This invention relates to improvements in the electrowinning of manganese. More particularly it relates to improvements in controlling the purity of the electrolyte and of the manganese deposited therefrom on the cathode.

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.

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 magnesium 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.

If the magnesium content is 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 outlets 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 contaminate it, or else tend to clog the diaphragm and the overflow pipes connecting the catholyte with the anolyte chamber. It is apparent that the deposition of contaminating influences on the cathode will also disturb electrical conditions in the cell.

As previously stated, the problem of controlling the content of magnesium in the electrolyte has been a serious one in the commercial electrowinning of manganese, and a great deal of effort has been expended in attempts to solve the problem without, however, arriving at a wholly satisfactory solution prior to the present invention. In general attempts to solve the problem by the addition of reagents to precipitate the magnesium have not been satisfactory, partly at least
because of side reactions caused by the introduction of the precipitating reagents.

The manganese electrolyte may be considered as a solution of manganese sulfate and ammonium sulfate contained as principal ingredients with other sulfates present chief among which are magnesium and iron sulfates due to the presence of these in the ore along with the manganese. The quantity of calcium sulfate might be considered as small and limited by the low solubility of the calcium sulfate in comparison to that of the other materials. Manganese sulfate is thought of as having relatively high solubility. Extensive experimental studies have shown that the solubility of magnesium sulfate is an inverse function of the concentration of ammonium sulfate and manganese sulfate and a direct function of temperature. It has been discovered that within the ranges of concentration of ammonium sulfate and manganese sulfate employed in the electrolytes for manganese electro-winning, complex sulfates of manganese, ammonium, magnesium, and calcium are formed, which complex sulfates have markedly different solubilities from any of the simple sulfates or double or triple sulfate combinations of these. A typical analysis of such complex sulfate is as follows:

<table>
<thead>
<tr>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
</tr>
<tr>
<td>MgSO₄</td>
</tr>
<tr>
<td>MnSO₄</td>
</tr>
<tr>
<td>CaSO₄</td>
</tr>
</tbody>
</table>

In addition these complex sulfates are not stable over a wide range of temperature but only exist over rather narrow ranges of temperature and in turn show low solubilities over these temperature ranges as evidenced by the fact that they readily crystallize out. These salts have been discovered to contain a higher proportion of magnesium than does the electrolyte from which they have been crystallized. It therefore follows that, if the complex salts are crystallized out of an electrolyte containing principally manganese and ammonium sulfates with magnesium as a contaminant in the form of its sulfate, the removal of this complex salt will serve as a mechanism for controlling the magnesium content of the electrolyte.

As previously stated, the electrolytic cell is a part of a path of circulation including the cell, the ore digesting station, and one or more purification stations for the removal of iron, nickel, and cobalt. Since the circulated electrolyte passes from the anolyte chamber to the catholyte chamber via the ore digesting station and purification stations mentioned, the impurities introduced into the electrolyte from the ore are cumulative and will continually build up unless removed, and this of course is true of magnesium as it is with the other impurities. For any given range of composition of electrolyte in terms of manganese sulfate and ammonium sulfate, separation of complex salts could in theory be prevented by increasing the temperature to a point where these salts are no longer stable and where they are soluble. However, in practice this would be wholly impractical because, due to the crystallization of magnesium and therefore continual increase in the concentration of complex salt, it would be necessary to continually increase the temperature. With increasing concentrations of magnesium and increasing temperature, electrical effects enter such as changes in overvoltage, electrical resistance, diaphragm potential differences, anode potentials, etc. It is therefore necessary to provide a commercially satisfactory practical method for removing magnesium and controlling the composition of the electrolyte so that the concentration of magnesium may be controlled at a point below a desired maximum whereby uniform conditions, including operation within a predetermined range of temperature, may be maintained.

It may be stated at this point that high temperatures accentuate the harmful effect of the impurities in the electrolyte, increase the anode corrosion, and often make working conditions difficult.

Attempts have been made to remove the magnesium and effect the control above mentioned by circulating cold water through a cooling coil placed at the ends of the platting cells or in a separate tank. These attempts have been found to be attended with serious objections on both technical and economic grounds. In the first place, the complex salt referred to above crystallizes or separates out on the heat exchange surfaces and reduces the heat transfer coefficient to such a low value that cooling efficiency is destroyed. Moreover, the removal of the crystals from a pipe cooling system is very difficult and costly. The most practical way of effecting this removal is to wash or flush them off with hot water. The complex salt is a valuable fertilizer and in order to realize its economic value must be sold in solid or crystalline form. Therefore the solution resulting from the washing of the crystals from the pipe coils must be concentrated by boiling, a process which is uneconomical.

