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MAGNESIUM CONTROL IN MANGANESE ELECTROWINNING

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2 Sheets-Sheet 1

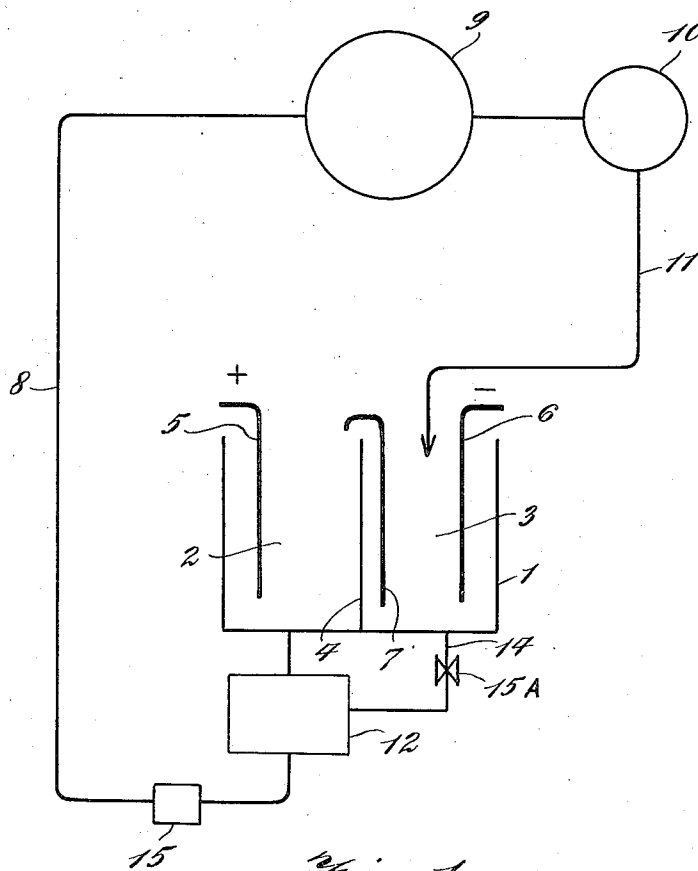


Fig. 1.

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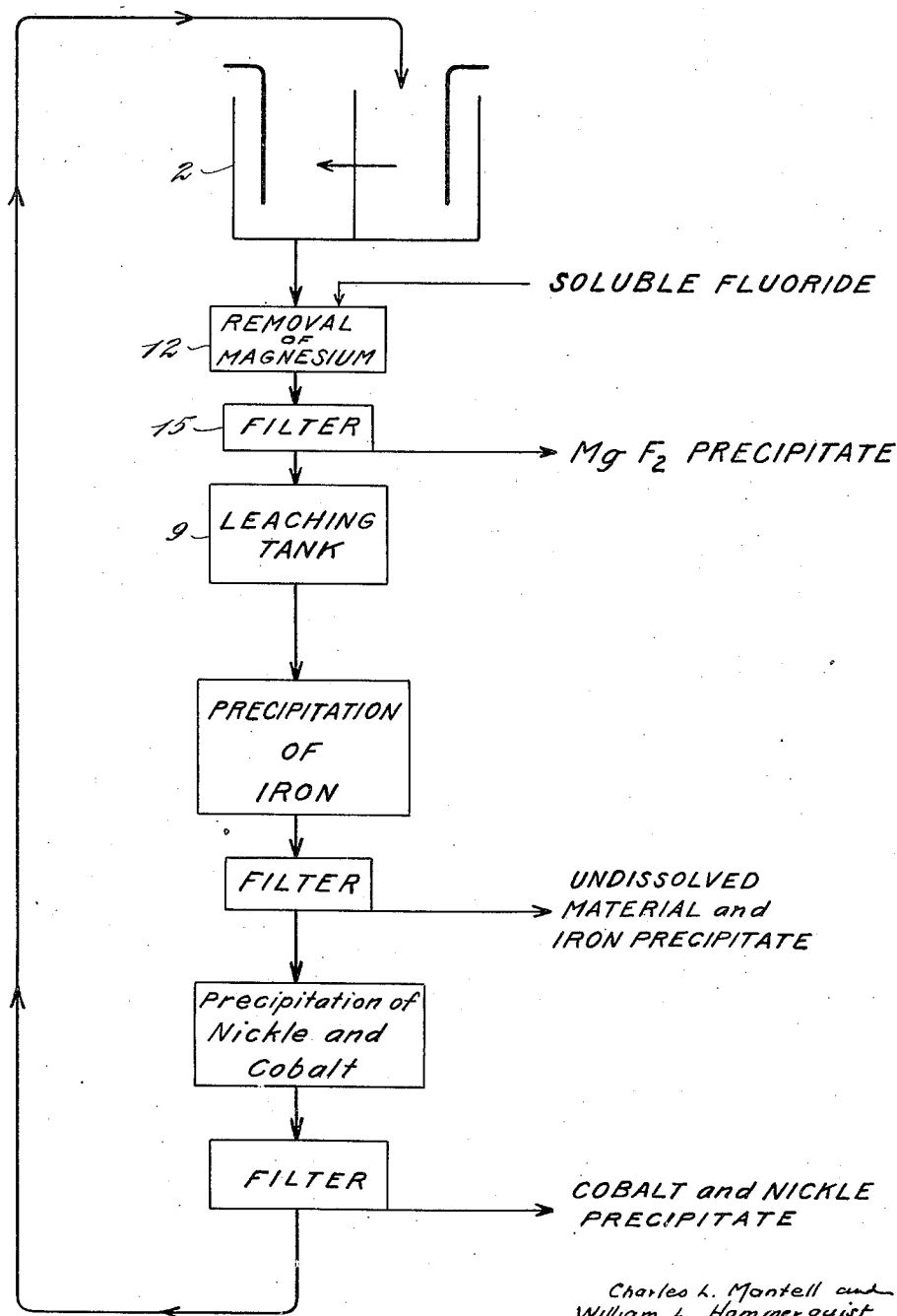
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Fig. 2.

