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ELECTROLYTIC TREATMENT OF MANGANESE BEARING MATERIAL

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Fig. 1.

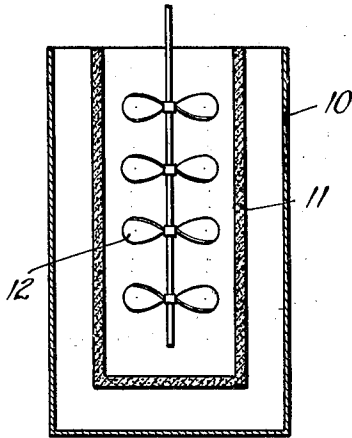


Fig. 2.

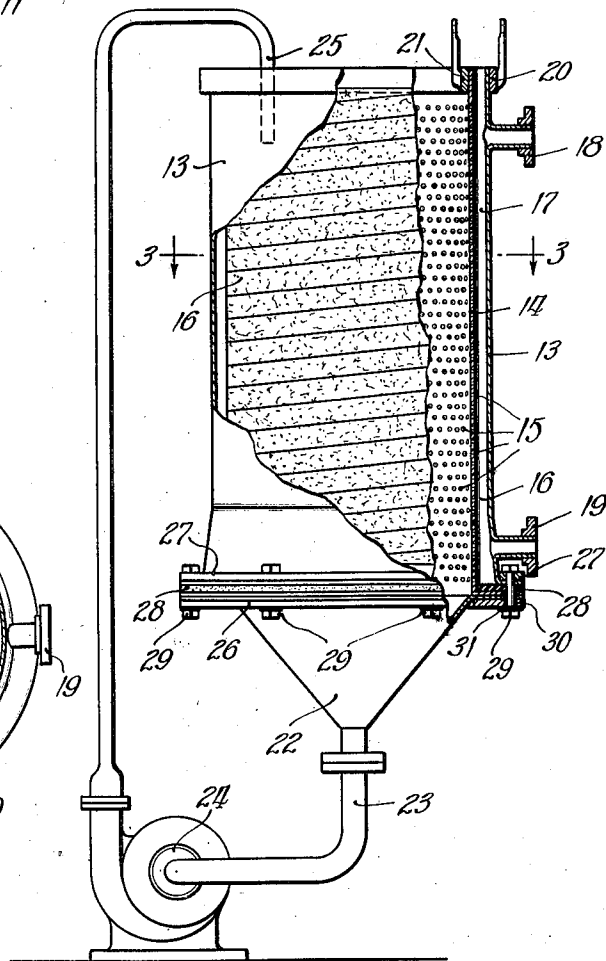
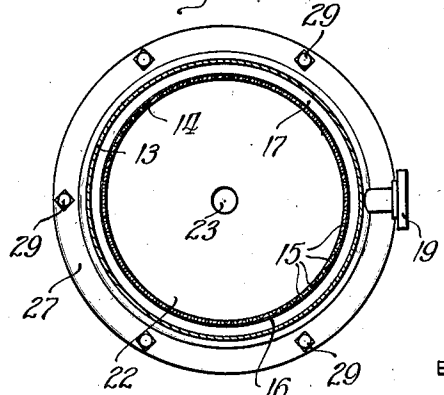


Fig. 3.



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ELECTROLYTIC TREATMENT OF MANGANESE BEARING MATERIAL

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The present invention relates to the electrolysis of manganese compounds, and is directed particularly to the production of manganese dioxide or other higher oxides of manganese directly from a natural ore or from other manganese bearing materials.

The invention also provides an electrolytic cell capable of carrying out the process of the invention in its various modifications.

One object of the invention is to utilize both anode and cathode reactions during the electrolysis, whereby both low and high grade ores or manganese bearing materials may be treated efficiently in a single cell to form the higher oxide in a comparatively high state of purity.

Another object of the invention is the treatment of the lower oxides of manganese by electrolysis to form higher oxides of greater purity.

Still another object of the invention is the provision of a cell which can be operated with current in either direction according to the character of process practiced.

Manganese occurs to a large extent as MnO_2 , manganese dioxide, and there are, especially in Minnesota, large deposits of low grade ore of this type containing less than 20% manganese, with large amounts of silica and iron. The present invention aims to produce a high grade manganese dioxide from such low grade ores, but it is not to be considered as limited to this type of raw material. For example manganese carbonate may be employed.

The electrolysis of a neutral solution of manganous sulphate produces at the cathode a deposit of manganese metal, and at the anode manganese dioxide, or other higher and hydrated oxides. If a diaphragm cell is used with such a neutral solution the cathode compartment becomes exhausted in its acid radical with the resulting formation of a white manganous hydroxide precipitate. However, when excess acid is present, for example, with a solution containing 5% sulphuric acid and 10% manganous sulphate, no manganese metal is deposited nor is a hydroxide precipitated. Instead, all the manganese forms a manganous salt of the acid,

that is, manganous sulphate where sulphuric acid is used. The presence of acid does not prevent the formation of the higher oxide in the anode compartment. When a high current density is used under these conditions, the oxide formed in the anode compartment is precipitated rather than accumulated on the surface of the electrode. Therefore, it is apparent that under conditions created by the presence of acid, the only solid product of electrolysis is the desired higher oxides of manganese.

