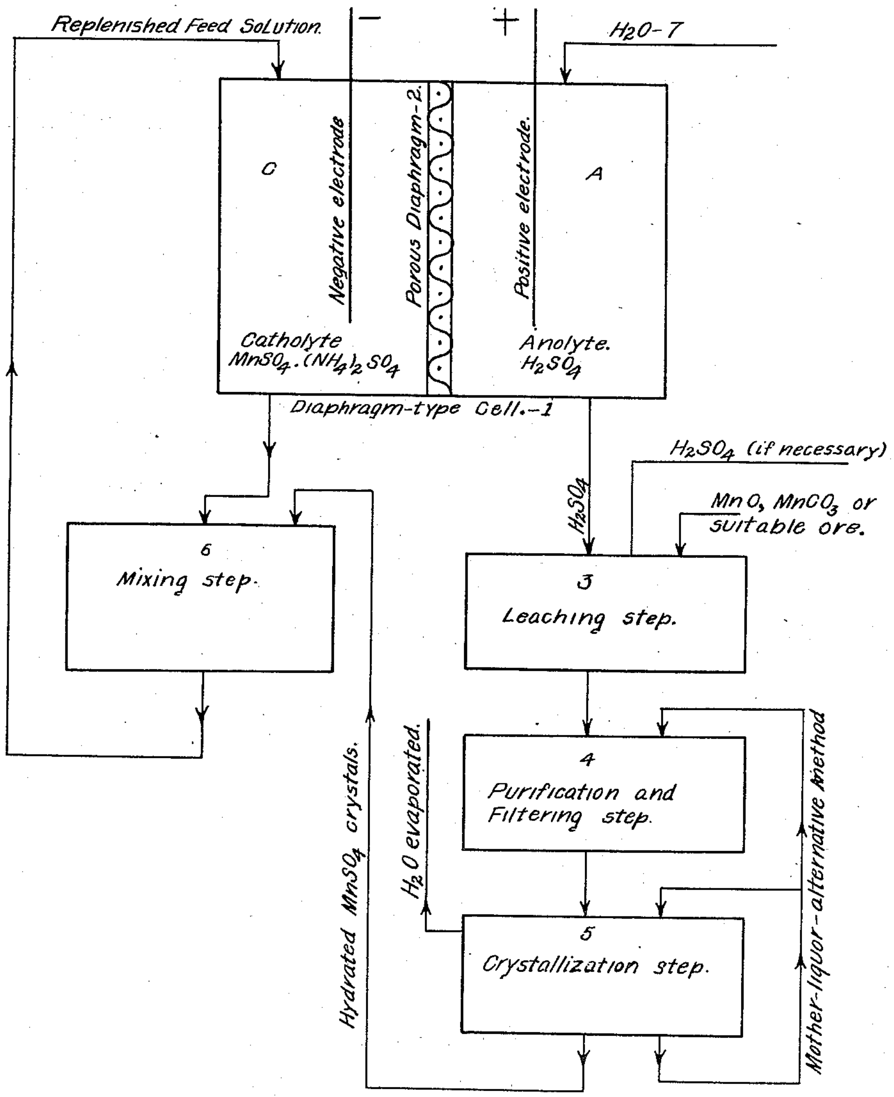
Oct. 14, 1941. W. H. HANNAY ET AL 2,259,418

ELECTROLYTIC MANGANESE PROCESS

Filed April 3, 1939



WILLIAM HENRY HANNAY
BASIL JOSEPH WALSH
INVENTORS

T. Harold Nichols

ATTORNEY

Patented Oct. 14, 1941

2,259,418

UNITED STATES PATENT OFFICE

2,259,418

ELECTROLYTIC MANGANESE PROCESS

William Henry Hannay and Basil Joseph Walsh, Trail, British Columbia, Canada, assignors to The Consolidated Mining & Smelting Company of Canada, Limited, Montreal, Quebec, Canada, a corporation of Canada

Application April 3, 1939, Serial No. 265,632

6 Claims. (Cl. 204—105)

Our invention relates to a continuous cyclic process for the extraction of manganese from its ores and the recovery, through electrodeposition, or substantially pure metallic manganese.