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UNITED STATES PATENT OFFICE

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MAGNESIUM CONTROL IN MANGANESE
ELECTROWINNING

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8 Claims. (Cl. 204—105)

This invention relates to improvements in the commercial electrowinning of manganese from its ores.

In the commercial electrowinning of manganese a body of electrolyte is maintained in an electrolytic cell provided with an anode and a cathode, separated by a permeable membrane or diaphragm into anolyte and catholyte chambers, respectively. From this body of liquid, specifically from the catholyte in the catholyte chamber, manganese is removed in the form of metallic manganese and deposited on the cathode. To this body of liquid a manganese salt is added to replenish the solution with manganese ions and compensate for the removal of metallic manganese. The manganese salt is obtained by leaching a suitably conditioned manganese ore with an acid solution and in practice this acid solution is the anolyte from the anolyte chamber. Nothing is removed from the electrolyte except metallic manganese and the volatile products of electrolysis whereas there is a continuous or progressive addition to the electrolyte of the products obtained by leaching ore with the anolyte liquid.

Consequently the concentration of impurities, specifically metallic elements other than manganese, continuously increases unless steps are taken to prevent this increase in concentration of impurities. Among these impurities magnesium is a common constituent of manganese ores. To illustrate this, reference may be had to the accompanying drawings in which Fig. 1 shows diagrammatically a cell for the electrowinning of manganese and its associated leaching and purification system. The cell 1 is divided into an anolyte compartment 2 and a catholyte compartment 3 by the permeable diaphragm 4. An electric current may be passed through the cell between the anode 5 and cathode 6. The permeable diaphragm may be made of textile material or other permeable substance. There is a transfer of catholyte to anolyte by diffusion through this diaphragm and an overflow pipe 7 permits flow of catholyte from the catholyte to the anolyte chamber. In practice the cell contains a series of anodes and cathodes arranged alternately in a row and separated by a corresponding series of diaphragms. The catholyte and anolyte compartments are respectively connected together by suitable manifolds. The cathodes and anodes are also respectively electrically connected. Fig. 1, however, shows a single catholyte and single anolyte chamber separated by a diaphragm and provided with

electrodes as shown, for the sake of simplicity since the particular construction of the cell is not a part of the present invention. Line 8 conducts anolyte from the anolyte chamber to a tank 9 in which suitably conditioned manganese ore is extracted. After the removal of insoluble material the liquid extract is then subjected to a series of operations to remove impurities including iron, nickel, cobalt and arsenic, the tank 10 being designated diagrammatically to indicate apparatus in which this series of operations may be performed.

Owing to the different electrolytic changes occurring in catholyte and anolyte the composition of the liquids in these respective compartments is different. For example, the composition of the anolyte may be represented as follows: pH 0.5 to 1.5 represented by sulfuric acid in the case where manganese is used as manganese sulfate, ammonium sulfate 150 to 175 grams per liter, manganese (for example as manganese sulfate) 5 to 15 grams per liter, a preferred range being 13 to 15 grams per liter.

