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METHOD OF SEPARATING COPPER, NICKEL, AND OTHER METALS FROM COPPER-NICKEL MATTE.

940,292.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that I, HORACE L. WELLS, a citizen of the United States, residing at New Haven, in the county of New Haven and State of Connecticut, have invented a new and useful Improved Method of Separating Copper and Nickel and other Metals from Copper-Nickel Matte; and I do hereby declare the following to be a full, clear, and exact description of the same.

My invention relates to an improved method for extracting and separating nickel and copper from a matte consisting largely of nickel and copper sulfids and commonly known as "rich copper-nickel matte". This matte is the well known product resulting from refining crude copper-nickel matte in a Bessemer converter, or otherwise, until the iron sulfid of the crude matte has been nearly all removed. The matte usually contains in the neighborhood of eighty per cent. of copper, nickel and cobalt, taken together, and it may also contain small quantities of iron, gold, silver as well as metals of the platinum group. To be satisfactorily applicable to my process, the matte should contain at least about thirty per cent. of nickel and cobalt together and not more than about fifty per cent. of copper; since when the matte contains too great a proportion of copper sulfid, the same by its mass to some extent protects the nickel and other soluble sulfids from the action of hydrochloric acid.

The object of my present invention is to provide a simple, effective, rapid and comparatively inexpensive method for directly extracting and separating the nickel and the copper present in such mattes as above specified. By directly extracting and separating, I mean without roasting, or without further smelting, or without first reducing to metallic form. I should here explain that the method forming the subject of my present invention does not aim to separate from the nickel, any cobalt or iron in the matte, nor does it aim to separate from the copper, any gold, silver or metals of the platinum group in the matte. These other metals may afterward be separated, if desired, from the nickel and copper in any of the usual ways.

With these ends in view my invention consists in subjecting a matte containing

nickel and copper sulfids to the action of a heated hydrochloric acid solution.

My invention further consists in treating fresh matte and any of its derived solid residues which are not exhausted of their nickel with fresh hydrochloric acid and any of its derived liquids which are not exhausted of their free acid in a progressive manner until exhausted or substantially exhausted solid residues and liquids are obtained.

My invention further consists in certain other details as will be hereinafter described and pointed out in the claims.

In practicing my improved method, I pulverize the matte, and agitate it with heated hydrochloric acid solutions. A fine pulverization of the matte greatly promotes the action of the acid. A pulverization representing a sieve of at least eighty meshes to the linear inch secures good results. I prefer to use a solution containing as a maximum not more than about twenty to twenty-five per cent. of actual hydrochloric acid since when acid solutions stronger than this are heated the acid may pass off and be wasted. Care must be taken not to actually boil the solutions, since when boiling takes place too much copper dissolves with, or in place of, the nickel. It is possible by using a very large excess of acid to dissolve substantially all of the nickel out of the matte in a single operation. It is also possible by using a very large excess of matte to change substantially all the hydrochloric acid in a solution into nickel chlorid in a single operation. It is more convenient and expeditious, however, to apply the acid to the matte and its resulting residues in two or more separate portions, and also to apply the matte to the acid and its resulting solutions in two or more separate portions. By agitating a matte containing in the neighborhood of forty per cent. each of nickel and copper, with the amount of hydrochloric acid solution required by calculation to convert the nickel into nickel chlorid and heated to about 180° F., a large portion of the nickel contained in the matte will be removed in two or three hours. At the expiration of this time the heated hydrochloric acid solution has been converted into a nickeliferous solution containing some unconverted or free hydrochloric acid and the

matte into a cupriferous residue containing some nickel. For the conversion of all or substantially all of the hydrochloric acid into nickel chlorid, I propose to treat the nickeliferous solution so derived with matte, either fresh or its solid derivatives until all, or substantially all of the free acid in the initial solution has been converted into nickel chlorid. Furthermore, for the extraction of all, or substantially all of the nickel from the cupriferous solid residue so derived, I propose to treat the same with heated hydrochloric acid solution either fresh or its liquid derivatives until all of the nickel in the initial charge of matte has been extracted. The solid and liquid derivatives just above referred to are intermediate products obtained in the progress of my improved process and consist on the one hand of matte from which the nickel has been partially extracted, and on the other hand liquid which has been partially exhausted of its free acid. The progressive treatment of the nickeliferous solution with matte and its solid derivatives and the progressive treatment of the cupriferous residue with hydrochloric acid solution or its liquid derivatives may be conducted in a variety of ways. The number of treatments will depend upon circumstances, such as the length of time of each treatment, the temperature and the composition of the original matte. The liquid solution will, of course, grow weaker and weaker in free acid, while on the other hand the solid residue will be more and more depleted of nickel, and the extent to which the treatment of the liquid and the residue will be carried on will be determined by considerations of economy, as obviously there may be a point beyond which it will not pay to convert the last trace of free acid into nickel chlorid and to extract the last trace of nickel from the residue. The described treatment of the nickeliferous solution with matte and of the cupriferous residue with acid solution are reciprocal operations in which nearly exhausted acid solution can be advantageously treated with fresh matte or a residual matte still rich in nickel, while on the other hand, cupriferous residue nearly depleted of its nickel may be advantageously treated with fresh acid solution or acid solution still containing considerable free acid. From this it follows that each charge of matte is subjected as fresh matte and its derivatives in the form of solid residue, to a cycle of treatments with acid solution, and its liquid derivatives, and that each given quantity of fresh acid is subjected as fresh acid and its derivatives in the form of nickeliferous solution, to a reciprocal cycle of treatments with matte or its solid derivatives.

