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METHODS FOR PRODUCING MANGANESE IN METAL STATE AND PURE MANGANESE DIOXIDE IF DESIRED, FROM MANGANESE ORES

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This invention has for its object a method for producing manganese in metal state and if desired pure manganese dioxide, from manganese ores.

In the method of this invention the manganese ore is converted into manganese sulphate by an attack by means of sulphuric acid or, at least in part, by the anolyte recovered from a final electrolysis step in the process, and by operating in presence of a reducing agent which converts the manganese dioxide, being by itself slightly responsive to attack by diluted acids, into manganese monoxide which on the contrary is easily attacked. A mixed solution of manganese sulphate and of sulphate of the element used as reducing agent is thus obtained; said solution is subsequently neutralised for the precipitation of the reducing agent from the solution and the precipitate is subsequently carried again into the process.

Finally the solution of manganese sulphate is electrolysed and thus manganese in metal state and, if desired, pure manganese dioxide is obtained; the electrolysis is carried out with advantage in such a manner as to obtain and keep the anolyte and catholyte separate for their reuse in the process.

As reducing agent a solution of a soluble iron salt in ferrous state is used with advantage in that the most of impurities present in the ore and consisting usually mainly of iron, arsenic, antimony, etc. precipitate with said salt at the time of the neutralisation step.

An embodiment of the method of this invention is hereinafter described by way of example assuming that pyrolusite is treated and that iron is used as reducing agent.

Pyrolusite is attacked by means of sulphuric acid in the presence of ferrous sulphate which acts as a reducing agent; the manganese oxides are thus reduced into manganese monoxide and are attacked by sulphuric acid thus producing a solution of $MnSO_4$ and $Fe_2(SO_4)_3$.

Say for the purpose of treating 100 Kg. of pyrolusite having a 50% content of MnO_2, 70 Kg. of iron are used said iron being recovered in the process, and 600 Kg. of diluted (20%) sulphuric acid, this acid also being recovered.

The removal of impurities of the class of copper, zinc, cadmium, etc. from the solution is effected by precipitating said metals by pure electrolytic manganese in powder state, said manganese being taken from the manganese obtained by electrolysis in the final step of the process.

Subsequently iron is precipitated by neutralising the solution; said neutralisation may be effected as usually by means of calcium carbonate or ammonia in gas state or in solution state in presence of ammonium salts, or preferably, in accordance with this invention, by taking advantage of the catholyte recovered from the subsequent electrolysis step and consisting of an alkaline solution of ammonium salts with manganese sulphate; for such a purpose the electrolysis step is carried out with the aid of porous separating partitions in conditions proper to obtain the anolyte and catholyte separately.

The neutralisation step may be improved by having the residual ferrous salts, if any, converted into ferric state by a previous addition of manganese dioxide obtained in the electrolysis step.

The ferric hydrate which precipitates as an effect of the neutralisation may be regenerated into ferrous sulphate which is subsequently carried again in the process in the ore attack step; for this purpose the ferric hydrate is dissolved into sulphuric acid in the presence of sulphur dioxide or of an alkali sulphide or, in accordance with a feature of this invention, in the anolyte recovered from the electrolysis step and consisting of an acid solution of manganese sulphate and of ammonium sulphate.

The solution thus obtained, consisting of pure manganese sulphate, is treated by an electrolysis step in which manganese in metal state is obtained at the cathode, a portion of said manganese being used if desired for the purification of the solution as above stated; by a proper control of the electrolysis step it is also possible to obtain pure manganese dioxide on the anode, which may be used in oxidising steps preceding the neutralisation step.

The electrolysis is effected with advantage by means of cells having porous partitions to secure the separation of the anolyte and catholyte from each other; in these circumstances the acid anolyte is obtained separately for further use either in the attack of the ore or for regenerating the ferric hydrate which has been precipitated as an effect of the neutralisation step, said ferric hydrate being regenerated into ferrous sulphate by treatment with said anolyte in presence of a reducing agent; on the other hand the recovered catholyte may be used again in the process for neutralizing the acid solution of manganese sulphate, ferric sulphate and ammonium sulphate.

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