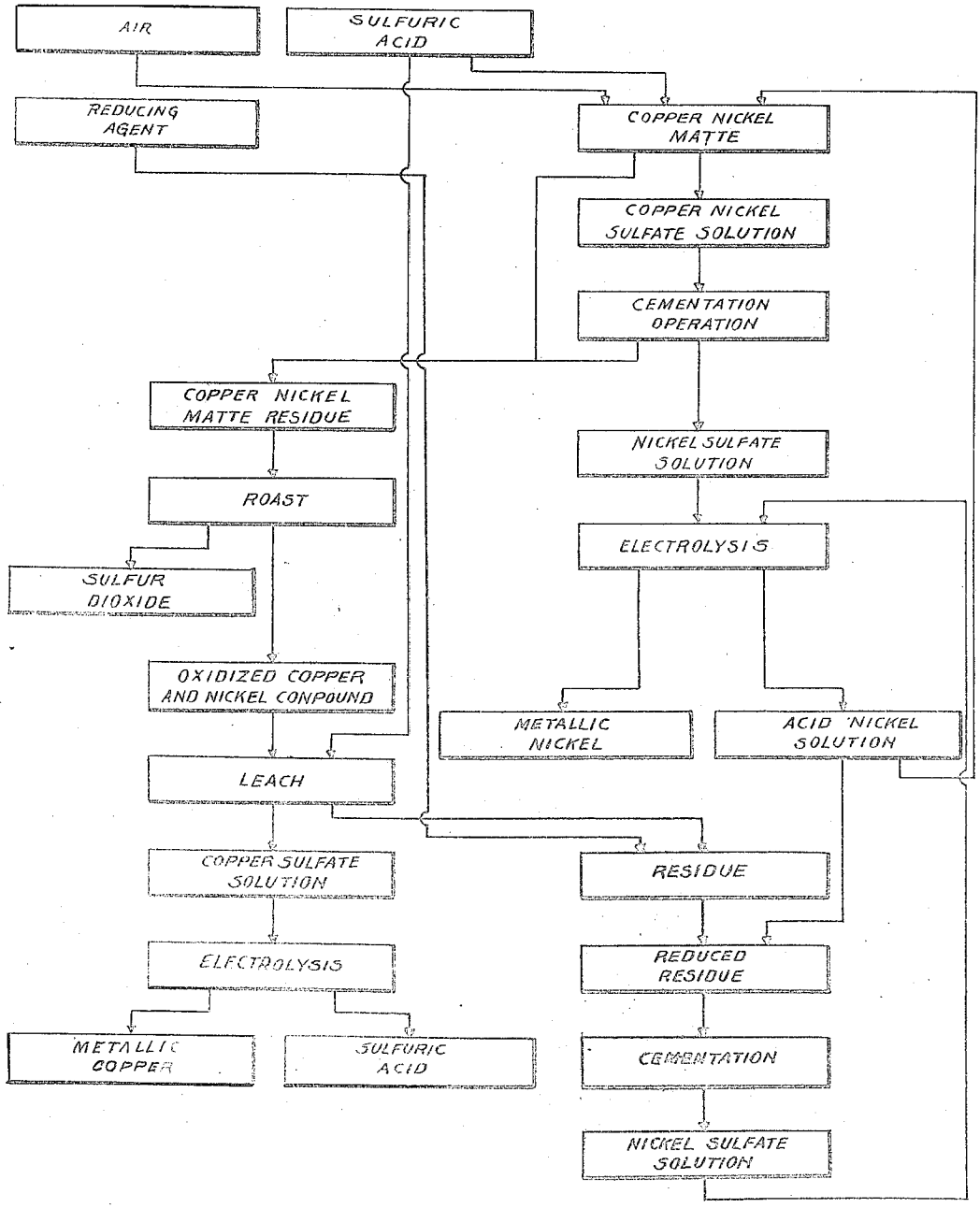
March 16, 1926. 1,577,422

N. V. HYBINETTE

REFINING COPPER NICKEL MATTE, ETC

Filed Jan. 13, 1921



INVENTOR
Noak Victor Hybinette

BY
Paine, Davis, Merriman & Edwards

ATTORNEYS

Patented Mar. 16, 1926. 1,577,422

UNITED STATES PATENT OFFICE.

