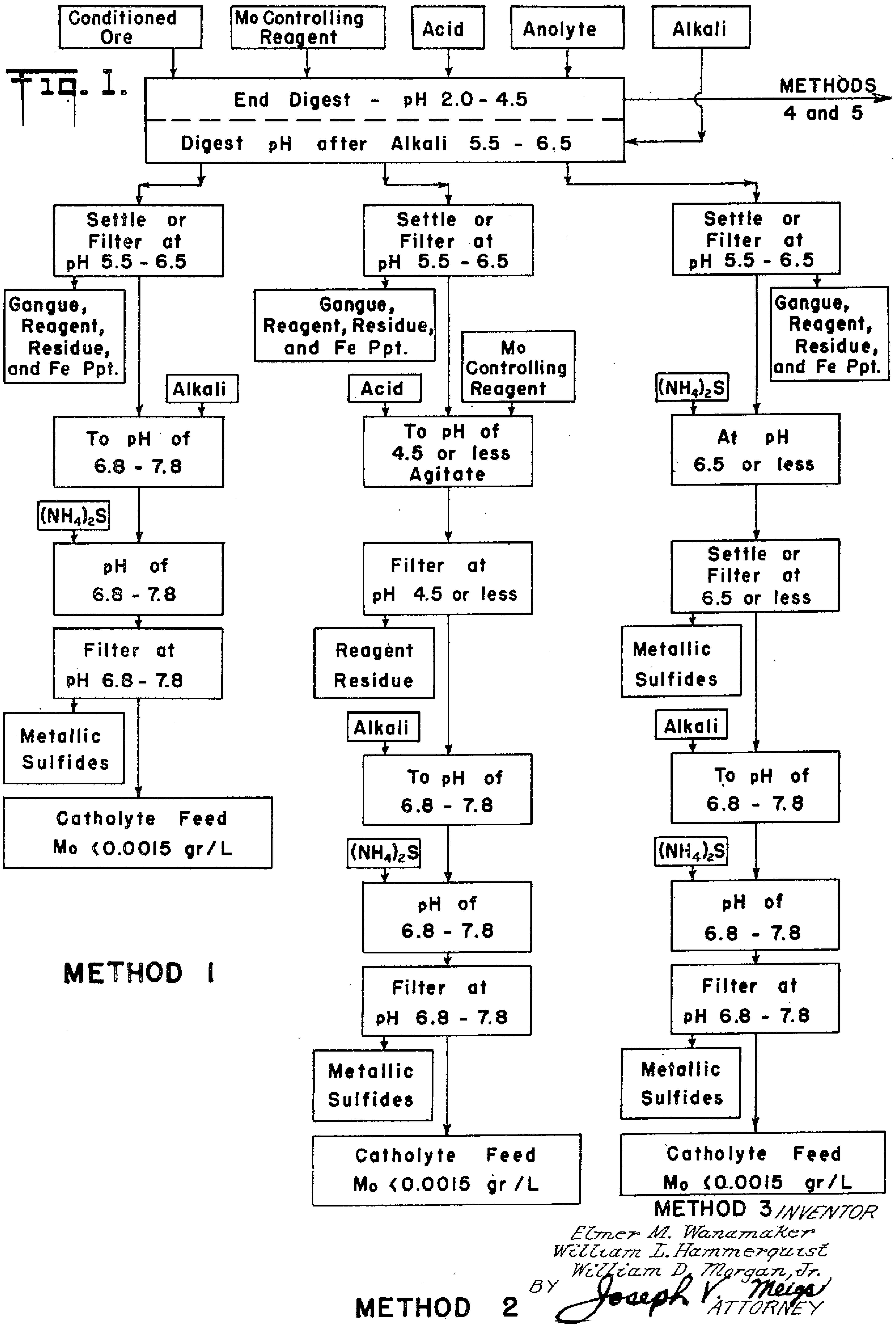
Jan. 23, 1951 E. M. WANAMAKER ET AL 2,538,995

MOLYBDENUM CONTROL FOR MANGANESE ELECTROWINNING

Filed May 15, 1948 2 Sheets-Sheet 1

Fig. 1.



INVENTOR

Elmer M. Wanamaker
William L. Hammerquist
William D. Morgan, Jr.

