METHOD OF PRODUCING PURE NICKEL BY ELECTROLYTIC REFINING

Fig. 1

Fig. 2
METHOD OF PRODUCING PURE NICKEL BY ELECTROLYTIC REFINING

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ABSTRACT OF THE DISCLOSURE

Ferronickel anodes are corroded in a nickel chloride electrolyte containing nickel, calcium and sodium, which is purified outside the electrolytic cell, fed as a catholyte into the cathodic compartment of the cell where nickel is deposited on the cathode and returned to the anodic compartment by diffusion through porous cloths, said catholyte being recycled in said cathodic compartment so as to sweep the cathode faces when the cathodic current density ranges from 1,500 to 4,500 amps/sq. ft. This process, being essentially all chloride, results in a nickel deposit of high purity (about 99.95% by weight).

This invention relates in general to the manufacture of high-purity (about 99.95% by weight) nickel from ferronickel and more particularly to a method of producing high-purity nickel cathodes by electrolytic refining from ferronickel anodes.

It is a primary object of this invention to provide a method of producing high-purity electrolytic nickel directly from ferronickel alloys.

The anode slime comprises a light fraction and a heavy fraction. Light slime (about 92% of the slimes) is reddish and has a high iron content. Heavy slime is black (about 8% of the slimes). By way of example, in a specific case the slimes showed the following compositions:

<table>
<thead>
<tr>
<th>Anodes, initial composition, weight kg</th>
<th>Anode slimes, elements remaining in the anode slimes</th>
<th>Anode wastes, elements remaining in the form of anode wastes (immersed portion alone)</th>
<th>Anolyte, elements dissolved in the anolyte, weight kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>88.90</td>
<td>9.44</td>
<td>4.20</td>
</tr>
<tr>
<td>Co</td>
<td>3.20</td>
<td>0.07</td>
<td>1.34</td>
</tr>
<tr>
<td>Fe</td>
<td>0.24</td>
<td>0.07</td>
<td>0.13</td>
</tr>
<tr>
<td>As</td>
<td>7.15</td>
<td>0.24</td>
<td>0.33</td>
</tr>
<tr>
<td>Other impurities</td>
<td>1.81</td>
<td>0.23</td>
<td>0.07</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>4.20</td>
</tr>
</tbody>
</table>

This invention provides a method of forming cathode deposits of electrolytic nickel and notably a method of producing electrolytic nickel plates.

The method of this invention is applicable under both low and high current density values; however, a high cathode current density (of the order of 2,000 to 3,000 amps/sq. ft.) permits of increasing appreciably the production rate of electrolytic cells and, therefore, of reducing the corresponding investments.

This invention proposes the use of an aqueous electrolyte affording a satisfactory anode corrosion and a proper cathode deposit.

Other objects and advantageous features of this invention will appear during the following description of the method constituting the primary object thereof.

As a rule, the present invention provides a method of producing high-purity electrolytic nickel by electrolytic refining from ferronickel anodes, this method comprising the following steps:

An anodic corrosion of ferronickel anodes in anodic compartments containing a nickel-chloride aqueous electrolyte to form a high-nickel impure anolyte including iron, cobalt, etc., and an anode slime comprising mainly iron, cobalt, etc.

A chemical treatment of the impure anolyte for removing all the iron, cobalt, etc., thus delivering a purified electrolyte which is subsequently used as a catholyte.

A cathode deposit, the nickel being electrodosed on metal plates such as stainless or nickel plates in cathodic compartments from the aforesaid catholyte, the nickel-impoverished catholyte being transferred into the anodic cells by diffusion through pervious cloths bounding the cathodic compartment.

If the method is applied by using a high-density current, one fraction of the catholyte must be recirculated with a high output at least equal to 0.66 to 0.8 gallon per hour per amp/ir. and the nickel concentration in the electrolyte must be relatively high in order to yield a satisfactory homogeneous deposit.

Ferronickel anodes contain mainly nickel and iron. The method is applicable irrespective of the nickel content of the anodes; however, for the sake of economy it is desirable to use ferronickel anodes having a nickel content higher than 80% by weight.