NOAK VICTOR HYBINETTE, OF OTTAWA, ONTARIO, CANADA, ASSIGNOR, BY MESNE ASSIGNMENTS, TO ANGLO-CANADIAN MINING AND REFINING COMPANY, LIMITED.

REFINING COPPER-NICKEL MATTE, ETC.

Application filed January 13, 1921. Serial No. 437,021.

To all whom it may concern:

Be it known that I, NOAK VICTOR HYBINETTE, a subject of the King of Norway, residing at Ottawa, in the Province of Ontario, Dominion of Canada, have invented certain new and useful Improvements in Refining Copper-Nickel Matte, Etc.; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to improvements in the refining of copper-nickel matte, and includes improvements in the production of a purified nickel sulfate solution, and in the electrolytic process of refining nickel.

In my prior United States application Serial No. 358,968, I have set forth an improved method of producing nickel by electrolysis from an acid nickel-sulfate solution, in which method a filtering diaphragm is used and in which the excess acid is removed by the migration of acid ions from the cathode compartment to the anode compartment.

The present invention relates to further improvements in such electrolytic refining methods in which an acid nickel sulfate solution is employed, and more particularly to the carrying out of the process with the use of insoluble anodes, and the production and supply of a suitable nickel sulfate solution free from copper.

The present invention also relates to improvements in the treatment of bessemerized copper-nickel matte, which may be more or less desulfurized, for the production therefrom of a purified acid nickel sulfate solution by treatment of the matte with acid with introduction of air, until the acidity is reduced to the desired degree, and then removing the copper from the acid copper-nickel sulfate solution by cementation on a further portion of such matte without introduction of air.

The present invention also includes improvements in the treatment of bessemerized copper-nickel matte, according to which the matte is utilized for the removal of copper from copper-nickel sulfate solutions by cementation, until the cementing capacity of the matte is partially or completely exhausted, and the remaining matte and cement copper then roasted and the roasted and oxidized product leached with sulfuric acid, thereby dissolving the oxidized cement copper as well as part of the copper of the matte, then reducing the residue to the metallic state and dissolving the same by the action of acid copper-nickel sulfate solution with the aid of air. This process can advantageously be carried out as a balanced cyclic process in which the acid electrolyte from the electrolytic cells is utilized to dissolve the reduced copper-nickel residue, and in which the copper is cemented out from the resulting solution upon the bessemerized copper-nickel matte, the cementing capacity of the matte being utilized to such an extent, that, after roasting and leaching of the matte residue and cement copper, and reducing the leached material, the amount of copper contained therein will be such that it can be cemented out in the cementing operation referred to, upon the bessemerized copper-nickel matte.

The present invention includes also certain improvements in the combination of the processes of the two preceding paragraphs in which both the bessemerized copper-nickel matte itself, and the reduced copper-nickel material ultimately produced therefrom (after the cementing, roasting, leaching and reducing operations) may be utilized in either the cementing operation or in the dissolving and acidity neutralizing operation, or in both operations.

When bessemerized copper-nickel matte is treated with an acid solution, such as is produced in the anode compartment when insoluble anodes are used, it is acted upon but slowly and this action is unsatisfactory even at higher temperatures in that only a small amount of nickel goes into solution, but if a large quantity of air is blown into the solution at the same time, or otherwise introduced, the matte will be rapidly dissolved as long as there is an excess of acid. The operation can be continued to complete neutralization, but this involves additional time and expense, and is unnecessary for the production of an acid nickel sulfate electrolyte of the character above referred to, adapted for use in the electrolytic process of my said prior application. During the treatment of the matte with acid, in the presence of air, both copper and nickel go

into solution, and it is necessary to remove the copper from the solution to make it available for use in the electrolytic cell.