BY Joseph V. Meigs
ATTORNEY

MOLYBDENUM CONTROL FOR MANGANESE ELECTROWINNING

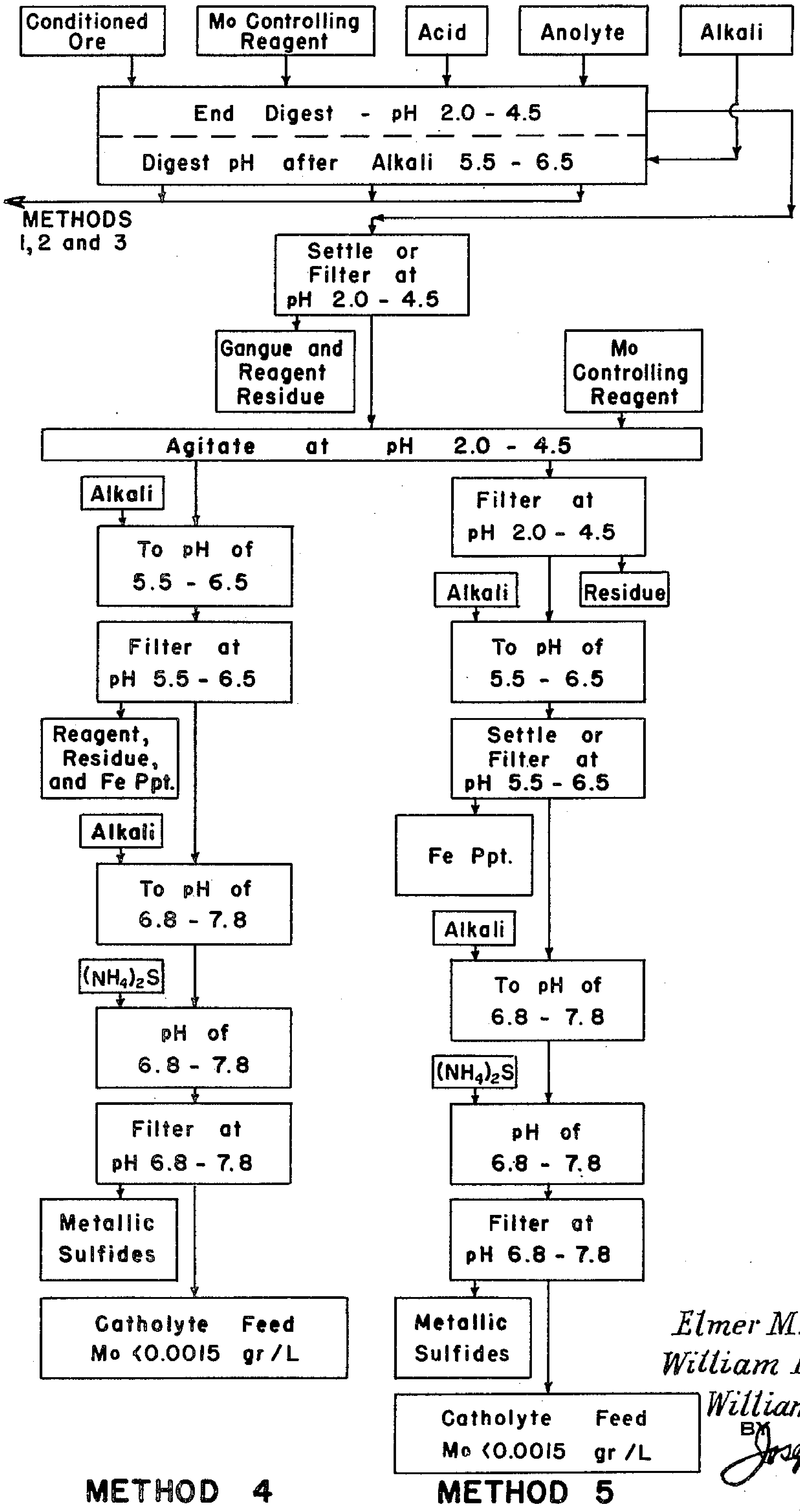


FIG. 2.

INVENTORS
Elmer M. Wanamaker
William L. Hammerquist
William D. Morgan, Jr.
BY *Joseph K. Meigs*
ATTORNEY

Patented Jan. 23, 1951

2,538,995

UNITED STATES PATENT OFFICE

2,538,995

MOLYBDENUM CONTROL FOR MANGANESE ELECTROWINNING

Elmer M. Wanamaker, William L. Hammerquist, and William D. Morgan, Jr., Knoxville, Tenn., assignors to Electro Manganese Corporation, Knoxville, Tenn., a corporation of Delaware

Application May 15, 1948, Serial No. 27,316

6 Claims. (Cl. 204—105)

This invention relates to processes for the electrowinning of manganese whereby improved operating results are obtained by controlling the molybdenum content of the solutions and this application is a continuation-in-part of our copending application, Serial No. 704,510, filed October 19th, 1946, now abandoned.

In this art, electrolytic cells are employed in which the electrolyte is divided into separate parts called anolyte and catholyte, respectively. Sometimes there are a plurality of catholyte chambers, each containing a cathode, arranged in a row and separated by porous diaphragms from the remaining space within the cell, constituting the anolyte chamber in which the anodes are disposed in spaced relation to and between the several cathode chambers. Sometimes this relation is reversed, i. e., the catholyte chambers are substituted by anolyte chambers and the remaining space in the cell constitutes the catholyte chamber, the cathodes being disposed in this chamber in spaced relation to and between the several anode chambers. Other arrangements may be used. In any event, the anodes and cathodes are respectively connected in parallel electrically and the two groups connected electrically in series and current is passed from the anode group to a cathode group to deposit manganese on the cathode.

For the purpose of simplicity of description the anolyte and catholyte will each be assumed to be a single body of liquid, these bodies being separated by a porous diaphragm through which spent catholyte passes from the catholyte chamber to the anolyte chamber.

In the catholyte chamber the electrolyte, containing for example from 130 to 200 grams of ammonium sulfate per liter, is partially stripped of its manganese content from a value which may be, illustratively, 25 to 35 grams per liter of manganese as manganous sulfate, down to a value which may be about 15 grams per liter in a typical case. The catholyte is alkaline and may have a pH of about 7 to 9. The spent catholyte passes to the anolyte chamber and becomes anolyte, the pH undergoing a marked change from the alkaline to the acid condition due to electrochemical changes.

In order to regenerate catholyte, anolyte which is acid and may have a pH of about 0.5 to 2, as an illustration, is commonly withdrawn from the cell and submitted to a series of treatments having two primary purposes (1) the addition of manganese in soluble form and in the manganous condition and (2) the purification of the solution

obtained by the enrichment step. After these treatments, the liquid is returned to the catholyte compartment or compartments of the cell.

It will thus be seen that a path of liquid circulation is established beginning, let us say, in the catholyte chamber and ending there, the purpose being to continuously supply the catholyte chamber with properly conditioned liquid to provide a solution from which manganese may satisfactorily be plated on the cathode or cathodes.

