Patented Feb. 16, 1932 1,844,937

UNITED STATES PATENT OFFICE

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PROCESS OF ELECTROLYTIC COPPER REFINING

No Drawing. Application filed June 28, 1928. Serial No. 289,080.

This invention is particularly designed for refining of matte from copper-nickel ores in which copper is present in the proportion of 2–4 parts to one part of nickel. The process is operated very much on the same lines as an ordinary modern electrolytic copper refinery, and as small quantities of nickel are present in nearly all copper anodes, certain steps in the process are applicable to such general refining practice.

In giving a broad outline of the process, we presume that the raw material, Bessemerized matte, is composed of approximately 60% copper, 20% nickel, 20% sulphur, 1% iron, and some precious metals. This matte is dead roasted in the ordinary way. It is divided in two parts of about two-thirds of the tonnage in one part and one-third in the other. The larger portion is turned into metallic anodes by ordinary processes of reduction and smelting. These anodes are electrolyzed in an ordinary refinery where the standard electrolyte is composed about as follows:

	Grams per liter
Copper	50
Nickel	50
Iron	5
H_2SO_4	125

The amount of free acid is adjusted to this comparatively high figure for the purposes of the later steps in the process.

The current density may be 20 amperes per square foot of anode surface. Perfect quality of copper is thus produced. It is evident that steps must be taken to maintain the balance of composition of electrolyte, by adding copper sulphate and withdrawing nickel and iron sulphate.

The second part of the roasted matte is, therefore, leached with sulphuric acid to produce such necessary copper sulphate. The residue from such leaching will contain a much larger proportion of nickel to copper than the original matte, say about half and half copper and nickel. This material is smelted to anodes. These anodes are preferably used in certain cells where the standard electrolyte is gradually depleted in copper and enriched in nickel by the withholding of any addition of copper sulphate solution from the copper leaching operation. As the copper becomes depleted the current density is lowered until at the end the electrolyte contains about 5 grams copper per liter and the current density may be 5 amperes per square foot of anodes. This is about the extreme limit for production of solid cathodes, but it will be found that the metal is contaminated with nickel and can only be marketed as ingots, not as wire bars. This quality is undesirable and by using the high nickel anodes in this division of the tankroom I obtain the benefit of producing only a smaller proportion of such inferior copper. In the present case about 15% of the total copper tonnage will be produced in this division, but not all of that will be inferior.

In this division, standard electrolyte runs in and the outgoing electrolyte, so called "foul electrolyte" is composed of about

5 grams copper per liter,
100 grams nickel per liter,
125 grams free H_2SO_4 per liter.

This foul electrolyte is the raw material for nickel production, and all nickel finds its way into this solution. A certain quantity of sulphuric acid is now added. It is evident that a certain amount of sulphuric acid must be supplied to the process, and an acid factory producing sulphuric acid from roast or smelter gases is, therefore, part of the general scheme of this invention. As will be seen hereinafter, nickel is removed from the process in the shape of nickel sulphate containing a certain amount of free sulphuric acid. It is then evident that a certain amount of acid must be brought in. I add that amount to the foul electrolyte. It brings up the total free acid to about 275 grams per liter. This concentration is by way of example only. The free acid may be adjustable between concentrations of about 200 to 300 grams per liter if desired.

The iron contained in this solution is present partly as ferrous and partly as ferric iron. It is desirable to have it all ferrous. It is also desirable to remove all the copper. This is now easily done by a simple

process of cementation on anode scrap of the anodes high in nickel. The cement copper so produced is inseparably mixed with the residue of the anode scrap on which it was cemented, and the mixture is preferably sent to the main anode furnace for production of anodes high in copper. The tonnage of cement copper will in this case amount to about 2% of the total copper production.

It is evident that this step of cementation with simultaneous reduction of iron to the ferrous state could as well be carried out before the adding of the new acid, but such cementation is faster and more complete in a stronger acid.

With the copper removed the composition of the solution is about:

	Grams per liter
Nickel	100
Iron	5
Free H_2SO_4	275

The nickel sulphate is now separated from the acid by cooling.