I have found that the dissolving of the bessemerized matte practically ceases when the supply of air or oxygen is cut off; and that, as soon as the aeration or oxidation is discontinued, cementation begins, irrespective of whether the solution is still acid or completely neutralized. I have also found that the cementation, as well as the solution of the metals, works best in a solution that is not brought to complete neutralization of free acid.

Accordingly, in the process of the present invention, according to one method of procedure, I subject the bessemerized copper-nickel matte, which may be desulfurized to a greater or less extent, to the action of the acid liquor, in the presence of air or oxygen, until the acidity has been reduced to the desired degree, thereby dissolving part of the nickel and copper of the matte; and I then subject the resulting solution, while still slightly acid, to cementation by treatment with a further portion of such matte for the removal of the copper from the solution and the production of a purified acid nickel sulfate solution. Instead of discontinuing the aeration while the solution is still acid, the aeration and solution of the metals can be continued to complete neutrality; and neutral copper-nickel sulfate solutions can thus be prepared where a neutral solution is required. I have found it of advantage, however, to stop the aeration and solution of the metal prior to complete neutralization, as above pointed out, and to treat the resulting still acid solution with further amounts of matte, without aeration, in order to free the solution from copper by cementation, thereby producing an acid nickel sulfate solution well adapted for use in the process of my said prior application.

The electrolyte supplied to the electrolytic cell should have a suitable composition, for example, about 4 to 5% of nickel as sulfate and about 0.1 to 0.2% of free sulfuric acid. Such an electrolyte, after the electroplating operation, will have a reduced nickel content and an increased acidity, for example, containing about 3 to 4% of nickel and about 1.6 to 1.7% free sulfuric acid. In order to carry out the process in a continuous and cyclic manner, the last mentioned solution must be replenished in nickel and must have its acidity neutralized to the proper degree. According to the present invention, the replenishment in nickel and neutralization of acid can be carried out simultaneously by treating the solution with the bessemerized copper-nickel matte, in the presence of air, and the resulting replenished and partly neutralized solution is then freed from copper, and the nickel content correspondingly increased, by cementation using further amounts of the bessemerized matte. The solution before cementation may contain, for example, about 3.7% to 4.7% nickel, about 0.3% copper, and about 0.1 to 0.2% free sulfuric acid. This solution is then brought into contact with the matte at a suitable temperature, e. g., 40 to 100° C., without blowing in air, with resulting cementation of copper and the production of a purified nickel sulfate solution of suitable nickel and acid content for further use in the electrolytic operation.

The bessemerized copper-nickel matte which is used for the production of the solution and for the cementation may contain the usual sulfur content, e. g., about 18% sulfur, or this sulfur content can be further reduced; that is, the matte may be more or less depleted in sulfur by different procedures, and matte varying in its sulfur content can be used in the process. The matte may vary in its copper and nickel, as well as in its sulfur, content, for example, it may contain about 50% nickel, 30% copper, 18% sulfur, and the remainder iron and slag.

During the treatment of the matte with the acid solution, in the presence of air, part of the sulfur in the matte will be oxidized and sulfuric acid formed. The lower the raw material is in sulfur, the less tendency for acid to be formed, and it is therefore sometimes advantageous to remove the sulfur to a considerable extent before the matte is used, although the production of the copper-nickel sulfate solution and the cementation of the copper therefrom can be carried out with matte or metal of varying sulfur content, for example, from 18 to 20% down to as low as 2 to 3%. Where excess acid is formed, the process can be continued until the resulting acidity has been reduced to the proper degree, so that the excess acid is converted into a corresponding amount of nickel sulfate. Where the nickel sulfate solution thus produced contains an excess of nickel sulfate above that required for the electrolytic operation, it can be reduced to the proper nickel content, for example, by concentration of part of the solution and subsequent crystallization of the excess nickel sulfate.