While the process sounds simple and easy, actually it is extremely complex in respect to the known and unknown electrical, electrochemical and chemical reactions occurring. If a pure manganese salt, e. g., pure manganous sulfate were commercially available at a sufficiently low cost, it would be greatly simplified. However, when it is appreciated that the raw materials are manganese compounds associated or combined with other materials, e. g., a manganese bearing ore containing many other elements and compounds, and the final product is metallic manganese having a purity of over 99.9 per cent, some of the difficulties become more apparent.

Ordinarily, manganese bearing ore is the source from which the liquid withdrawn from the cell is enriched in its manganese content although other sources may be employed, e. g., manganese bearing solutions obtained as a by-product in the chemical arts where manganese dioxide or ores containing higher oxides of manganese are used as oxidizing agents, e. g., in the oxidation of aniline to make quinone or hydroquinone.

It will be seen that the liquid in its path of circulation constitutes a body or reservoir, that at one point in the cyclic path manganese is removed (in the cell) and that at another point or points manganese is added.

There are many elements and compounds associated or combined with manganese in ores and other manganese bearing raw materials, e. g., iron, arsenic, silicon, molybdenum, cobalt, nickel and copper, to mention some of the more common elements.

The control of these elements so as to obtain catholyte from which manganese may be readily and satisfactorily deposited is an important consideration. It will be understood that some of the elements associated with manganese occur, as for example in the ore, in considerable quantities, others in smaller or even minute proportions. In view of the nature of the process above described, the concentration, in the body or reservoir of circulatory liquid, or elements occurring even in minute proportions in the source of manganese, will result in an accumulation of those elements in the electrolyte in the cell unless proper control is exercised.

The problem is not merely one of preventing contamination of the manganese cathodic deposit by the impurities. Some of the elements exercise a far more serious and subtle effect, i. e., they tend to interfere with the electrochemical reactions, more particularly with current efficiency and satisfactory deposition and in some cases actually inhibit deposition of manganese.

Molybdenum has been found to be a particularly insidious enemy to economical and successful plating operations in manganese electrowinning. Its source is in the manganese containing ore or other material used to replenish the spent anolyte. It occurs in various valence forms and combinations with other elements, and in widely varying proportions depending on the source of the molybdenum bearing material. Its effect on the plating of manganese varies as a function of numerous variables including the source, the proportion of molybdenum in the source and the teatment, if any, to which that source, e. g., manganese bearing ore has been submitted prior to contact or admixture with spent anolyte. In the absence of proper control, the presence of molybdenum in the electrolyte is a source of erratic results and phenomena difficult to explain or understand, such as blackened plates accompanied by marked decrease in current efficiency, and in some cases by characteristic striations in the metallic surface, usually followed by complete cessation of manganese deposition.

With short plating cycles the bad effects of molybdenum are less marked than when plating cycles of 24 to 48 hours, necessary in the commerical electrowinning of manganese, are employed.

Notwithstanding the numerous variables affecting the behaviour of molybdenum as related to manganese electrowinning, it has been found that its deleterious effects can be obviated by controlling the proportion thereof in the solutions used for plating, so that that proportion does not exceed a maximum critical value. The invention therefore provides a method of control whereby dependable and uniform plating results may be obtained, insofar as the effects of molybdenum are concerned, notwithstanding wide and uncontrollable variations in the factors above-mentioned including, for example, the kind of ore, the form or forms of molybdenum therein, the proportion of molybdenum therein, the treatment of the ore prior to extraction of the manganese content thereof, etc.

It has been found that if the molybdenum content of the solutions employed for manganese electrowinning, more specifically the molybdenum content of the catholyte which is fed to the electrolytic cell is so controlled as not to exceed a critical value of about 0.0015 gram per liter that the above-mentioned deleterious effects are avoided and adequate control of molybdenum effected.

One of the important considerations is the ratio of manganese to molybdenum in the ore. It is not so much the absolute percentage in the ore of molybdenum which is important as the ratio of manganese to molybdenum. This is so because a certain proportion of ore has to be digested with the anolyte withdrawn from the cell in order to replenish therein the content of manganese from the relatively low concentration of the manganese in the anolyte as withdrawn from the anolyte chamber to the higher concentration which is necessary in order that the solution may be satisfactorily used as catholyte. The proportion of ore which is necessary to effect this increase in manganese concentration varies with the manganese content of the ore. Therefore a relatively low grade ore containing a relatively low proportion of manganese and a relatively low proportion of molybdenum will introduce as much molybdenum into the solution as a higher grade ore containing a higher percentage of manganese and a higher percentage of molybdenum. A ratio of manganese to molybdenum of 25,000/1 may be regarded as high (low Mo) and a ratio of manganese to molybdenum of 500/1 may be regarded as low (high Mo). It has been found that certain methods which are effective in the case of a low molybdenum ore are quite ineffective in the case of a high molybdenum ore.

A principal object of the present invention is to provide processes which will be generally effective in the case of all ores which may be encountered and except as hereinafter specifically noted the methods of the present invention are effective to control the molybdenum content of ores in general containing manganese and molybdenum.

The principles of the invention will be defined in the claims and certain typical or specific methods will be described in order to illustrate those principles.

In the description of the invention reference may be had to the accompanying drawings wherein Fig. 1 is a flow sheet outlining three methods which illustrate the principles of the invention and Fig. 2 comprises a flow sheet outlining two additional methods illustrating the principles of the invention.