As the strength of the solution in free acid determines its rapidity of action, and as the richness of the solid residue in nickel

determines its rapidity of action, it follows that the most advantageous results can be secured by simultaneously treating two or more charges consisting of matte and its progressively exhausted derivatives with two or more given amounts of hydrochloric acid solution and its progressively exhausted liquid derivatives. In other words, several charges of matte in their progress of exhaustion may be advantageously treated simultaneously with several acid solutions in their progress of exhaustion. Excellent results will be obtained by using acid and matte according to its strength in free acid on the one hand, and according to its depletion of nickel on the other hand, the employment of the acid being in one direction and of the residue in the other direction, in so far as the weaker the acid the richer the matte placed with it for treatment, and the richer the matte in nickel the weaker the acid placed with it for treatment. The number of steps in each cycle and the correlation of concurrent cycles by borrowing, so to speak, acid from one to use on the residue of another, and vice versa, is obviously capable of great variations and will be chiefly determined according to economy of time and labor. The progressive feature of my improved process may be summarized by the statement that the matte is treated successively by three or more solutions, the first of which it finishes, and the last of which is fresh acid which finishes it; while at the same time the liquid starting as fresh acid, acts upon three or more solids in the other direction meeting the fresh matte at the last step and being finished by it. I have found that the process may be advantageously carried on by the use of three vessels, but do not limit myself to any number or arrangement of vessels. I will explain further that since it is more convenient to remove a liquid than a solid from one vessel to another, I prefer to bring about the successive action of the partially exhausted liquids upon the appropriate solids and vice versa, by pouring the liquids from one vessel to another, and thus decanting them from the solids upon which they have previously acted. I will state also that I prefer to leave behind in these decantations the small portion of liquid which adheres to the solid residue and wets it and that I prefer to permit any small amount of solid matter that may be in suspension in the decanted liquids to pass with them from one vessel to another, except in the cases of the finished solid residue and the finished liquid. The finished solid residue I propose to wash with water, the resulting washings being saved for absorbing hydrochloric acid gas in another part of the process, or for diluting strong hydrochloric acid solution. The finished solution I propose to clarify, either by settling and decan-

tation from the sediment, or by filtration or by both.

In practicing my improved process, I prefer to use equal charges of matte and of acid carefully calculated according to the amount of acid necessary to react with the nickel, cobalt and iron in the matte, and vary these charges only as it may be desired to equalize, for convenience, the length of time required to finish the two end products. For instance, if it is found that the extraction of the nickel from the final cupriferous solid residue is requiring more time than the neutralization of the nickeliferous final solution, I shall use temporarily a proportionately larger amount of acid; if, on the other hand, the neutralization of the nickeliferous final solution is requiring more time than the extraction of the last nickel from the final cupriferous solid residue, I shall use temporarily a proportionately larger amount of fresh matte. I may add that the described nickeliferous solutions particularly when strongly acid, contain a considerable amount of copper the greater part of which is precipitated as copper sulfid and thus removed from the solutions when the same are heated and agitated with matte or its derivatives rich in nickel sulfid presumably on account of the abundant production of hydrogen sulfid which acts upon the copper in the solutions and precipitates it as copper sulfid. Most of the copper contained in the more acid solutions is therefore removed when these solutions have been exhausted of substantially all of their hydrochloric acid. The finished solution as far as treatment with matte is concerned, is a nearly neutral nickel chlorid solution containing, besides a possible small amount of copper chlorid, any iron and cobalt, also as chlorids, that the matte may have contained. Any last trace of copper may be removed from the finished solution preferably after cooling it, by agitating it with gas given off abundantly in the initial treatment of fresh or nearly fresh matte with a strongly acid solution; or any last trace of copper may be removed from the solution by the use of hydrogen sulfid made in some other way. Whatever the details may be, I secure as the result of my improved method of treatment, a nickel chlorid solution on the one hand in which there is no free acid or practically none, and on the other hand, a cupriferous residue in which there is no nickel or practically none. The solution contains an amount of nickel practically corresponding to the amount of nickel in an original charge of matte of given quantity, is practically free from copper, nearly free from hydrochloric acid, and contains also any iron and cobalt that may have been present in the matte. This solution is eminently suitable for the preparation of me-