In carrying out the electrolytic operation, in combination with the procedure above described, the acid nickel sulfate solution is electrolyzed with the use of insoluble anodes, and the nickel sulfate electrolyte is regenerated by first treating the solution with the matte in the presence of air and then cementing out copper upon a further amount of matte in the absence of air. The electrolyte may thus be supplied to the cathode compartment of a cell, for example, as described in my said prior application, and the anode liquor, depleted in nickel and of in-

creased acidity, regenerated in the manner above described.

It will be seen that the invention as thus described, in certain of its aspects, is not limited to an electrolytic refining process, inasmuch as the invention is adapted for the production of nickel sulfate solutions, either acid or neutral, adapted for use for other purposes than as electrolytes. So also, the invention, in certain of its aspects, is not limited to the carrying out of the electrolytic operation in a cell provided with a filtering diaphragm, although the invention is of particular advantage in conjunction therewith.

It will be evident that the treatment of the bessemerized matte with acid, in the presence of air, and the subsequent cementation, in the absence of air, can be carried out in various kinds of apparatus, and in such a way that sufficient matte will be used to obtain the desired rapidity of reaction. The treatment of the matte with the liquor can thus be carried out on the counter-current principle, with progressive dissolving of the metals and progressive neutralization, and the subsequent cementation can be similarly carried out, with progressive impoverishment of the solution in copper and corresponding enrichment in nickel, and with progressive depletion of the matte in nickel and corresponding increase in copper.

When the bessemerized copper-nickel matte is utilized both for the cementation and for the production of further amounts of copper-nickel sulfate solution, according to the process above described, the matte will not be completely utilized either in the cementation operation or in the dissolving operation. The matte used in the cementing operation will still contain considerable amounts of nickel and sulfur, together with the copper originally present therein and the cement copper resulting from cementation. The bessemerized matte used in the dissolving operation may likewise contain such portions of the matte as have not been dissolved in the treatment of the matte with the acid copper-nickel sulfate solution. Furthermore, it may be more advantageous to use a considerable excess of the matte and not attempt complete utilization so far as possible of its cementing capacity.

The matte which has been utilized in the cementing operation can advantageously be employed for the separation and recovery of its nickel and copper content.

The matte, after the cementation, and containing the cement copper, can thus be roasted to free it or substantially free it from sulfur and to convert the nickel and copper into oxides, and a considerable part of the copper can be dissolved from the oxidized material with sulfuric acid to give a solution of copper-sulfate relatively free from nickel which can be used for the recovery of copper therefrom by electrodeposition. After the oxidized material has thus been leached with the acid, the copper-nickel residue is then reduced by the action of a suitable reducing agent, such as carbon, hydrogen, carbon monoxide, hydro-carbons, etc., preferably at the lowest temperature so that the metallic powder shall be in a correspondingly fine state of sub-division and highly reactive. The reduced copper-nickel residue is then utilized for the production of a copper-nickel sulfate solution therefrom, for example, by treating it with the acid electrolyte from the electrolytic operation, with aeration to neutralize the greater part of the acidity of the electrolyte and to take into solution a corresponding amount of copper and nickel as sulfates, and the resulting solution is them subjected to cementation upon further amounts of bessemerized copper-nickel matte to remove the copper therefrom as cement copper and to give an acid nickel sulfate electrolyte for reuse in the electrolytic cells.

The combined operation just described can with advantage be carried out in such a way that the amount of copper contained in the reduced metal (after the cementing, roasting, leaching and reducing operations) can readily be cemented out on a corresponding amount of bessemerized copper-nickel matte, and so that the matte upon which the copper is thus cemented out will, after the roasting, leaching, and reducing operations, contain an amount of copper corresponding to that cemented out. The process, as thus carried out is made a balanced process in which the matte is utilized for the cementation and in which the reduced copper-nickel metal (remaining after the cementation, roasting, leaching and reducing operations) is utilized for replenishing the electrolyte and neutralizing the greater part of its acidity. The entire metal content of the matte can thus be utilized to advantage in conjunction with the electrolytic production of nickel in cells with an insoluble anode.