In accordance with the invention spent anolyte containing manganese sulfate, ammonium sulfate, and sulphuric acid is withdrawn from the anolyte chambers of one or more cells and is sent to a digester or tank where it is treated in accordance with the present invention, that treatment including the addition of conditioned manganese ore and a reagent which is composed of cell sludge or raw manganese ore or a mixture thereof to produce a digest slurry. The anolyte, as it comes from the cell, is "spent," and in a typical case contains from about 8 to 18 grams per liter of manganese as manganous sulfate, about 100 to 180 grams per liter of ammonium sulfate, and has a pH of about 0.5 to 2.0. In the digest tank the anolyte is mixed with conditioned ore, primarily for the purpose of increasing the content of manganese to the value which is desirable in order that the resulting solution may be used as catholyte, that increase in value being equal to the decrease in concentration of the manganese in the electrolyte caused by cathodic deposition of manganese. Specific examples of such decreases are 15, 20 and 25 grams per liter. The proportion of ore to accomplish this purpose depends upon the percent of manganese in the ore and the solubility in the solution of the manganese compound or compounds in the ore. The acidity of the solution is due to the presence of sulphuric acid in the anolyte and additional sulphuric acid may be added. In a typical case 2100 pounds of ore are digested with 8,000 gallons of anolyte containing 15 grams per liter of manganese as manganous sulfate and having a pH of about 0.5 to 2.0 and about 700 to 900 pounds of 60° Bé. sulphuric acid is added to complete the extraction of the manganese at a maximum pH of about 4.5. In that typical case 99 per cent or more of the manganese is extracted and the resulting digest solution contains 30 grams per liter of manganese as manganous sulfate. In accordance with the present invention the major portion, e. g., about 95% and preferably over 99% of the manganese content of the ore, is soluble in the acid solution which might perhaps better be termed slurry or digest solution, those being terms employed in the art. Such solubility is rare in a native or raw ore. Most ores contain manganese in a higher state of oxidation, that is, higher than corresponds to a valence of 2, and the manganese in those ores is difficultly soluble or insoluble. To transform the manganese therein to a soluble condition, it is necessary to give the ore a conditioning or heat treatment. Suitable conditioning treatments will be seen by reference to Wanamaker, et al., U. S. Patents 2,397,824, April 2, 1946, and 2,384,862, September 18, 1945. The treatment described in those patents includes heating the ore to a high temperature in the presence of carbon. However, some ores do not require said treatment because the manganese is found therein in nature in the form of a salt or compound, e. g., $MnCO_3$ which is readily soluble in dilute sulphuric acid. The invention is applicable to the electrowinning of manganese from those ores. Indeed, the invention is not limited to the electrowinning of manganese solely from ores but extends to the electrowinning of manganese from any source thereof capable of providing manganous sulfate, where the problem of molybdenum control arises. One of such sources is represented by the solutions obtained as by-products in the chemical industries, e. g., where pyrolusite or other products containing higher oxides of manganese (associated with molybdenum) have been used as a reagent. Examples of such by-products are aqueous solutions obtained by the oxidation of aniline by means of pyrolusite or other ores containing higher oxides of manganese associated with molybdenum, said by-product solutions containing components as shown below:

Solution No.	1	2
Ratio Mn/Mo	22,000/1	6,000/1
Manganese (as $MnSO_4$) g./l.	107.5	107.8
Molybdenum g./l.	0.0049	0.018
Ammonium sulfate g./l.	54	50

It is to be noted that in accordance with the present invention the source of electrodeposited manganese is material in which the manganese exists practically wholly in the manganous condition as for example, an ore in which at least 95% of the manganese and preferably 99% or more is in the manganous soluble condition. Nevertheless it is an essential feature of this invention that the reaction mixture including the anolyte contains a measured but appreciable quantity of manganese components in stages of higher oxidation and which are insoluble in the anolyte. In accordance with the present invention deliberate addition of such components, e. g., raw or unconditioned ore is made. It is recognized that the introduction of these manganese components which are unconditioned represents a deliberate inefficiency in the extraction of manganese and its conversion into soluble form. This inefficiency is however more than compensated for by the resulting advantages. The above-mentioned manganese components in which the manganese has a valence higher than two are, preferably, added to the spent anolyte at a pH range (of said anolyte) of 0.5 to 2.0.

The molybdenum controlling reagents employed herein include either cell sludge or raw ore in which the major portion of the manganese is in a state of oxidation higher than corresponds to a valence of two, or a mixture thereof, that is, said cell sludge or raw ore are the preferred forms of the above-mentioned manganese components in which the manganese exists in a state of oxidation corresponding to a valence greater than two. Cell sludge is sometimes referred to as anode sludge or anode mud. It is a product formed as a result of anodic oxidation. The anodes employed in manganese electrowinning commonly contain a preponderating proportion of lead. Some of the anodes contain such preponderating proportions of lead along with other elements such as tin, antimony, and cobalt. Others may consist wholly of lead or lead with a small proportion of silver. The anode sludge or cell sludge consists largely of manganese dioxide together with the peroxide or dioxide of the element or elements of which the anode is composed. It is necessary to remove said sludge from the anode compartments to maintain satisfactory operation of the cells and as this material is removed it commonly contains about 70% by weight of dry solids and about 30% by weight of water. It exists in the form of granules or aggregates the size of which is indicated by the fact that in a typical case about ⅓ passes through a 200 mesh screen and ⅔ is retained thereon. When this material is ground, as for example in a ball mill, slurry is formed and in a typical case the fineness of the particles thereof is indicated by the fact that over 97% passes through a 200 mesh screen, indeed, the major portion, e. g., over 80 per cent, passes through a 400 mesh screen. The ground anode sludge is preferred because its action is more rapid than that of the unground material. In respect of the raw ore containing higher oxides of manganese which may be employed as one of the reagents of the present invention, this material preferably is in accordance with the invention ground to a fineness comparable to that of unground cell sludge, i. e., such that at least about ⅓ passes through a 200 mesh screen. The products of the grinding operation are commonly delivered to a cyclone separator. The portion thereof which does not settle out in the separator and remains suspended in the air is collected in filters known as bags. This material is known as "bag-house dust" in the art. The particle size is so small that practically all of it passes through a 200 mesh screen, the major portion, e. g., over 90 per cent, passes through a 400 mesh screen.