The anode corrosion takes place regularly and uniformly. The weight of the noncorroded anode portion may be as low as about 4 to 5% of the initial weight, without taking into account the anode portion emerging from the bath.

By way of example, in the specific case contemplated hereinafter, the anode corrosion for 100 kilograms of ferronickel led to the following results concerning the division on the one hand of the elements dissolved in the anolyte and on the other hand of the elements remaining on the anode in the form of anode wastes, and finally, the elements transferred to the anode slimes:

The surface area of the electrodes used in these examples, whether anodes or cathodes, may range from 2 to 13 sq. ft.
The original cathode may be a stainless mother plate the surfaces of which are properly prepared for example by sandblasting so as to be slightly but very regularly rough, the electrodeposition of nickel forming on both faces of this plate a commercial nickel cathode having a thickness ranging from 3/16" to 9/16", which is separated from the mother plate after the electrolysis.

The original cathode may also consist of a nickel mother sheet having a thickness ranging from about 0.02" to 0.04", obtained by electrodeposition of nickel on a stainless-steel mother plate and separation of the thus deposited nickel sheets when their thickness attains a value of about 0.02" to 0.04"; the internal texture and the surface of these sheets are carefully prepared for example by effecting the following sequence of operation:

Grinding to remove a surface "skin" and thus providing a smooth, regular surface; planishing to obtain a straight, flat sheet, and annealing and stamping to form grooves in the sheet and make it nondeformable; the thus treated sheets are used as mother sheets for producing commercial nickel cathodes of a thickness ranging from about 0.35" to 0.47" and incorporating the mother sheet constituting the intermediate portion of the commercial cathode.

This invention is also concerned with commercial nickel cathodes obtained by carrying out the method described hereinabove.

Various types of electrolytic cells may be used for carrying out the method of this invention.

In the attached drawing, FIGURE 1 is a diagrammatic vertical section showing a specific form of embodiment of an electrolytic cell; FIGURE 2 is a similar vertical section but taken at right angles to the former in the cathode compartment portion of the assembly, and FIGURE 3 is a block diagram showing the various steps of an electrolysis carried out according to the method of this invention.

The anodeless cathodes are corroded anodically in electrolytic cells 2 filled with a nickel-chloride electrolyte to produce a high-nickel impure anolyte 3.

The impure liquid anolyte produced with a pH approximating 4 contains about 70 to 85 grams per liter of nickel, 30 to 60 grams per liter of calcium, 15 to 20 grams per liter of sodium, about 0.5 to 1 gram per liter of iron, 0.10 to 0.20 gram per liter of cobalt, 0.010 to 0.020 gram per liter of copper. This concentrated solution is at a temperature of about 90° to 95° (113° F. to 140° F.).

The impure anolyte is treated at 4, outside the electrolytic cell, to remove the greater portion of its iron and cobalt contents, notably in order to produce a pure catholyte 5 before causing the impure anolyte 3 to flow through. The impure anolyte 3 contains the impure nickel cathode 6 and is formed which contain at least 99.85% nickel, less than 0.1% cobalt, less than 0.01% iron, less than 0.01% copper. The iron precipitation takes place under a pH value ranging from 1.8 to 3.5 by chlorine peroxidization in the presence of precipitation agent which should be a basic nickel material such as hydrate or carbonate of nickel. If hydrate of nickel is used (a product which can be prepared by electrolysis) an amount of hydrate of nickel which corresponds to the stoichiometric quantity of iron dissolved in the electrolyte should be introduced. Copper and arsenic are eliminated with iron. The precipitation of cobalt takes place under a pH value of 3.5 to 4.5 in the presence of example of milk of lime and chlorine; calcium and sodium remain in the solution.