If the solution is cooled to about +12° C., a slight precipitation of salts crystals is noticeable. As the temperature is lowered, further amounts of salts are crystallized out in finely divided condition. At −15° C. about 90% of all nickel is thus precipitated. This may be an unnecessarily low temperature, and I cool to say −10° C. and obtain a precipitation of about 80–85% of the total nickel. About 70% of the iron is at the same time brought down. A trace of copper will all stay in the mother liquor. Were it not for the high percentage of free acid no such separation would be economically possible. If the iron had been in the ferric state it would not crystallize.

The crystals need not be washed. On account of the absence of copper the solution is readily handled in acid-proof machinery which separates the crystals and carries them to a furnace where they are roasted to oxide of nickel, contaminated only with such iron as was contained in the anodes. It is further refined by well-known processes.

The mother liquor is returned to the leaching division of the plant. Such mother liquor as is excessive of the needs of the main electrolyte may be mixed with the crystals. Such mother liquor contains 10–12 grams of nickel per liter.

It will be seen that the process is remarkable for the absence of insoluble anodes, chemicals, diaphragms, filter-presses and washing operations. It lends itself to mechanical operation with a minimum of labor.

Certain variations are obviously possible. In its simplest form the process may be carried out with only one kind of anodes. The cementation may be used to a greater or less extent or not at all. Insoluble anodes may be used. The foul electrolyte may be oxidized preferably by ozone to oxidize the iron and prevent it from contaminating the nickel. The mother liquor may be reduced preferably by sulphurous acid gas to allow the freezing out of iron sulphate crystals separately. Cobalt may be separated in the same way. Cooling may be substituted by the use of ammonium sulphate or potassium sulphate at least partly. Excess mother liquor may also be thrown in with the crystals so as to recover the nickel contained therein. Also the concentration of the sulphuric acid in the liquor may be increased by the use of insoluble anodes in the electrolytic bath or by evaporation or otherwise.

The important element of the invention is the discovery that nickel sulphate can be precipitated from strongly acid solutions as a dry, granular salt which can be separated and handled easily and roasted to oxide without difficulty.

I claim:

1. The method of recovering nickel from electrolytic solutions containing nickel, copper and free sulfuric acid which comprises separating the copper by electrolysis, then increasing the sulphuric acid concentration until the total free acid is about 200–300 grams per liter, and cooling to about −10° to −20° C., and thereby separating nickel sulphate crystals.

2. The method of recovering nickel from electrolytic solutions containing nickel, copper and free sulfuric acid which comprises separating the copper by electrolysis, then adding sulphuric acid until the total free acid is about 200–300 grams per liter, and separating nickel sulphate crystals by cooling to about −10° to −20° C.

3. In the process of claim 1, the removal of the last part of copper from the foul electrolyte by cementation on material containing metallic nickel while maintaining the free sulfuric acid concentration in the electrolyte at about 125 to 300 grams per liter.

4. In the process of claim 1, electrolyzing the copper from a bath containing free sulfuric acid and nicked in proportions such that the addition of sulphuric acid to the foul electrolyte in a quantity equal to that bound to the nickel will make a total of about 250 grams per liter.

5. The method of recovering nickel from electrolytic solutions containing nickel, copper, free sulfuric acid and small amounts of iron, which comprises separating the copper by electrolysis, reducing the dissolved iron to the ferrous state and then increasing the sulfuric acid concentration until the total free acid is about 200 to 300 grams per liter, and cooling to about −10° to −20° C. whereby the major portion of the iron and nickel is separated as a crystalline precipitate.

6. The method of recovering nickel from electrolytic solutions containing nickel, copper and free sulfuric acid, which comprises

separating the copper by electrolysis, then building up a high concentration of nickel in the foul electrolyte by further electrolyzing copper-nickel anodes comparatively high in nickel content, whereby a less proportion of copper of poor quality is obtained, then increasing the sulfuric acid concentration of the foul electrolyte until the total free acid is about 200 to 300 grams per liter, and cooling the solution to about $-10°$ to $-20°$ C.

In testimony whereof I affix my signature.

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