When this solution is used to extract conditioned manganese ore in the tank 9 the basic character of the ore changes the pH and the liquid removed from the extract tank 9 may have a pH of about 2.0 to 4.0. Simultaneously, of course, the concentration of manganese is increased to a value which may be represented by 25 to 55 grams of manganese per liter, a preferred range being 35 to 55 grams per liter, in the form of a soluble manganese salt, as for example the sulfate. In the extraction tank 9 the anolyte liquor becomes contaminated with impurities, as for example iron, cobalt, nickel, arsenic, calcium and magnesium. The extent of this contamination is controlled by the solubility of the respective sulfates.

If the concentration of these impurities is not satisfactorily controlled it is impossible to secure a deposit of manganese having the required purity and the maintenance of satisfactory electrical conditions in the cell is seriously impaired. The seriousness of the problem is increased by the fact that even though the impurities may be reduced to a concentration of very low magnitude, nevertheless the concentration of these impurities in the electrolyte tends to continuously increase because of the fact that the body of the electrolyte is maintained substantially constant and there is continuously added thereto catholyte liquid obtained by extracting fresh ore containing said impurities. In other words, even though the catholyte liquid entering the

catholyte chamber through the line 11 contains very small concentrations of impurities, the continuous addition of these impurities to the body of electrolyte gradually builds up higher concentrations unless adequate means are devised for the control thereof.

Among the advantages of manganese obtained by the electrowinning thereof are not only the low cost of manganese produced by this process as compared with the thermal process and the fact that it is possible to employ low grade manganese ores, but also the fact that manganese may be produced by electrowinning in a high state of purity. In fact the purity of manganese produced by the electrowinning process must be extremely high as this is one of the outstanding advantages of electrolytic manganese as compared with manganese obtained by other methods. Consequently the control of impurities introduced into the electrolyte is an important matter not only in respect of controlling the impurities of the manganese deposit but also in preventing side reactions introduced by the impurities and maintaining the efficiency of operation, and has presented a serious problem. Not only do these impurities when less adequately controlled seriously contaminate the deposit of manganese, but also seriously interfere with the successful operation of the electrolytic process.

The problem is particularly acute in the case of magnesium owing to the difficulty of successfully separating it from the manganese. Iron can be removed satisfactorily to a large extent by precipitating as ferric hydroxide. Cobalt and nickel can be precipitated to a very large extent by means of ammonium sulfide. Since manganese is commonly in the form of manganese sulfate, the anolyte liquid contains a considerable concentration of sulfuric acid and the relative insolubility of calcium sulfate prevents undue contamination of the electrolyte with calcium. Difficulty has, however, been experienced in adequately separating magnesium and various attempts have been made to remove magnesium and control the proportion thereof in the electrolyte without success, however, prior to the present invention. For example, it has been attempted to precipitate magnesium as magnesium ammonium phosphate. This attempt has been a failure, however, because manganese is simultaneously precipitated.

If the magnesium content be allowed to build up without control complex sulfates of magnesium with manganese and ammonium ion are formed in the anolyte. These complex sulfates precipitate out in the anolyte and tend to cause clogging of the diaphragm, the anolyte outlet and the anolyte manifolds. In addition these complex sulfates cause a loss of manganese and ammonium sulfate which is obviously undesirable. With clogging of the diaphragm increased voltages are necessary to overcome the increased electrical resistance of the diaphragm with subsequent increase in the voltage distribution in the cell and a disturbance of the necessary cathode potential for the deposit of manganese metal from the catholyte. If the magnesium content were allowed to build up in an uncontrolled amount in the catholyte with increased alkalinity of the catholyte, basic salts of magnesium tend to be formed which in turn may be mechanically carried to the cathode and deposited with the manganese metal thereby contaminating it, or else tend to clog the diaphragm and the overflow pipes connecting the catholyte with the ano-

lyte chamber. It is apparent that the deposition of contaminating influences on the cathode will also disturb electrical conditions in the cell.

It has been discovered that it is not necessary to completely remove magnesium because a certain small concentration not exceeding about 4 grams of magnesium per liter does not cause the formation of troublesome precipitates and therefore can be tolerated.

It is an object of the present invention to control the proportion of magnesium in an electrolyte containing magnesium and manganese.

It is a further object to limit the proportion of magnesium to an amount not exceeding about 4 grams of magnesium per liter.

It is a further object to efficiently and economically separate magnesium from manganese in an electrolyte containing salts of these metals.

It has been discovered that soluble fluorides preferentially precipitate magnesium in the presence of manganese.