As above-mentioned, the ore contains in addition to manganese numerous other elements among which iron, arsenic, nickel, cobalt and copper may be mentioned. Owing to the prevalence of iron in ores, the result of the conditioning treatment involving the use of carbon as reducing agent may introduce ferrous iron into the digest solution or slurry in amounts of from 0.1 to 0.3 gram per liter of ferrous ion. Should however the ore be deficient in iron then from 0.1 to 0.3 gram per liter of ferric or ferrous ion, preferably in the form of ferrous or ferric sulfate, are added as hereinafter described.

In the five methods described specifically below there is a series of steps generic to and found in all methods and that series of steps may be described as follows:

Spent anolyte having a pH of 0.5 to 2.0 is reacted with conditioned ore and a molybdenum controlling reagent which is generically a manganese compound containing on a dry basis not less than 50 per cent by weight of manganese dioxide and may be anode sludge or raw ore. Other species are the manganese dioxide produced for use in dry batteries and the manganese dioxide produced as a by-product in zinc electrowinning. The reaction is carried out in the presence of iron sulfate in an amount to provide a concentration of from 0.1 to 0.3 gram per liter of an ion of the group consisting of ferrous and ferric ion. The molybdenum controlling reagent is used in the proportion of from 25 to 100 pounds of said reagent, calculated on a dry basis, per 8,000 gallons of digest solution. The conditioned ore is used in a proportion which will effect an increase in the concentration of manganese in the digest solution equal to the decrease in concentration of manganese in the electrolyte caused by cathodic deposition of manganese.

The above-mentioned reaction is completed at a pH not exceeding 4.5 and within the range of 2.0 to 4.5. At a subsequent stage of the process the pH of the solution is raised to 5.5 to 6.5 and insoluble matter is separated within that pH range that insoluble matter including insoluble residues of the molybdenum controlling reagent, molybdenum compounds and insoluble iron compounds. Thereafter the pH of the solution is raised to 6.8 to 7.8 and the solution is treated with a sulfide ion supplying material in that proportion which is supplied by 30 to 100 liters of commercial ammonium sulfide (containing 40 to 45 per cent $(NH_4)_2S$) per 10,000 gallons of solution. The result of that treatment is not only to precipitate the sulfides of cobalt and nickel but also to complete the treatment for the precipitation of molybdenum to the required extent. Insoluble material including said nickel and cobalt sulfides is separated and there is obtained a solution containing not more than 0.0015 gram per liter of molybdenum, said solution being ready for feeding to the catholyte chambers of the cells.

Five specific methods will now be described falling within the above described genus and employing the principles of the above described generic method.

Method No. 1

This method is applicable to ores where the Mn/Mo ratio varies from 25,000/1 to 1500/1.

Spent anolyte is reacted with conditioned ore and a molybdenum controlling reagent which may be raw ore or anode sludge. The reaction is carried out in the presence of iron sulfate in an amount to provide a concentration of from 0.1 to 0.3 gram per liter of ferrous iron or ferric iron. The said molybdenum controlling reagent is used in a proportion of from 25 to 100 pounds of said reagent, calculated on a dry basis, per 8,000 gallons of solution. The conditioned ore is used in sufficient proportion to effect an increase of 15 grams per liter in the concentration of manganese in the digest solution, i. e., concentration of manganese as manganous sulfate greater than the concentration of that manganese in the spent anolyte to the extent of 15 grams per liter. The reaction as above described is carried out so that the necessary increase in manganese concentration is effected at a pH not exceeding 4.5 and within the range of 2.0 to 4.5, it being understood that the pH of the spent analyte may be less than 2.0, e. g., 0.5 up to 2.0. Thereafter the pH of the slurry is raised to 5.5 to 6.5 and then within that range insoluble material is separated by filtration or otherwise, the insoluble material including gangue, reagent residues, molybdenum compounds and iron precipitate and the resulting solution having a pH of 5.5 to 6.5. Then the pH of that solution is raised to 6.8 to 7.8 and is treated with a sulfide ion supplying material not only to precipitate the sulfides of cobalt and nickel, but also as the final step in the series of steps to decrease the concentration of molybdenum in the solution to be obtained to a value not greater than 0.0015 gram per liter. The proportion of sulfide ion material used for this purpose is or is equivalent to that supplied by from 30 to 100 liters of commercial ammonium sulfide (containing 40 to 45 per cent $(NH_4)_2S$) per 10,000 gallons of solution. The insoluble material produced by that treatment is then separated and the resulting solution contains not more than 0.0015 gram per liter of molybdenum and is ready to be fed to the catholyte chambers of the solution.

Method No. 2

This method is applicable to the treatment of ores where the Mn–Mo ratio varies from 25,000/1 to 500/1.

This method differs from Method No. 1 in the following respects, such differences being readily ascertainable not only by the description of this method but also by reference to the accompanying flow sheet:

After the spent anolyte has been reacted with the ore in the presence of a soluble iron compound as described in Method No. 1 so as to produce the stated increase in concentration of manganese to the extent of 15 grams per liter and after said reaction has been completed at a pH not exceeding 4.5 and within a range of 2.0 to 4.5 and after the pH of the slurry has been raised to 5.5 to 6.5 and insoluble compounds separated, then prior to the step of raising the pH of the solution to 6.8 to 7.8 and treating with a sulfide ion supplying material the solution is given a second treatment with said molybdenum controlling reagent within the same range of proportions as described in Method No. 1 and at a pH not exceeding 4.5 and within the range of 2.0 to 4.5, then insoluble compounds including residues of said reagent are separated at a pH not exceeding 4.5 and within the range of 2.0 to 4.5. The pH of the resulting solution is then raised to 6.8 to 7.8 and treated with a sulfide ion supplying material as in Method No. 1.