We are aware that processes for the extraction of manganese from its ores and the subsequent electro-deposition of metallic manganese from manganous sulphate electrolytes have been the subject of exhaustive investigation for a number of years. Until recent years, however, it has not been feasible to apply electro-chemical methods on a commercial scale, due to the lack of fundamental knowledge of essential operating conditions, the difficulty in maintaining the electrolyte substantially free from impurities which tend to inhibit the deposition of manganese, and the low current efficiency which increases the cost of the manganese above economic limits.

We are also aware that manganese has been electrolytically deposited from electrolytes formed of a solution of manganous sulphate-ammonium sulphate as exemplified by Allmand and Campbell, (Transactions of the Faraday Society, 1924); by technical literature, such as the article by Fink and Kolodney, "Electrodeposition of Metallic Manganese Using Insoluble Anodes" which appeared in Transactions of the Electrochemical Society, 1937; and by Shelton in his U. S. Patent No. 2,119,560.

One of the principal features of our invention resides in the manner in which we continuously electrolyze a separately cycling electrolyte formed of a solution of manganous sulphate and ammonium sulphate, in the cathode compartment of an electrolytic cell, while maintaining, in the anode compartment, an entirely different electrolyte consisting of an aqueous sulphuric acid solution. The two compartments are separated from each other by means of a porous diaphragm; the anolyte and the catholyte do not intermix except to the extent to which there is a transfer of ions through the diaphragm during electrolysis, and to the extent to which sulphuric acid enters the catholyte from the anolyte as the result of diffusion. The additions to the anolyte and catholyte, necessary to maintain the electrolysis, are made separately and each electrolyte is separately discharged from its respective compartment.

A further feature of our invention resides in the manner in which we continuously produce sulphuric acid in the anolyte and, maintaining it at a predetermined concentration by the addition of water, use the solution thus generated for the subsequent leaching step of the process.

Further features of our invention reside in the manner in which we continuously purify the solution from the leaching step and obtain therefrom hydrated manganous sulphate crystals in a highly purified condition and also in the manner in which we use these purified crystals to replenish the spent catholyte. By the addition of the hydrated manganous sulphate crystals to the depleted catholyte, we form a solution which is suitable for returning to the cathode compartment as feed solution. The concentrations of the constituents of the replenished solution are controlled within predetermined ranges which have been found essential to maintain optimum operating conditions.

The manner in which we operate our process to realize the above and other features will be apparent from the following description and accompanying drawing in which the various steps of the process are illustrated diagrammatically.

Like reference characters refer to like parts throughout the specification and drawing.

The numeral 1 indicates a diaphragm type cell in which the cathode compartment C is separated from the anode compartment A by means of the porous diaphragm 2, formed of such material as alundum. The cathode may be formed of iron, aluminum or of a suitable chromium iron alloy or stainless steel. The anode is preferably formed of lead. While the cell shown has only two compartments, one compartment containing the anolyte and the other, the catholyte, other types of cell, such as a cell divided into three compartments with an anode compartment on each side of the cathode compartment, would be suitable.

The electrolyte circulating through the cathode compartment consists of a compound manganous sulphate-ammonium sulphate solution. The electrolyte in the anode compartment consists of a sulphuric acid solution. Each of the electrolytes is constantly maintained within a predetermined range of concentration.

Water is continuously added to the anolyte at 7. The rate at which the water is added is regulated so that sulphuric acid of a desired concentration is formed on reaction of the water with the sulphate ions entering the anolyte from the cathode compartment.

The numeral 3 indicates the leaching step of the process wherein manganous oxide or manganous carbonate is leached with the sulphuric acid solution withdrawn from the anode compartment. Additional sulphuric acid from other sources may be added, if necessary, during this step to replace losses of sulphuric acid which may occur in this or in the subsequent filtering step of the process.

The solution obtained from the leaching step is filtered at 4 and the filtrate is purified to remove impurities such as nickel, cobalt, zinc, lead, iron, arsenic and antimony. While we do not wish to limit the scope of our present invention to any particular purification step, we have found that the use of hydrogen sulphide for the precipitation of metallic impurities present in solutions containing manganese is particularly suitable in this step of the process, after removal of iron by standard methods.

