

UNITED STATES PATENT OFFICE.

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ELECTROLYTIC RECOVERY OF ZINC AND MANGANESE.

1,055,157.

Specification of Letters Patent.

Patented Mar. 4, 1913.

No Drawing.

Application filed September 4, 1912. Serial No. 718,508.

To all whom it may concern:

Be it known that I, ANDREW GORDON FRENCH, a citizen of the Dominion of Canada, residing at Nelson, in the Province of British Columbia, Canada, have invented a new and useful Electrolytic Recovery of Zinc and Manganese, of which the following is a specification.

This invention relates to a process for the recovery of metallic zinc and manganese dioxid by electrolysis, the object being to recover these materials in a dense, pure form in the case of zinc, and in a pure marketable condition in the case of the manganese dioxid. It forms part of a treatment for the recovery of these materials from refractory complex zinc-lead ores containing manganese. The preparatory treatment of these ores is set forth in an application for a patent, now pending, which was filed on the 30th of September, 1911, under Serial No. 652,047, patented October 15, 1912, #1,041,060.

In the process set forth in that application the final result was a strong, aqueous solution of sulfate of zinc with neutral sulfate of sodium and containing more or less sulfate of manganese, which is usually present in the complex ores which this process is designed to treat. These three salts, when in solution together, are easily split up by a low voltage direct electric current and yields on the cathode a dense deposit of very pure, metallic zinc and on the anode pure manganese dioxid. It is on the favorable combination of these three salts that the success of this process depends and where the manganese is not in sufficient quantity to form that favorable combination, this element should be added in order to obtain the most satisfactory results.

The following specification fully describes the process as conducted.

The aqueous solution of the sulfates of zinc and manganese with neutral sulfate of sodium is delivered into an electrolytic tank having lead anodes and thin, sheet zinc cathodes and a direct current of from two and a half to four and a half volts with a current density of from twenty to thirty amperes per square foot of cathode surface is passed through the solution. Under this current a very pure metallic zinc is formed as a dense deposit on the cathodes and a pure manganese dioxid at the anodes.

The purity of the zinc, particularly in its

absolute freedom from oxid of zinc and sulfur compounds, the presence of which in previous attempts at electrolytic recovery have caused sponginess and deterioration of the deposit, is attributable chiefly to the association with the zinc in the electrolyte, of the manganese and sodium sulfates. These three salts in solution together, when crystallized out do so as a triple salt. A further advantageous feature of this treatment lies in the fact that the sulfuric acid which is liberated from the zinc and manganese sulfates combines in its nascent condition with the neutral sulfate of sodium to form bisulfate and persulfate of sodium in the electrolyte, and as these reactions are exothermic the current is correspondingly reinforced. A second reinforcement in a similar manner is obtained from the formation of the manganese dioxid at the anode.

In the practice of the process, the solution, which forms the electrolyte, is made to flow continuously from the ore leaching tanks into the electrolytic tank, in a nearly saturated condition and free from acidity, and a return flow of the electrolyte, after having been partially acted upon by the current, is returned from the electrolytic tank to the ore leaching tank. A proportion of the zinc and the manganese having been abstracted from the solution and deposited respectively on the cathodes and at the anodes, the return flow of the solution to the leaching tank is in an acid condition, having from one and a half to two and a half per cent. of acidity as bisulfate and persulfate of sodium. This acidity enables it to dissolve out a fresh supply of zinc and manganese in the leaching tank, and this process is continued until the ore in the leaching tank is depleted of its zinc and manganese.

As described above, when treating solutions from ores which are poor in manganese, it is necessary to mix it with others richer in that element so as to give one unit of manganese to from four to six units of zinc, which I find to be a good working proportion although if a greater proportion of manganese be employed the operation may still be successfully performed.

In circumstances where ores sufficiently rich in manganese are not obtainable, I obtain the required sulfate of manganese by treating a proportion of the manganese dioxid mud, as deposited at the anodes, with

sulfurous acid gas, either free or in solution, while the dioxid is carried in as small a quantity of water as will hold it in suspension. This immediately takes oxygen from the dioxid forming the soluble manganese sulfate which is required to add to the electrolyte.

The sulfurous acid may be obtained from the flues of the furnace used for calcining the sulfid ores in the earlier treatment referred to, as being the subject of the application filed September 30, 1911 and hereinbefore referred to.

The process here described is advantageous in that it produces a particularly dense and pure form of metallic zinc, and similarly the dioxid of manganese is commercially pure, and these results are obtained with a very low voltage current owing to the electrolyte being a solution of the three salts above referred to and to the fact that the reactions in the electrolytic tank are exothermic, reinforcing the current.

In this application I make no specific claim to that species of the invention in which, when the percentage of manganese is below the minimum amount the regeneration of the required sulfate of manganese by treating dioxid of manganese in suspension in water by sulfurous acid gas or a sulfurous acid solution, is employed, since that form of the invention constitutes the subject-matter of my divisional application filed on February 4, 1913, Serial No. 746121.

Having now particularly described my invention I hereby declare that what I claim as new and desire to be protected in by Letters Patent, is:

1. A process for the recovery of pure metallic zinc and manganese dioxid, said process comprising the electrolytic decomposition of a solution containing sulfate of zinc, sulfate of manganese and neutral sulfate of sodium.

2. A process for the recovery of pure metallic zinc and manganese dioxid, said process comprising the electrolytic decomposition of an aqueous solution of sulfate of zinc, sulfate of manganese and neutral sulfate of sodium.

3. A process for the recovery of pure metallic zinc and manganese dioxid, said process comprising the passage of an electric current of from two and a half to four and a half volts from a lead anode to a zinc cathode immersed in a solution containing sulfate of zinc, sulfate of manganese and neutral sulfate of sodium.

4. A process for the recovery of pure metallic zinc and manganese dioxid, said process comprising the electrolytic decomposition of a solution containing sulfate of zinc, sulfate of manganese and neutral sulfate of sodium the electrolyte after being acted upon being continuously delivered to the leaching tank from which the original supply was obtained and continually replaced in the electrolytic tank by a supply drawn from the same leaching tank.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

ANDREW GORDON FRENCH.

Witnesses:

WM. C. McCLELLAND,
W. F. TEETZEL.