

UNITED STATES PATENT OFFICE.

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ELECTROLYTIC RECOVERY OF ZINC AND MANGANESE.

1,055,158.

Specification of Letters Patent.

Patented Mar. 4, 1913.

No Drawing. Original application filed September 4, 1912, Serial No. 718,506. Divided and this application filed February 4, 1913. Serial No. 746,121.

To all whom it may concern:

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

10 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
15 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
20 ores is set forth in my Patent #1,041,060 of October 15, 1912. 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 contain-
25 ing 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 elec-
30 tric 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
35 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
40 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
45 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
50 current a very pure metallic zinc is formed as a dense deposit on the cathodes and pure manganese dioxid at the anodes. The purity of the zinc, particularly in its absolute freedom from oxid of zinc and sulfur
55 compounds, the presence of which in previ-

ous 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
60 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 sul-
65 fates 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.
70 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
75 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 cur-
80 rent, 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 res-
85 pectively 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-
90 cent. of acidity as bisulfate and persulfate of sodium. This acidity enables it to dissolve out a fresh supply of zinc and man-
95 ganese 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 in the preamble, when treat-
100 ing 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
105 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 per-
110 formed. 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 Patent #1,041,060 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.

While I have described herein the complete process I do not broadly claim the same in this application, nor do I claim the species of the process which has relation to the treatment of ores that contain plenty of manganese, as such forms the subject matter of my original application filed September 4, 1912, #718,506, of which this application is a divisional part, and has particular relation to the process as employed in connection with ores which are not sufficiently rich

in manganese but require the regeneration of sulfate of manganese in carrying out the process.

What I claim is:—

1. In a process for the production of metallic zinc and dioxid of manganese, by the electrolytic decomposition of a solution containing sulfate of zinc, sulfate of manganese, and neutral sulfate of sodium, 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.

2. A process for the recovery of pure metallic zinc and manganese dioxid which comprises 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 treated to effect the regeneration of the required sulfate of manganese by treating dioxid of manganese in suspension by sulfurous acid gas or a sulfurous acid solution, and then delivering the electrolyte after being regenerated to the leaching tank from which the original supply was obtained and replaced in the electrolytic tank by a supply drawn from the same leaching tank.

ANDREW GORDON FRENCH.

Witnesses:

ALBERT E. DIETERICH,
GEO. B. PITTS.