Instead of using the bessemerized copper-nickel matte only in the cementation operation, it may in part be directly roasted, then leached to remove part of the copper, and the residue reduced to give reduced metals which can be used in the main process in the manner above described, that is, in the cementation operation, or in the dissolving operation, or in both operations; although I regard it as more advantageous to make use of the bessemerized matte itself for the cementation, or for the greater part of the cementation, and to utilize the reduced metals (produced as above described) in the dissolving operation.

It will thus be seen that the present in-

vention includes various improvements which can be combined to advantage for the complete utilization of bessemerized copper-nickel matte for the production of nickel therefrom, as well as the separation of copper (by roasting of the matte or matte and cement copper and leaching of the roasted material with sulfuric acid); and that the various features of improvement are capable of combination to particular advantage for the complete utilization of the matte and the separation and recovery of copper and nickel therefrom.

It will also be seen that the invention includes improvements in the electrolytic deposition of nickel from acid nickel sulfate solutions with insoluble anodes in which the acid electrolyte from the cells, of increased acidity and decreased nickel content due to the electrolysis, is utilized for dissolving further amounts of copper and nickel, with introduction of air, to bring about partial and incomplete neutralization of the acidity, and in which the copper is cemented out from the still acid solution, without neutralization of the remaining acidity, so that the electrolyte is returned to the electrolytic cells replenished in nickel and with a regulated acidity such as is advantageous in the electrolytic operation. The dissolving of copper and nickel in the acid electrolyte from the cells can be carried out with a reduced metal (produced as above described), or with bessemerized matte, with introduction of air, or partly with matte and partly with reduced metal; while the cementation of the copper from the solution, without complete neutralization of its acidity, can be carried out either upon the bessemerized matte or upon the reduced metal, or in part upon both, but advantageously upon the matte, in the manner above described, and with utilization of the reduced metal produced from the matte (after the cementation, roasting, leaching and reducing operations) for supplying the copper and nickel to be dissolved in the acid electrolyte.

A typical process embodying the invention is illustrated in the flow sheet of the accompanying drawing.

The bessemerized copper-nickel matte is utilized by leaching with a sulphuric acid solution or the acid nickel solution resulting from electrolysis in the presence of air. The resulting copper-nickel sulphate solution is subjected to the cementing action of a further quantity of bessemerized copper-nickel matte, thus removing the copper from the solution, and is then passed to electrolytic vats for recovery of the nickel. The acid solution resulting from the electrolysis thus partially depleted of nickel is returned to the first operation step of the process; namely, the solution step.

The copper-nickel matte residue resulting from the solution step and from the cementation step is roasted evolving sulphur dioxide and producing oxidized compounds of copper and nickel which are leached with a sulphuric acid solution wherein a copper sulphate solution is formed practically free of nickel. This copper sulphate solution is then subjected to electrolysis for the recovery of the copper.

The oxidized residue resulting from the last-mentioned leaching operation is subjected to the action of a reducing agent, such as hydrogen or carbon monoxide, or the like. The thus reduced residue is then leached with an acid solution, such as the acid nickel solution resulting from the first-mentioned electrolysis step, and the thus formed solution is subjected to cementation with the bessemerized copper-nickel matte, thereby removing the copper from the solution which may be returned to the first-mentioned electrolytic vats for recovery of the nickel.

I claim:—

1. The method of utilizing bessemerized copper-nickel matte which comprises cementing copper thereon from a copper-nickel sulfate solution, roasting the remaining matte and cement copper, leaching the roasted material with sulfuric acid to form a copper sulfate solution, reducing the leached residue, dissolving the reduced material to form a copper-nickel solution and cementing copper from such solution upon a further amount of bessemerized matte.

2. The method of utilizing bessemerized copper-nickel matte which comprises cementing copper thereon from a copper-nickel sulfate solution, roasting the remaining matte and cement copper, leaching the roasted material with sulfuric acid to form a copper sulfate solution, reducing the leached residue, and dissolving the reduced material by the action of an acid copper-nickel sulfate solution with introduction of air.