Method No. 3

This method is applicable to ores having Mn/Mo ratio varying from 25,000/1 to 500/1.

This method differs from Method No. 1 in the following respects:

After the reaction or digestion of the spent anolyte with conditioned ore, molybdenum controlling reagent and ferrous or ferric ion has been completed so as to effect an increase in the concentration of manganese as manganous sulfate in the digest solution to the extent of 15 grams per liter (i. e. 15 grams per liter greater than the concentration of said manganese in the spent anolyte) and said increase in manganese concentration has been completed at a pH not greater than 4.5 and within the range of 2.0 to 4.5, and after the pH of the digest slurry has been increased to 5.5 to 6.5 and insoluble compounds separated within that pH range, then before increasing the pH of the solution to 6.8 to 7.8 and treating with a sulfide ion supplying material the following steps are carried out, as described herein and also as clearly indicated on the accompanying flow sheet for Method No. 3:

The solution having a pH of 5.5 to 6.5 is given an intermediate treatment with sulfide ion supplying material at a pH not exceeding 6.5 and within the range of 1.5 to 6.5, the proportion of sulfide ion supplying material being equivalent to that supplied by 25 to 75 liters of commercial ammonium sulfide having a content of 40 to 45 per cent of $(NH_4)_2S$. The insoluble material produced is separated at a pH not exceeding 6.5. Then the pH of the resulting solution is raised to 6.8 to 7.8 and treated with sulfide ion supplying material as in Method No. 1.

Method No. 4

This method is applicable to the treatment of ores where the Mn/Mo ratio varies from 25,000/1 to 500/1.

This method differs from Method No. 1 in the following respects:

After the reaction of the spent anolyte with conditioned ore and molybdenum controlling reagent in the presence of ferrous or ferric ion has been completed at a pH not exceeding 4.5 and within the range of 2.0 to 4.5 so as to effect an increase in the concentration of manganese as manganous sulfate to the extent of 15 grams per liter (such increase having been effected at a pH not exceeding 4.5), then instead of increasing the pH of the digest slurry to 5.5 to 6.5, insoluble material resulting from such reaction is separated at a pH not exceeding 4.5 and within a range of 2.0 to 4.5 and the resulting solution having a pH within the range of 2.0 to 4.5 is given a second treatment with molybdenum controlling reagent within the same range of proportions that was used in the first treatment. Said second treatment with said reagent occurs within a pH range of 2.0 to 4.5. Then, without separating insoluble material the pH of the reaction mixture is raised to 5.5 to 6.5 and insoluble material is separated within that pH range, that insoluble material including residues of said molybdenum controlling reagent, molybdenum compounds and insoluble iron compounds. Then the pH of the resulting solution is raised to 6.8 to 7.8 and given a treatment with sulfide ion supplying material as in Method No. 1, i. e., by using a proportion of sulfide ion material equal or equivalent to that supplied by 30 to 100 liters of commercial ammonium sulfide (containing 40 to 50 per cent $(NH_4)_2S$) per 10,000 gallons of solution.

Method No. 5

This method is applicable to ores where the Mn/Mo ratio varies from 25,000/1 to 500/1.

This method is the same as Method No. 4 except for the following, the differences being described herein and also being clearly shown on the accompanying flow sheet:

After the second treatment with molybdenum controlling reagent at a pH within the range of 2.0 to 4.5 insoluble material is separated within that pH range, that insoluble material including residues of said reagent, then the pH of the resulting solution is raised to 5.5 to 6.5 and insoluble material is separated within that pH range, that insoluble material including insoluble iron compounds. Then the pH of the resulting solution is raised to 6.8 to 7.8 and given a treatment with sulfide ion supplying material as in Method No. 4 (and also as in Method No. 1).

What is claimed is:

1. In the electrowinning of manganese from ores containing manganese in a state of oxidation higher than that corresponding to a valence of two together with molybdenum and other impurities, and employing an electrolytic cell containing anolyte and catholyte liquids, the passage of the electric current between the anodes and cathodes and through said liquids containing manganous sulfate and ammonium sulfate causing the deposition of metallic manganese on the cathodes, and employing the use of steps including heating said raw ore with a reducing agent until a conditioned ore is obtained in which at least 95 per cent by weight of the manganese therein is soluble in dilute sulfuric acid and using spent anolyte having a pH of about 0.5 to 2.0, about 8 to 18 grams per liter of manganese as manganous sulfate and ammonium sulfate to extract manganese from said conditioned ore, the process which comprises reacting the spent anolyte together with conditioned ore and a molybdenum controlling reagent which is a manganese compound containing on a dry basis not less than 50 per cent by weight of manganese dioxide, the reaction being carried out in the presence of iron sulfate in an amount to provide concentration of from 0.1 to 0.3 gram per liter of an ion of the group consisting of ferrous and ferric ion, the said molybdenum controlling reagent being used in the proportion of from 25 to 100 pounds of said reagent, calculated on a dry basis, per 8,000 gallons of digest solution, the said conditioned ore being used in a proportion to effect an increase in the concentration of manganese in the digest solution equal to the decrease in concentration of the manganese in the electrolyte caused by cathodic deposition of manganese, completing the above mentioned reaction at a pH within the range of 2.0 to 4.5; thereafter raising the pH of the solution to 5.5 to 6.5 and separating insoluble material within that pH range, and thereafter raising the pH of said solution to 6.8 to 7.8 and treating said solution with that proportion of sulfide ion supplied by 30 to 100 liters of commercial ammonium sulfide (containing 40 to 45 per cent of $(NH_4)_2S$) per 10,000 gallons of solution, separating insoluble material and obtaining a solution containing not more than 0.0015 gram per liter of molybdenum.