tallic nickel by the usual methods, (for instance, by electrolysis,) after its purification from iron, and the separation of the cobalt by the customary methods if these steps are desired. The solid residue consists chiefly of copper sulfid, and contains practically all of the copper in the initial charge of matte as well as any gold, silver and metals of the platinum group that may have been present therein, but it contains practically no nickel. This solid residue is very suitable for the production of metallic copper and the recovery of the precious metals by the usual methods.

In order to make my method more economical, I have devised means for recovering the chlorin of the nickel chlorid solution in the form of hydrochloric acid which may be used again for the treatment of matte, and at the same time converting the nickel into commercial products, nickel chlorid being a salt not extensively used in the arts.

First method: When the nickel chlorid solution is evaporated to dryness and the residual solid nickel chlorid is heated to a temperature approaching low redness in an atmosphere containing hydrogen, for example in water-gas which consists chiefly of hydrogen and carbon monoxid, the nickel chlorid is changed to metallic nickel which is left in a pulverulent condition, while hydrochloric acid goes off and may be absorbed by water in the customary manner to make the aqueous solution commonly called hydrochloric acid. In case calcium chlorid or sodium chlorid, or both, or other salts of similar behavior, have been introduced into the nickel chlorid solution in freeing it from iron, or the separation of its cobalt, these salts will remain unchanged, mixed with the metallic nickel powder, and they can be removed therefrom by simple treatment with water, which dissolves them. In case that the iron and cobalt have not been removed from the nickel chlorid solution, they will be contained in the metallic nickel.

Second method: Another method of recovering the hydrochloric acid from the nickel chlorid solution for use again in the treatment of matte, consists in adding to the solution sulfuric acid and ammonium sulfate in amounts calculated to correspond to the amount of nickel present in the nickel chlorid solution. The mixture is allowed to stand for a short time and to become cool if necessary. The greater part of the nickel will be precipitated in the form of nickel-ammonium sulfate, a salt much used in the process of electro-plating nickeled goods. The solution separated from this precipitate contains hydrochloric acid corresponding in amount to the nickel chlorid that has been changed to sulfate, together with the constituents of a small amount of ammonium-nickel sulfate remaining dissolved in the

liquid. This acid liquid can then be used for the treatment of matte according to the method already described. The small amounts of sulfates present in this liquid do not interfere with this process, as they pass through it unchanged and may ultimately be recovered.

The two methods above described of recovering the hydrochloric acid, will form the subject of separate applications.

I claim:—

1. The herein described method of separating nickel and copper from a rich matte containing their sulfids, the said method consisting in pulverizing the matte and agitating it with hydrochloric acid solution heated below the boiling point and containing not more than 25% of actual hydrochloric acid, the solution resulting containing the nickel and the solid residue resulting containing the copper.

2. The herein described method of separating nickel and copper from a matte containing their sulfids consisting in treating fresh matte and any of its derived solid residues which are not exhausted of their nickel with fresh hydrochloric acid and any of its derived liquids which are not exhausted of their free acid, in a progressive manner until exhausted or substantially exhausted solid residues and liquids are obtained.

3. The herein described method of separating nickel and copper from a matte containing their sulfids, the said method consisting in pulverizing the matte and treating it with heated hydrochloric acid solution, and then progressively treating the resulting solution and its derivatives with matte and its solid derivatives, and the resulting solid residue and its derivatives with hydrochloric acid solution and its acid liquid derivatives.

4. The herein described method of separating nickel and copper from a matte containing their sulfids, the said method consisting in pulverizing the matte and treating it with heated hydrochloric acid solution, and then progressively treating the resulting nickeliferous solution and the resulting solid cupriferous residue respectively with matte and its solid derivatives and hydrochloric acid solution and its acid liquid derivatives until substantially all of the hydrochloric acid in the initial solution has been changed to nickel chlorid and until substantially all of the nickel in the initial charge of matte has been removed.

In testimony whereof, I have signed this specification in the presence of two subscribing witnesses.

HORACE L. WELLS.

Witnesses:

CLARA L. WEED,

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