As above described the process of electro-winning of manganese involves a cyclical operation and the circulation of the electrolyte in a path of circulation from the anolyte chamber to the catholyte chamber via certain purification stations.

In accordance with this invention the electrolyte or any predetermined or desired fraction thereof is treated to remove magnesium in the form of a complex salt thereof by cooling said electrolyte or fraction or portion thereof by reducing the temperature of said electrolyte by evaporative cooling in direct contact with the atmosphere, that is to say, the liquid to be cooled is subdivided into a plurality of parts having a plurality of surfaces. These parts and surfaces are exposed to direct contact with air at atmospheric temperatures. Cooling occurs largely by evaporation. A preferred apparatus element for effecting such cooling is a cooling tower. For example, a cooling tower may be passed through the cooling tower or a predetermined portion may be passed through said tower and the remainder recirculated by returning it to the inlet of the said path. Also all of the cooled liquid from the cooling tower may be sent forward in the circulation path or a predetermined fraction thereof may be sent forward and the remainder returned to the circulation path and thereby recirculated. The proportion of liquid cooled by the method described will depend on
various conditions including prevailing temperature and humidity conditions and the temperature range at which it is desired to maintain the electrolyte. By the method described the electrolyte is cooled to that range necessary to crystallize or precipitate the complex salt. In the case of a cooling tower the complex salt separates out on the baffle surfaces thereof and may be readily removed therefrom in solid form. The heat transfer involved is directly from the liquid to the atmosphere as contrasted with the transfer through metallic walls as in the case of cooling coils, the separation of the salt in no way reduces the efficiency of cooling. Moreover, as will more fully hereinafter be discussed, the cooling by evaporation effects the desired volume control.

While the principal purpose and advantage of the method and apparatus of this invention are directed to and connected with the removal of magnesium, there are at least two important corollary advantages, one in temperature control and the other volume control. By the method of the present invention it is possible to control the temperature of the electrolyte at any point in the path of circulation thereof. For example, liquid may be withdrawn from the anolyte chamber, a predetermined fraction thereof sent to a cooling tower, cooled and recirculated back to the anolyte chamber, and the remaining portion sent forward to the digester. In this way the temperature of the anolyte may be maintained within any desired temperature range. In another case anolyte may be withdrawn from the anolyte chamber, sent to a cooling tower and cooled, a portion of the cooled anolyte recirculated back to the anolyte chamber and the remainder sent forward to the ore digester, and by controlling the degree of cooling in the tower and the rate of recirculation not only may the temperature of the anolyte be maintained within a predetermined range, but also the temperature of the reaction in the digester may also be controlled. It may be added at this point that temperature control is particularly necessary in manganese electrowinning for reasons already stated. In respect of controlling the temperature in the digester, it may be pointed out that in some cases it is desirable to be able to cool the liquid delivered to the digester because of the exothermic reaction occurring in the digester as a result of reaction between anolyte and certain kinds of ores.

A further important corollary advantage of this invention is the provision of an efficient and economic control for the volume of the electrolyte. Manganese ores in general contain insoluble portions which must be separated from the leach liquors. These insoluble portions or gangue may be removed and made available as values of manganese solutions or ammonium sulfate solutions, which for economic reasons should be recovered as far as possible. It is therefore quite desirable to wash these residues with water or dilute solutions. The same situation obtains where the leach liquors are utilized in the course of purification of the leach liquors. Common examples of the impurities removed are iron, arsenic, antimony, cobalt, and nickel which are rendered insoluble in the form of hydroxides or oxides in the case of iron, arsenic, and antimony, and sulfides in the case of cobalt and nickel. For most effective washing it is desirable to employ as large a quantity of water or dilute solutions as possible without the corresponding penalty of reduction of concentration of manganese sulfate and ammonium sulfate. The concentration of these materials is desired to be maintained within limits because of their effect upon the resulting electrolysis. If, therefore, as a function of cooling an electrolyte there is involved evaporation losses of water, these losses may be restored in the form of wash liquids to treat gangue residue or precipitate impurities without payment of the penalty of reduction of the manganese sulfate and ammonium sulfate to an extent greater than restoration of these to their desired values. It is obvious that if an electrolyte be cooled and during such cooling suffer evaporation losses, it is likewise concentrated in respect to the initial concentrations of manganese sulfate and ammonium sulfate. The wash water introduced to recover values from the gangue and precipitated impurities is thus a mechanism for the restoration of the manganese sulfate and ammonium sulfate to their preferred values.