The purified pregnant solution is passed into crystallizer 5 wherein hydrated manganous sulphate is crystallized by heating. We have found that the crystallization step may be readily effected by taking advantage of the fact that, within certain limits, the solubility of manganous sulphate in aqueous solution decreases with an increase in temperature. During this step, some water is removed by evaporation.

The mother-liquor from the crystallizing step may be added to the fresh solution from the purification step and thus re-circulated through the crystallizer or, if the impurities in the mother-liquor should build up to an undesirable extent, they may be removed by returning the solution to the circuit ahead of the purification step.

The crystallized hydrated manganous sulphate is mixed at 6 with spent catholyte withdrawn from the cell. The rate of addition of hydrated manganous sulphate crystals to the spent catholyte is sufficient to replenish the solution adequately before being returned as fresh pregnant feed solution to the cathode compartment. The rate of addition of manganese, in the form of hydrated manganous sulphate, to the spent catholyte is equivalent to the rate at which manganese is deposited on the cathode.

Referring now to specific operating conditions, we have found that the concentrations of ammonium sulphate and manganous sulphate that may be used in the electrolyte may be varied through a relatively wide range. We have found that these two salts may be used in the electrolyte in such relative amounts that the ratio of the weight of ammonia present in the solution to the weight of the manganese present is as low as 0.2. As the use of this minimum ratio is not commercially practicable, we prefer to use concentrations of ammonium sulphate and manganous sulphate such that the weight of ammonia present is not less than 1.4 times the weight of the manganese present. Using our preferred ammonia-manganese ratios, the actual concentrations of ammonium sulphate and of manganous sulphate may be varied within wide limits, which are governed by the maximum solubility of each of these two salts when in the same solution, at temperatures of about 25° C. to 35° C., and by the lowering of the cathode current efficiency to the point at which operation of the cell becomes uneconomical on a commercial scale. When operating the cell with an ammonia-manganese ratio such that the weight of ammonia is at least 1.4 times the weight of the manganese, we prefer to use, in the feed solution, concentrations of the order of 50 grams of ammonia, as NH_3, per litre and of 35 grams of manganese, as Mn, per litre, the corresponding concentrations of ammonium sulphate and manganous sulphate being approximately 194 and 96 grams per litre respectively.

The catholyte, as it flows through its compartment of the cell, is depleted of manganese by the electro-deposition of that metal. The rate of flow of the solution through the cathode compartment of the cell, and also its composition at entrance and exit are readily regulated to give the most satisfactory results. As electrolysis proceeds, however, the pH of the catholyte, unless suitable provision is made, will drop from the preferred value of about pH 8 to a point where no further deposition of manganese can be obtained.

The drop in pH value of the catholyte is caused by an accumulation of sulphuric acid as a result of the diffusion of sulphuric acid from the anolyte and it is necessary, therefore, to control the pH value of the catholyte by the addition of ammonia.

We have found that when the pH of the solution drops below a value of about 4, the manganese deposits are unsatisfactory, and therefore we prefer to maintain the pH value of the solution within the range of from pH 4 to pH 8 by the addition of ammonia.

We have also found that very satisfactory results are obtained when the rate of flow of the catholyte from the cell is so regulated that the fresh pregnant solution contains about 50 grams of ammonia, as NH_3, per litre, and 35–40 grams of manganese, as Mn, per litre, and the depleted solution contains about 55 grams of ammonia, as NH_3, per litre, and 20–25 grams of manganese, as Mn, per litre.

An increase in ammonia content of the outlet solution over the inlet solution is caused by the addition of ammonia to control the pH value of the catholyte, as outlined above, and it will be apparent that the ratio of the weight of ammonia to the weight of manganese is much higher in the depleted solution than it is in the fresh pregnant solution. In the present illustration, for example, the ratio is approximately 1.4 in the feed solution and from 2.0 to 3.0 in the depleted solution.

As set out above, ammonia is added to the catholyte to maintain the pH value thereof within the range of from pH 4 to pH 8 which, in forming ammonium sulphate, adds to the ammonium sulphate already present. If necessary, the spent catholyte may be treated to render the excess ammonia content available for recirculation.