2. In the electrowinning of manganese from raw ores containing manganese in a state of oxidation higher than that corresponding to a valence of two, together with molybdenum and other impurities, the Mn to Mo ratio lying within a range of about 25,000/1 to 1500/1 and employing an electrolytic cell containing anolyte and catholyte liquids the passage of the electric current between the anodes and cathodes and through said liquids containing manganous sulfate and ammonium sulfate causing the deposition of metallic manganese on the cathodes, and employing a series of steps including heating said raw ore with a reducing agent until a conditioned ore is obtained in which at least 95 per cent by weight of the manganese therein is soluble in dilute sulfuric acid, and using spent anolyte having a pH of about 0.5 to 2.0, about 8 to 18 grams per liter of manganese as manganous sulfate, and ammonium sulfate, to extract manganese from said conditioned ore, the process which comprises

reacting the spent anolyte together with conditioned ore and a molybdenum controlling reagent of the group consisting of said raw ore and anode sludge, the reaction being carried out in the presence of iron sulfate in an amount to provide a concentration of from 0.1 to 0.3 gram per liter of an ion of the group consisting of ferrous and ferric ion, the said molybdenum controlling reagent being used in the proportion of from 25 to 100 pounds of said reagent, calculated on a dry basis, per 8,000 gallons of digest solution, the said conditioned ore being used in a proportion to effect an increase of 15 grams per liter in the concentration of manganese in the digest solution, completing the above mentioned reaction at a pH of 2.0 to 4.5, then raising the pH of the digest slurry to 5.5 to 6.5 and separating insoluble material within that pH range, then raising the pH of the resulting solution to 6.8 to 7.8 and treating said solution with that proportion of sulfide ion supplied by 30 to 100 liters of commercial ammonium sulfide (containing 40 to 45 per cent $(NH_4)_2S$) per 10,000 gallons of solution, separating insoluble material including nickel and cobalt sulfides and obtaining a solution containing not more than 0.0015 gram per liter of molybdenum.

3. In the electrowinning of maganese from raw ores containing magnanese in a state of oxidation higher than that corresponding to a valence of two, together with molybdenum and other impurities, the Mn to Mo ratio lying within a range of about 25,000/1 to 500/1 and employing an electrolytic cell containing anolyte and catholyte liquids, the passage of electric current between the anodes and cathodes and through said liquids containing manganous sulfate and ammonium sulfate causing the deposition of metallic manganese on the cathodes, and employing a series of steps including heating said raw ore with a reducing agent until a conditioned ore is obtained in which at least 95 per cent by weight of the manganese therein is soluble in dilute sulfuric acid and using spent anolyte having a pH of about 0.5 to 2.0, about 8 to 18 grams per liter of manganese as manganous sulfate, and ammonium sulfate, to extract manganese from said conditioned ore, the process which comprises reacting the spent anolyte together with conditioned ore and a molybdenum controlling reagent of the group consisting of said raw ore and anode sludge, the reaction being carried out in the presence of iron sulfate in an amount to provide a concentration of from 0.1 to 0.3 gram per liter of an ion of the group consisting of ferrous and ferric ion, the said molybdenum controlling reagent being used in the proportion of from 25 to 100 pounds of said reagent, calculated on a dry basis, per 8,000 gallons of digest solution, the said conditioned ore being used in a proportion to effect an increase of 15 grams per liter in the concentration of manganese in the digest solution, completing the above mentioned reaction at a pH of 2.0 to 4.5 then raising the pH of the digest slurry to 5.5 to 6.5 and separating insoluble material within that range, then decreasing the pH of the resulting solution to a value of 0.5 to 4.5 and again digesting said solution at a pH not exceeding 4.5 with the above mentioned proportion of molybdenum controlling reagent, then separating insoluble material at a pH not exceeding 4.5, then raising the pH of the resulting solution to 6.8 to 7.8 and treating said solution with that proportion of sulfide ion supplied by 30 to 100 liters of commercial ammoinum sulfide (containing 40 to 45 per cent $(NH_4)_2S$) per 10,000 gallons of solution, separating insoluble material including nickel and cobalt sulfides and obtaining a solution containing not more than 0.0015 gram per liter of molybdenum.

4. In the electrowinning of manganese from raw ores containing manganese in a state of oxidation higher than that corresponding to a valence of two, together with molybdenum and other impurities, the Mn to Mo ratio lying within a range of about 25,000/1 to 500/1 and employing an electrolytic cell containing anolyte and catholyte liquids, the passage of electric current between the anodes and cathodes and through said liquids containing manganous sulfate and ammonium sulfate causing the deposition of metallic manganese on the cathodes, and employing a series of steps including heating said raw ore with a reducing agent until a conditioned ore is obtained in which at least 95 per cent by weight of the manganese therein is soluble in dilute sulfuric acid and using spent anolyte having a pH of about 0.5 to 2.0, about 8 to 18 grams per liter of manganese as manganous sulfate and ammonium sulfate, to extract manganese from said conditioned ore, the process which comprises reacting the spent anolyte together with conditioned ore and a molybdenum controlling reagent of the group consisting of said raw ore and anode sludge, the reaction being carried out in the presence of iron sulfate in an amount to provide a concentration of from 0.1 to 0.3 gram per liter of an ion of the group consisting of ferrous and ferric ion, the said molybdenum controlling reagent being used in the proportion of from 25 to 100 pounds of said reagent, calculated on a dry basis, per 8,000 gallons of digest solution, the said conditioned ore being used in a proportion to effect an increase of 15 grams per liter in the concentration of manganese in the digest solution, completing the above mentioned reaction at a pH of 2.0 to 4.5 then raising the pH of the digest slurry to 5.5 to 6.5 and separating insoluble material within that pH range, then treating the solution at a pH of 1.5 to 6.5 with that proportion of sulfide ion equivalent to that supplied by 25 to 75 liters of commercial ammonium sulfide (containing 40 to 45 per cent $(NH_4)_2S$) per 10,000 gallons of solution, then separating insoluble material produced by that treatment at a pH not exceeding 6.5 then raising the pH of the resulting solution to 6.8 to 7.8 and treating said solution with that proportion of sulfide ion supplied by 30 to 100 liters of commercial ammonium sulfide (containing 40 to 45 per cent $(NH_4)_2S$) per 10,000 gallons of solution, separating insoluble material including nickel and cobalt sulfides and obtaining a solution containing not more than 0.0015 gram per liter of molybdenum.