3. The method of utilizing bessemerized copper-nickel matte which comprises cementing copper thereon from a copper-nickel sulfate solution, roasting the remaining matte and cement copper, leaching the roasted material with sulfuric acid to form a copper sulfate solution, reducing the leached residue, and dissolving the reduced material by the action of an acid sulfate solution, such solution being the acid solution from an electrolytic operation carried out upon a nickel sulfate electrolyte with insoluble anodes, and the nickel-sulfate solution produced by the cementing operation being supplied as the electrolyte to the electrolytic cell.

4. The process of treating bessemerized copper-nickel matte which comprises subjecting the same to the action of an acid nickel sulfate solution, with introduction of air to effect partial neutralization of the free acid, and subjecting the resulting still somewhat

acid solution to the action of material containing nickel, without introduction of air, for the separation of copper by cementation, thereby producing a purified acid nickel sulfate solution.

5. The process of treating bessemerized copper-nickel matte, which comprises subjecting the same to the action of a sulfuric acid solution, with introduction of air, and thereby producing a solution of nickel and copper sulfate, discontinuing the operation before complete neutralization of the acid, and treating the resulting acid solution with material containing nickel, without introduction of air, for the separation of copper by cementation, thereby producing a purified acid nickel sulfate solution.

6. The method of refining bessemerized copper-nickel matte, which comprises dissolving the matte in an acid nickel sulfate solution, with introduction of air, to effect partial neutralization of the free acid, subjecting the resulting still somewhat acid solution to the action of material containing nickel, without introduction of air, for the separation of copper by cementation, electrolyzing the resulting purified acid nickel sulfate solution and thereby obtaining metallic nickel and regenerating the acid nickel sulfate solution for treating further amounts of matte.

7. The method of refining bessemerized copper-nickel matte, which comprises subjecting an acid nickel sulfate solution to electrolysis in an electrolytic cell with insoluble anode and filtering diaphragm between the anode and cathode through which the solution travels from the cathode to the anode compartments and through which the excess acidity is removed from the cathode compartment, drawing off the acid solution from the anode compartment, treating the matte with such solution with introduction of air until the acidity is neutralized to the appropriate degree, and subjecting the resulting still somewhat acid solution to the action of material containing nickel, without introduction of air, for the separation of copper by cementation, thereby producing a purified acid nickel sulfate solution for use in the further carrying out of the electrolytic operation.

8. The method of refining bessemerized copper-nickel matte which comprises dissolving the matte in an acid nickel sulfate solution, with introduction of air, converting the excess sulfuric acid resulting from the operation to nickel sulfate, removing the excess nickel sulfate from the solution by a crystallizing operation, and utilizing the acid nickel sulfate solution for the electrolytic deposition of nickel therefrom and the regeneration of an acid nickel sulfate solution for dissolving further amounts of matte, whereby the excess acid is separated from the cyclic operation in the form of nickel sulfate by crystallization.

9. The method of refining bessemerized copper-nickel matte, which comprises electrolyzing an acid nickel sulfate solution with insoluble anodes, regenerating the resulting acid solution by dissolving copper and nickel therein from copper-nickel containing material, with introduction of air, until the acidity is incompletely neutralized, cementing out copper from the resulting solution without neutralization of the remaining acidity, and returning the still acid nickel sulfate solution to the electrolytic operation.

10. The method of refining bessemerized copper-nickel matte, which comprises electrolyzing an acid nickel sulfate solution with insoluble anodes, regenerating the nickel sulfate electrolyte by treating the solution with reduced copper-nickel material with introduction of air until the acidity is partially neutralized, cementing out copper from the resulting acid copper-nickel sulfate solution upon bessemerized copper-nickel matte without neutralization of the remaining acidity, returning the still acid nickel sulfate solution to the electrolytic cells, subjecting the matte and cement copper remaining after the cementation to roasting and subsequent leaching with sulfuric acid to remove copper therefrom, and reducing the remaining copper-nickel material and utilizing the same as the copper-nickel material for supplying further amounts of copper and nickel to the acid electrolyte from the cells.

In testimony whereof I affix my signature.

NOAK VICTOR HYBINETTE.