It will therefore be noted that the invention is characterized by a number of important advantages including the following: 1. Control of the purity of the electrolyte in terms of magnesium.

2. Economic recovery of the manganese and other values in the complex salt separated out.

3. Temperature control of the electrolyte at any desired point in the circulation system.

4. Effecting this temperature control by a highly efficient method.

5. Accurate control over the volume of the electrolyte in the entire circuit.

6. Effecting this volume control without substantial loss of ammonia.

7. Provision for utilization of wash water to recover values from gangues and precipitates without the disadvantage of dilution and without the necessity of discarding solutions or wash waters.

There are various ways of effecting the subdivision of the liquid and direct contact of the subdivided parts with air. At present, the most convenient apparatus for this purpose is the cooling tower of which there are various designs.

The invention will be defined in the claims and further described and illustrated by reference to the accompanying diagrammatic drawing, in which:

Fig. 1 shows diagrammatically a form of circulation and recirculation system; and

Fig. 2 shows diagrammatically a cooling tower.

Referring to Fig. 1, the cell 9 has a cathode 1 in a catholyte chamber 2 and an anode 3 in an anolyte chamber 4, these chambers being separated by diaphragm 20. From chamber 4 the line 7 provided with pump 6 and valve 6A leads to cooling tower 8. From collecting trough 8A provided with valve 8A leads back to chamber 4 via anolyte feed tank 25. Line 10 provided with valve 10A leads to the ore digesting station 11. Line 12 leads to mud filter 16 and purifying station 13 and from there, via filter 14, catholyte storage tank 16A and catholyte feed 17, line 15 leads to catholyte chamber 2. Line 22 provided with valves 22A and 22B leads from anolyte feed tank 25 to digester 11.

Referring to Fig. 2, the cooling tower 8 which may be of the natural or forced draft variety has baffles 18 as shown, collecting trough 8A and feed trough 19.

To illustrate an application of the process of the invention, current is passed through the
4. Anolyte in chamber 4 and the catholyte in chamber 2 from anode 3 to cathode 1 and, coincidental with the deposition of manganese, heat is developed. Anolyte (which may contain for example 150 to 175 grams ammonium sulfate and 5 to 15 grams manganese, as manganese sulfate, per liter and also containing magnesium and sulfuric acid corresponding to a pH of 1.5 to 2 and having a temperature of 35° to 50°C) is withdrawn by means of pump 6 and line 7 and delivered to cooling tower 8 where it is cooled to a temperature sufficient to precipitate magnesium as a complex salt, e.g., MgSO₄·7H₂O. The cooled liquid is returned to chamber 4 by line 8, valve 22A being closed and valve 9A open, and thus recirculated and the rate of recirculation is adjusted to maintain the temperature of the liquid in the cooling tower between the desired limits under the prevailing conditions of atmospheric temperature and humidity. Solid material, e.g., crystals of the complex salt above referred to, are deposited on the baffles 18 and may readily be removed therefrom.

Part of the warm anolyte from chamber 4 is sent forward to the ore digestion station 11, via line 10, where manganese ore is extracted. The extract, which may be partly purified in the digester, is then sent to mud filters 16 and then to purification station 13 where such further purification as may be necessary is effected by precipitation of impurities which are filtered in filter 14. Washing with fresh water of the filter cake of filter 16 (or of the filter cakes produced at any other stage of the process, whether or not specifically shown) may be accomplished with an amount of water equal to that removed by evaporation in the cooling tower without any substantial change in the total volume of liquid. Solid material separated in the cooling tower is readily and efficiently removable therefrom.

Another example of operation is as follows: Anolyte from chamber 4 is withdrawn through pipe 7 by means of pump 6 (valve 10A being closed) and all of said anolyte is sent to cooling tower 8 and then to anolyte feed tank 25 through line 8A. A portion may be recirculated back to anolyte chamber 4 through line 8 (valve 8A being open to the desired extent) and the remainder sent to digester 11 (valve 22B being open and valve 22A being open to the desired extent).