5. In the electrowinning of manganese from raw ores containing manganese in a state of oxidation higher than that corresponding to a valence of two, together with molybdenum and other impurities, the Mn to Mo ratio lying within a range of about 25,000/1 to 500/1 and employing an electrolytic cell containing anolyte and catholyte liquids, the passage of electric current between the anodes and cathodes and through said liquids containing manganous sulfate and ammonium sulfate causing the deposition of metallic manganese on the cathodes, and employing a series of steps including heating said raw ore with a reducing agent until a conditioned ore is obtained in which at least 95 per cent by weight of the manganese therein is solu-

ble in dilute sulfuric acid and using spent anolyte having a pH of about 0.5 to 2.0, about 8 to 18 grams per liter of manganese as manganous sulfate, and ammonium sulfate, to extract manganese from said conditioned ore, the process which comprises reacting the spent anolyte together with conditioned ore and a molybdenum controlling reagent of the group consisting of said raw ore and anode sludge, the reaction being carried out in the presence of iron sulfate in an amount to provide a concentration of from 0.1 to 0.3 gram per liter of an ion of the group consisting of ferrous and ferric ion, the said molybdenum controlling reagent being used in the proportion of from 25 to 100 pounds of said reagent, calculated on a dry basis, per 8,000 gallons of digest solution, the said conditioned ore being used in a proportion to effect an increase of 15 grams per liter in the concentration of manganese in the digest solution, completing the above mentioned reaction at a pH of 2.0 to 4.5, then separating insoluble material within a pH range of 2.0 to 4.5, then again digesting the resulting solution with the above mentioned proportion of molybdenum controlling reagent at a pH of 2.0 to 4.5, then, without separating insoluble material, raising the pH to 5.5 to 6.5 and separating insoluble compounds within that pH range, then raising the pH of the resulting solution to 6.8 to 7.8 and treating said solution with that proportion of sulfide ion supplied by 30 to 100 liters of commercial ammonium sulfide (containing 40 to 45 per cent $(NH_4)_2S$) per 10,000 gallons of solution, separating insoluble material including nickel and cobalt sulfides and obtaining a solution containing not more than 0.0015 gram per liter of molybdenum.

6. In the electrowinning of manganese from raw ores containing manganese in a state of oxidation higher than that corresponding to a valence of two, together with molybdenum and other impurities, the Mn to Mo ratio lying within a range of about 25,000/1 to 500/1 and employing an electrolytic cell containing anolyte and catholyte liquids, the passage of electric current between the anodes and cathodes and through said liquids containing manganous sulfate and ammonium sulfate causing the deposition of metallic manganese on the cathodes, and employing a series of steps including heating said raw ore with a reducing agent until a conditioned ore is obtained in which at least 95 per cent by weight of the manganese therein is soluble in dilute sulfuric acid and using spent anolyte having a pH of about 0.5 to 2.0; about 8 to 18 grams per liter of manganese as manganous sulfate, and ammonium sulfate, to extract manganese from said conditioned ore, the process which comprises reacting the spent anolyte together with conditioned ore and a molybdenum controlling reagent of the group consisting of said raw ore and anode sludge, the reaction being carried out in the presence of iron sulfate in an amount to provide a concentration of from 0.1 to 0.3 gram per liter of an ion of the group consisting of ferrous and ferric ion, the said molybdenum controlling reagent being used in the proportion of from 25 to 100 pounds of said reagent, calculated on a dry basis, per 8,000 gallons of digest solution, the said conditioned ore being used in a proportion to effect an increase of 15 grams per liter in the concentration of manganese in the digest solution, completing the above mentioned reaction at a pH of 2.0 to 4.5, then separating insoluble material within said pH range of 2.0 to 4.5, then again digesting the resulting solution with the above mentioned proportion of molybdenum controlling reagent at a pH of 2.0 to 4.5, then separating insoluble material within said pH range of 2.0 to 4.5, then raising the pH of the resulting solution to 5.5 to 6.5, then separating insoluble compounds at said pH range of 5.5 to 6.5, then raising the pH of the resulting solution to 6.8 to 7.8 and treating said solution with that proportion of sulfide ion supplied by 30 to 100 liters of commercial ammonium sulfide (containing 40 to 45 per cent $(NH_4)_2S$) per 10,000 gallons of solution, separating insoluble material including nickel and cobalt sulfides and obtaining a solution containing not more than 0.0015 gram per liter of molybdenum.

ELMER M. WANAMAKER.
WILLIAM L. HAMMERQUIST.
WILLIAM D. MORGAN, JR.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,320,773	Fink et al.	June 1, 1943
2,325,723	Wanamaker et al.	Aug. 3, 1943
2,361,143	Leute et al.	Oct. 24, 1944
2,392,385	Hunter	Jan. 8, 1946

FOREIGN PATENTS

Number	Country	Date
528 112	Great Britain	of 1940