In the anode compartment, the concentration of sulphuric acid in the anolyte is maintained sufficiently high so that the solution obtained from the leaching step, on entering the crystallization step, is nearly saturated with manganous sulphate at ordinary temperatures, and contains from 150 to 200 grams of manganese per litre.

The sulphuric acid solution in the anode compartment is continuously formed by the reaction of the sulphate ions which migrate into that compartment with the water which is added thereto. The total amount of sulphuric acid produced in a given time, of course, depends on the amount of manganese deposited on the cathode in the same time; theoretically, for each pound of manganese deposited, 1.78 pounds of sulphuric acid are produced. We prefer to introduce water into the anode compartment at a rate such that the withdrawn solution contains from 10% to 35% sulphuric acid by weight. Having regard to evaporation losses, losses arising from the formation of hydrogen and oxygen at the electrodes, and also to the amount of acid that is neutralized in the cathode compartment, the amount of water introduced into the anode compartment is readily adjusted to give a desired concentration of sulphuric acid in the effluent solution.

The temperature of the leaching step is preferably maintained within the range of from 25° C. to 35° C. and an excess of manganous oxide or manganous carbonate is always present in that step to ensure that all the sulphuric acid present is neutralized.

Both manganous oxide and manganous carbonate, when prepared artificially, react readily with sulphuric acid of practically any strength, at temperatures as low as 25° C. On the other hand, manganous carbonate, if available in the form of an ore, requires to be leached with hot acid, and we have found it preferable to leach such an ore at a temperature of about 70° C., to ensure that the manganous carbonate will react readily with sulphuric acid. Leaching at this temperature will produce a supersaturated solution, and it will therefore be necessary, after cooling this solution, to agitate the solution for a sufficient period to dissolve any manganous sulphate which may have crystallized out. When the manganese ore is composed of a higher oxide which is not soluble, the ore is first reduced by conventional methods, such as by a reducing roast, to a lower oxide which is soluble in sulphuric acid.

The purification step of the process is operated within the temperature range of from 25° C. to 35° C., within which range the manganous sulphate is most soluble.

The conditions under which the crystallization step is operated depend upon the rate at which hydrated manganous sulphate crystals must be added to the depleted catholyte solution to maintain the rate of feed of fresh pregnant solution to the cathode compartment. We have found by introducing the purified solution into the crystallizer at about 27° C., the solution contains the greatest concentration of dissolved manganous sulphate. The crystallizer is preferably maintained within the temperature range of from 80° C. to 102° C.

The mother-liquor from the crystallizing step may be recirculated through that step, or, alternatively, it may be passed to the purification step to permit the removal of impurities.

The manganous sulphate crystals leaving the hot crystallizer are presumably combined with one molecule of water of crystallization as expressed by the formula $MnSO_4H_2O$. If the crystals are permitted to cool while exposed to the atmosphere, they absorb moisture until their formula may be expressed as $MnSO_4.4H_2O$. While sufficient water must be added to the catholyte to replace that lost by evaporation and by electrolysis, the addition of water in excess of that amount should be avoided, otherwise the catholyte will be diluted to an undesirable extent. We have found, therefore, that the hydrated manganous sulphate crystals on leaving the crystallizer should be introduced immediately into the mixing step.

The hydrated manganous sulphate crystals are passed to the mixing step of the process into which also flows the depleted catholyte solution withdrawn from the cathode compartment. The mixing can be effected either as a batch process or continuously as desired. The rate of addition of hydrated manganous sulphate crystals to the spent catholyte is controlled in such a manner that the effluent solution from the mixing step is of the composition desired for the fresh pregnant catholyte entering the cathode compartment, as set out hereinabove.

The cell is preferably operated at a current density of from 20–35 amperes per square foot of cathode surface and the temperature of the electrolyte is maintained at about 25 to 35° C. Under these conditions, we obtain a current efficiency of about 50%, substantially the remainder of the current being consumed in the generation of hydrogen at the cathode and oxygen at the anode.