It has been further discovered that this precipitation is best carried out at a pH between about 1 and 3, preferably, however, 1.5 to 2.75.

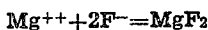
These discoveries and their application have enabled the above and other objects to be accomplished.

In view of the discovery that the separation of magnesium from manganese is best accomplished within a limited pH range, and further in view of the fact that it is possible to control the pH of the anolyte liquid between the desired limits, the invention further comprises as one of the objects thereof the removal of anolyte liquid from the anolyte chamber and treatment thereof with soluble fluorides at the above mentioned pH ranges to remove magnesium prior to employing the anolyte liquid as the means of extracting fresh ore.

The invention as to its principles and scope will be defined in the claims ultimately appended hereto. An illustrative embodiment will be set forth in the following description taken in conjunction with Fig. 1 and Fig. 2, the latter showing diagrammatically a flow-sheet of a process carried out in accordance with the present invention.

Referring specifically to Fig. 2 which shows this flow-sheet, anolyte liquid containing manganese, as manganese sulfate, at a concentration of about 5 to 15 grams of manganese per liter and ammonium sulfate at a concentration of, for example, about 150 to 175 grams per liter is withdrawn from the anolyte chamber 2 to the tank 12 where its pH concentration is adjusted to a preferred range of about 1.5 to 2.75. This may be accomplished by the addition of acid or alkali as necessary, and if alkali is required this is most advantageously supplied by adding the required proportion of catholyte liquid which may be supplied through the line 14 provided with valve 15A (see Fig. 1). Instead of catholyte liquid, ore may in some cases be employed. In the tank 12 the anolyte liquid having its pH adjusted as stated is then treated with a suitable soluble fluoride. This may be a fluoride of an alkali metal or ammonium or a double fluoride, as for example, ammonium hydrogen fluoride NH_4HF_2 . Hydrogen fluoride may be used but it is difficult to handle. Instead of using soluble fluorides as such, the reaction product of an insoluble fluoride and sulfuric acid may be used, e. g., the reaction product or a slurry of calcium fluoride and sulfuric acid. The proportion of soluble fluoride necessary to remove

a given quantity of magnesium is based upon the equation



In a typical case the concentration of magnesium withdrawn from the anolyte chamber 2 is about 4 grams per liter and by treatment with a soluble fluoride is reduced to about 2 grams per liter, so that when the fluoride treated anolyte is used to extract fresh ore the magnesium added by this extraction will not result in a concentration of magnesium greater than about 4 grams per liter in the resulting liquid fed from the purifying system 10 to the catholyte chamber through the line 11. It is to be understood that the magnesium increase or build-up per cycle may be so small that intermittent rather than continuous removal of magnesium from the anolyte is needed. In the typical case referred to the anolyte in the tank 12 is treated with ammonium hydrogen fluoride to the extent of 5 grams per liter. This provides the theoretical amount of fluoride ion to remove 2 grams per liter of magnesium and about 10 per cent excess. The anolyte liquid is then filtered in the filter 15. The filtrate is then passed to the leaching tank 9 and used therein to extract conditioned manganese ore. The ratio of ore to the filtrate is controlled so that the magnesium content of the extract does not exceed about 4 grams of magnesium per liter. The liquid extract, which may have a pH of 2.0 to 4.0, is then treated for the removal of iron and arsenic by oxidizing the iron to the ferric condition and adjusting the pH by addition of alkali to that value which will cause the precipitation of ferric hydroxide. The preferred pH is 5.6 but may be 5.5 to 7.2. The oxidation may be brought about by blowing with air or by treatment with other suitable oxidizing agents. The precipitate is filtered and the filtrate is then treated with an agent to remove nickel and cobalt as for example ammonium sulfide. The liquid at this stage is then treated with such soluble sulfide, as for example ammonium sulfide, and filtered to remove the precipitate of cobalt and nickel sulfides. The filtrate is then delivered as catholyte to the catholyte chamber 3.

Instead of causing magnesium separation in the anolyte prior to its use to extract ore in the digester, such separation may occur at any point in the system where the pH may advantageously be controlled at about 1 to 3, preferably 1.5 to 2.75 as for example in the digester or after digestion (of fresh ore) and prior to iron precipitation. In such a case anolyte having a pH range of about 0.5 to 1.5 is used to extract fresh ore and the pH of the extract is then increased to a range of about 1.5 to 2.75.