The present invention in its most practical aspect aims primarily to utilize the anode compartment of a cell to form manganese dioxide from a manganous sulphate solution, to form the manganous sulphate solution directly from raw material such as low grade ore, and to use the cathode compartment of the cell to effect what reduction of the raw material is necessary to form the manganous solution.

Accordingly, then, I provide a cell in which there are two compartments, each containing an electrode, one being used to act on raw material, and one being used to prepare the desired product. The diaphragm of the cell serves to separate the two solutions, to provide the electrical path, and to prevent the solid impurities in the raw material from contaminating the solid higher oxide formed.

Various types of cell may be employed, but for reasons later to be explained, I prefer a construction and arrangement of the parts which involve the important features of the cells illustrated in the drawing, in which:

Fig. 1 represents a simple diaphragm cell;

Fig. 2 illustrates a front elevation, partly broken away in section, of a modified cell;

Fig. 3 is a cross section of the cell of Fig. 2 along the line 3—3.

A container such as the cylindrical lead vessel 10 serves as one electrode for the cell. Within the vessel is a smaller and similarly shaped vessel 11 which is made of porous diaphragm material, such as porous silica or asbestos fiber. Within the porous vessel there is an electrode and an agitator which are herein combined into a metal stirrer of lead, indicated at 12.

In one use of this cell, the outer compartment is made the anode chamber, and the inside of the porous cell is made the cathode compartment. A 5% solution of sulphuric acid is placed in both compartments of the cell and finely ground ore of manganese is added to the cathode compartment in proportion to make a 10% solution of manganous sulphate. When current is applied to this filled cell, the higher manganese oxides in the ore are reduced to form soluble manganous sulphate. Any manganese dissolved initially in the anode compartment, or which may have diffused into the same is precipitated by the anode oxygen as a higher hydrated oxide. When most of the manganese in the ore is dissolved and reduced, the contents of the cell compartments are separately removed and treated. Filtration of the cathode material separates an acid manganous sulphate solution from the gangue of the ore. Filtration of the anode material separates a substantially sulphuric acid solution from the hydrated high manganese oxides. These can be washed and dried to form a high grade manganese dioxide. The acid filtrate from the anode material can be reused in the cathode compartment to dissolve more ore, and the cathode filtrate containing the reduced manganese is transferred to the anode chamber where the manganese is to be precipitated.

It will be seen that the first operation of the cell on the above basis is not efficient, in that there is little or no manganese initially present in the anode chamber. But after the first operation, each compartment will have prepared a solution to be reused in the other compartment during the next operation. The apparatus and the process then require no raw material but the ore or equivalent material supplied. Thus, there is provided a simple mechanical and a chemical purification of the raw material.

It is readily understood that this simple illustrative cell can be modified to make more continuous the process herein described, and that the process can be modified in suitable degree without departing from the principle of the present invention.

Figs. 2 and 3 illustrate another more practical form of cell suitable for the present invention. In this form two concentric lead cylinders 13 and 14 form the two electrodes. The inner one is perforated as indicated at 15 and wrapped with asbestos paper 16 to form the diaphragm. An annular cell compartment 17 is thus provided into which open two flanged openings 18 and 19. Copper current conductors 20 and 21 connect with each electrode. The bottom of the cell has a cone shaped closure 22 opening into a pipe line 23 containing a centrifugal pump 24, and discharging at the top into the inner chamber, as indicated at 25. The cone bottom is

carried by a ring of iron 26 which is bolted or clamped to a second iron ring 27 associated with the outer lead vessel and insulated from the other ring by the gasket 28. Bolts 29, have insulating sleeves 30 and washers 31, to prevent the current from passing between the iron rings 26 and 27.

Lead electrodes are preferred for the reason that they are more resistant to acids, especially sulphuric, and for the reason that as anode, they give a high oxidation potential. Both electrodes are made of lead so that either one may be used as anode as conditions of the process may warrant.

In any process wherein there is available a precipitate of manganous or manganic hydroxide, the present type of cell is useful with current reversed as above alluded to. Under such conditions the manganese hydroxides are added to acid in the cell, such as sulphuric acid, using the larger compartment as the anode chamber. It is immaterial whether all the hydroxide added is dissolved, for when any portion dissolves and is then reoxidized and precipitated, there is set free an equivalent amount of acid which will be effective to dissolve the excess undissolved hydroxide as the process proceeds.

It is to be understood that neither the process nor the method is limited to the details of the examples here given. Various other manganese bearing materials may be employed, other metals used as electrodes, etc., without in any way departing from the spirit and scope of the invention as expressed in the appended claims.

I claim:

1. The method of treating manganese-bearing ore which comprises subjecting the ore to the action of a cathode in the presence of sulphuric acid to form a manganous sulphate solution, and separating the solution from the insoluble portion of the ore.

2. The method of treating a manganese bearing material which comprises subjecting the same to the action of a cathode in the presence of an acid capable of forming a soluble manganous salt.

3. A method of electrolytically treating manganese compounds which consists of subjecting the material containing manganese to the action of a cathode in one compartment of a cell in the presence of sulphuric acid whereby to form a manganous salt solution, and simultaneously subjecting a manganous salt solution to the action of an anode in the other compartment.

In witness whereof, I hereunto subscribe my name this 29 day of November, 1927.

N ARTHUR LAURY.