We have found by operating our process in the manner set out above that the continuous operation thereof is effected on a commercial scale to result in a compact, coherent deposit of substantially pure manganese and at the same time permitting economies in the process which heretofore have been considered impossible to realize.

For example, by maintaining a separately circulating manganous sulphate-ammonium sulphate electrolyte in the cathode compartment and in the anode compartment an electrolyte consisting of an aqueous sulphuric acid solution, we increase the conductivity of the anolyte, thus making possible increased power efficiency. Furthermore, we avoid the formation of manganese dioxide at the anode which, in addition to increasing the circulating load on the system, necessitated shutting down the former type of cell at frequent intervals to remove the precipitated manganese dioxide.

We have found that economic advantages result from the smaller volume of ammonium sulphate and manganous sulphate solution required. Also, the crystallization step effects additional purification of the electrolyte.

It will be apparent, of course, that the process disclosed hereinabove is not limited to the examples set out. Various modifications of the preferred method may be made to meet specific operating conditions without departing from the scope of the appended claims.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. In a continuous process for the electrodeposition of manganese in a diaphragm type cell, the steps of feeding a manganous sulphate-ammonium sulphate electrolyte having a pH value within the range of from pH 4 to pH 8 into the cathode compartment, the anode compartment containing an electrolyte consisting of an aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, continuously feeding water into the anode compartment in amount sufficient to combine with the sulphate ions migrating through the diaphragm to form an aqueous sulphuric acid solution, and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

2. In a continuous process for the electrodeposition of manganese in a diaphragm type cell, the steps of feeding a manganous sulphate-ammonium sulphate electrolyte having a pH value within the range of from pH 4 to pH 8 into the cathode compartment, the anode compart-

ment containing an electrolyte consisting of an aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, maintaining the pH value of the catholyte within the predetermined range by the addition of ammonia, continuously feeding water into the anode compartment in amount sufficient to combine with the sulphate ions migrating through the diaphragm to form an aqueous sulphuric acid solution, and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

3. In a continuous process for the electro-deposition of manganese in a diaphragm type cell, the steps of feeding a manganous sulphate-ammonium sulphate electrolyte, in which the ratio of the weight of ammonia to manganese is maintained above 0.2 and having a pH value within the range of from pH 4 to pH 8, into the cathode compartment, the anode compartment containing an electrolyte consisting of an aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, continuously feeding water into the anode compartment in amount sufficient to combine with the sulphate ions migrating through the diaphragm to form an aqueous sulphuric acid solution, and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

4. In a continuous process for the electro-deposition of manganese in a diaphragm type cell, the steps of feeding a manganous sulphate-ammonium sulphate electrolyte having a pH value within the range of from pH 4 to pH 8 into the cathode compartment, the anode compartment containing an electrolyte consisting of an aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, continuously feeding water into the anode compartment to combine with the sulphate ions migrating through the diaphragm and in amount sufficient to form an aqueous sulphuric acid solution containing from 10% to 35% sulphuric acid by weight, and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

5. A continuous process for the electro-deposition of manganese which comprises electrolyzing a manganous sulphate-ammonium sulphate electrolyte, in which the ratio of the weight of ammonia to manganese is maintained above 1.4 and having a pH value maintained within the range of from pH 4 to pH 8 by the addition of ammonia, in the cathode compartment of a diaphragm type electrolytic cell, the anode compartment containing an electrolyte consisting of aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, continuously feeding water into the anode compartment in amount sufficient to combine with the sulphate ions migrating through the diaphragm to form an aqueous sulphuric acid solution, and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

6. A continuous process for the electro-deposition of manganese which comprises electrolyzing a manganous sulphate-ammonium sulphate electrolyte, in which the ratio of the weight of ammonia to manganese is maintained above 1.4 and having a pH value maintained within the range of from pH 4 to pH 8 by the addition of ammonia, in the cathode compartment of a diaphragm type electrolytic cell, the anode compartment containing an electrolyte consisting of an aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, continuously feeding water into the anode compartment to combine with the sulphate ions migrating through the diaphragm and in amount sufficient to form an aqueous sulphuric acid solution containing from 10% to 35% sulphuric acid by weight and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

WILLIAM HENRY HANNAY.
BASIL JOSEPH WALSH.