of 0.6 to 1.2 A/dm^2 at the anode.

4. A process according to claim **1**, wherein the aqueous sulfuric acid-manganous sulfate solution containing the alkaline earth metal salts comprises 10–60 g/l of

manganese, 20–100 g/l of sulfuric acid, 0.10–0.50 g/l of calcium and 20–60 g/l of magnesium.

5. A process according to claim **1,** wherein the aqueous sulfuric acid-manganous sulfate solution used in the electrolysis by the use of the cathode having the cluster deposited thereon as an anode contains the alkaline earth metal salts.

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