We claim:

1. The process of controlling the magnesium content of electrolytes used in the electrowinning of manganese containing manganese in the form of manganese sulfate together with magnesium sulfate as an impurity, which comprises treating said electrolyte with a soluble fluoride, partially precipitating magnesium as magnesium fluoride and separating it from the electrolyte, leaving the remainder of the magnesium in solution to an extent not greater than about 4 grams per liter and removing excess fluoride.

2. The process of controlling the magnesium content of an electrolyte used in the electrowinning of manganese, said electrolyte containing manganese sulfate, ammonium sulfate, sulfuric acid and magnesium sulfate, which com-

prises treating said electrolyte at a pH of about 1 to 3 with a soluble fluoride, partially precipitating magnesium as magnesium fluoride and separating it from the electrolyte, leaving the remainder of the magnesium in solution to an extent not greater than about 4 grams per liter and removing excess fluoride.

3. The process of controlling the magnesium content of an electrolyte used in the electrowinning of manganese, said electrolyte containing manganese sulfate, ammonium sulfate, sulfuric acid and magnesium sulfate, which comprises treating said electrolyte at a pH of about 1.5 to 2.75 with a proportion of soluble fluoride insufficient to precipitate all the magnesium, precipitating a portion of the magnesium fluoride and separating it from the electrolyte, leaving the remainder of the magnesium in solution and removing excess fluoride.

4. The process of controlling the magnesium content of the catholyte and anolyte in the electrowinning of manganese which comprises withdrawing anolyte from the anolyte chamber, said anolyte containing manganese sulfate, ammonium sulfate, magnesium sulfate and sulfuric acid, treating it with a proportion of soluble fluoride at a pH of about 1.5 to 2.75 insufficient to precipitate all of the magnesium, precipitating a portion of the magnesium as magnesium fluoride, leaving the remainder of the magnesium in solution to the extent of about 2 grams of magnesium per liter, filtering the precipitate and extracting conditioned manganese ore with the filtrate.

5. The process of limiting the magnesium content of the catholyte and anolyte in the electrowinning of manganese to a value not substantially above about 4 grams of magnesium per liter, which comprises withdrawing anolyte liquor from the anolyte chamber, said anolyte containing manganese sulfate, ammonium sulfate, magnesium sulfate and sulfuric acid, treating it with a proportion of a soluble fluoride insufficient to precipitate all of the magnesium, precipitating a portion of the magnesium and reducing its concentration to a value of about 2 grams per liter, filtering the precipitate, containing magnesium as an impurity, extracting conditioned manganese ore with said filtrate, and controlling the ratio of ore to said filtrate so that the magnesium content of the resulting extract is not substantially greater than about 4 grams per liter.

6. The process of controlling the magnesium content of the catholyte and anolyte in the electrowinning of manganese which comprises withdrawing anolyte from the anolyte chamber, said anolyte containing manganese sulfate, ammonium sulfate, magnesium sulfate and sulfuric acid, treating it with a proportion of soluble fluoride at a pH of about 1.5 to 2.75 insufficient to precipitate all of the magnesium, precipitating a portion of the magnesium as magnesium fluoride, leaving the remainder of the magnesium in solution to the extent of not more than about 4 grams of magnesium per liter, filtering the precipitate, extracting conditioned manganese ore with the filtrate, treating said extract to remove therefrom heavy metals other than manganese and to remove excess fluoride, separating said heavy metals and employing said purified extract as catholyte liquid.

7. The process of limiting the magnesium content of the catholyte and anolyte in the electrowinning of manganese to a value not substan-

tially above 4 grams of magnesium per liter, which comprises withdrawing anolyte liquor from the anolyte chamber, said anolyte containing manganese sulfate, ammonium sulfate, magnesium sulfate and sulfuric acid, treating it with a proportion of a soluble fluoride insufficient to precipitate all of the magnesium, precipitating a portion of the magnesium and reducing its concentration to a value substantially less than 4 grams per liter, filtering the precipitate, extracting conditioned manganese ore with said filtrate, treating said extract to remove therefrom heavy metals other than manganese and to remove excess fluoride, separating said heavy metals and employing said purified extract as catholyte liquid.

8. The process of controlling the magnesium

content of the catholyte and anolyte in the electrowinning of manganese which comprises extracting conditioned manganese ore containing magnesium as an impurity with said anolyte containing sulfuric acid and having a pH of 0.5 to 1.5 and obtaining an extract containing manganese sulfate and magnesium sulfate and having a pH of about 1.5 to 2.75, treating said extract with a proportion of a soluble fluoride insufficient to precipitate all of the magnesium, precipitating a portion of the magnesium and leaving the remainder in solution to the extent of not more than about 4 grams of magnesium per liter and removing excess fluoride.

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