Instead of a cooling tower, any device which provides evaporation by direct contact of liquid with air at normal atmospheric temperatures, by subdivision of the liquid and direct contact of the subdivided parts thereof with air, e.g., spraying devices, may be employed.

While anolyte is commonly contacted with manganese ore to replenish the manganese removed from the electrolyte by cathodic deposition, it will be clear that the anolyte may be contacted with any source of manganese sulfate. Where a manganese carbonate ore is employed the manganese carbonate is the source of the manganese sulfate since the carbonate reacts with the sulfuric acid of the anolyte to generate manganese sulfate. However, as stated, any suitable source of manganese sulfate may be employed instead of manganese ore. For example, manganese sulfate itself may be employed, or any source of which will constitute a source of manganese sulfate.

What is claimed is:

1. In a process for the electrowinning of manganese employing an electrolytic cell having a cathode in a catholyte in a catholyte chamber, said catholyte containing manganese sulfate, magnesium sulfate and ammonium sulfate, and an anode in an anolyte in an anolyte chamber, said anolyte containing manganese sulfate, magnesium sulfate, ammonium sulfate and sulfuric acid, and in which process the anolyte is withdrawn from the anolyte chamber, contacted with manganese carbonate, to produce an extract which is subjected to treatment to remove impurities and obtain a purified extract which is delivered to the catholyte chamber, thus establishing a path of circulation of liquid from anolyte chamber to catholyte chamber and in which process the solution of the electric current from anode to cathode causes the evolution of heat in the anolyte and catholyte, the improvement which comprises diverting liquid from said path of circulation, subdividing said liquid into a multiplicity of parts having a multiplicity of surfaces adapted for evaporation and cooling of said liquid, exposing said parts and surfaces to direct contact with air at atmospheric temperatures whereby evaporation and cooling of said liquid and separation of a complex magnesium salt therefrom occurs, returning cooled liquid to said path of circulation and collecting the said salt separate from said liquid.

2. In a process for the electrowinning of manganese from magnesium-containing manganese ore employing an electrolytic cell having a cathode in a catholyte in a catholyte chamber, said catholyte containing manganese sulfate, magnesium sulfate and ammonium sulfate, and an anode in an anolyte in an anolyte chamber, said anolyte containing manganese sulfate, magnesium sulfate, ammonium sulfate, and sulfuric acid, and in which process the anolyte is withdrawn from the anolyte chamber, contacted with manganese ore to produce an extract which is subjected to treatment to remove impurities and obtain a purified extract which is delivered to the catholyte chamber, thus establishing a path of circulation of liquid from anolyte chamber to catholyte chamber and in which process the solution of the electric current from anode to cathode causes the evolution of heat in the anolyte and catholyte, the improvement which comprises diverting liquid from said path of circulation, subdividing said liquid into a multiplicity of parts having a multiplicity of surfaces adapted for evaporation and cooling of said liquid, exposing said parts and surfaces to direct contact with air at atmospheric temperatures whereby evaporation and cooling of said liquid and separation of a complex magnesium salt therefrom occurs, returning cooled liquid to said path of circulation and collecting the said salt separate from said liquid.
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causes the evolution of heat in the anolyte and
catholyte, the improvement which comprises re-
moving liquid from said electrolytic cell, subdiv-
ding said liquid into a multiplicity of parts hav-
ing a multiplicity of surfaces adapted for evapo-
ration and cooling of said liquid, exposing said parts and surfaces to direct contact with
air at atmospheric temperatures whereby evap-
oration and cooling of said liquid and separation of a complex magne-
sium salt therefrom occurs, returning at least a portion of said cooled liquid to said cell
and thus establishing a path of recirculation of
cooled liquid.

5. In a process for the electrowinning of man-
ganese from magnesium-containing manganese
ore, employing an electrolytic cell having a cath-
yte in a catholyte chamber, said catholyte contain-
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tures whereby evaporation and cooling of said
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salt therefrom occurs, and returning at least a
portion of said cooled anolyte liquid to the
anolyte chamber of said cell.

6. In a process for the electrowinning of man-
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anolyte chamber of said cell.

7. In a process for the electrowinning of man-
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