The catholyte, that is, the electrolyte of purified aqueous chloride, has a pH value ranging from 4 to 5 set preferably by adding an amount of ferric hydroxide, for example approximately 0.01% iron, 0.010 gram/liter of cobalt and 0.003 gram/liter of copper. The nickel and chloride radical concentrations are practically the same as in the impure anolyte. The catholyte is electrolyzed in the cathode compartment 7 at a temperature ranging from 50° C. to 60° C. (122° F. to 140° F.) by causing electric current to flow through. The current density may be variable; however, very satisfactory results are observed with current density values ranging from about 1,500 amps/sq. ft. to about 4,500 amps/sq. ft. The catholyte is electrolysed under the above-described conditions between the anode 1 and the cathode 6 and permits of obtaining satisfactory cathodes of electrodeposited nickel. During the electrolysis, a potential ranging from 1.5 to 1.7 volts is maintained between the anode and cathode.

The use of high-density current, that is, about 1,500 amps/sq. ft. and notably from 2,000 to 4,500 amps/sq. ft. for electrodeposition nickel implies the stirring of the catholyte in the cathodic compartment to facilitate the diffusion through the cathodic film of the nickel ions to be discharged.

This stirring is obtained by resorting to a forced circulation of the catholyte along the path 8 in the cathodic compartment 7 by means of a circulation pump (not shown). The recirculated catholyte is preferably reheated along its path outside the cathode cell to a temperature ranging from 50° C. to 60° C. (122° F. to 140° F.).

The pure catholyte 5 from the anolyte purification is fed at 9 to the recirculated catholyte 8 and the mixture 12 of the two catholyte stream is reintroduced into the cathodic compartment 7. To effect a satisfactory nickel deposit under a current density of 3,000 amps/sq. ft., the catholyte circulation output should be at least from 0.66 to 0.8 gallon per hr. and per amp/hr. Of course, the catholyte circulation output should be adjusted as a function of the actual density of the current utilized.

Moreover, in order to ensure a proper nickel deposition at current density values higher than 2,000 to 2,500 amps/sq. ft., sudden variations in the electrolyte composition should be avoided and minimum contents of the order of 70 grams/liter of nickel and 40 grams/liter of calcium should be adhered to.

In practice, only 10 percent of the nickel contents of the high-nickel purified catholyte are removed during the electrodeposition of nickel in the cathodic compartment 7. The nickel-impoverished catholyte will then flow in the direction of the arrows 1 through the catholyte cloths 10 and causing the anodic compartment 7 in front of front the anode 1, towards the anolyte 3 where its nickel and impurity contents increase before flowing out from the cells in the form of impure anolyte 3 which is recirculated as shown in FIGURE 1.

With a current density of 3,000 amps/sq. ft. the anodic corrosion and the cathodic deposit takes place with an efficiency attaining 95% for the anodic current and 95% for the cathodic current.

The following example illustrates a typical and nonlimiting case of an electrolyte carried out according to the teachings of this invention:

EXAMPLE

The electrolysis is carried out in cells 11 (FIGURE 3) comprising sixty-one electrodes, that is, thirty-one anodes 1 and thirty cathodes 6; the rectangular anode dimensions are 30" x 40" with an initial thickness of 2.16"; the rectangular cathode consists of 32" x 42" x 0.2" stainless steel plates. The anodes constitute the raw material to be treated.

Each cathode 6 is disposed in a cathodic cell 7 consisting of a cathodic box of polyester reinforced with glass fabric, the two lateral faces of this box which register with the anode being hollowed and comprising cathodic cloths 10 permitting the gravity of a 4.5 cu. in., per hour output per amp/hr. of catholyte towards the anolyte.

The inner dimensions of the electrolytic cells are 51" x 227" x 55". These cells are lined internally with a corrosion-resistant material also adapted to withstand mechanical shocks and heat surges, such as polyester resin reinforced with glass fabric.

In the diagram of FIGURE 3 only one anode 1 and one cathode 6 is shown in the cell 11 in order to simplify the drawing.
The electrolysis is carried out under a current density of 3,000 amperes per sq. ft., thus giving 450 amperes admitted for each electrode or 13,600 amperes per electrolytic cell.

The catholyte 12 is distributed along the cathodes 6 by diffusion in the form of perforated plates 13 (see FIGURE 2) disposed in the cathodic boxes and adapted to sweep the cathodes in the direction of the arrows f2 with an hourly output of 0.66 gallon/hr. per amp/hr. One fraction of the catholyte (0.0211 gallon/hr. per amp/hr.) is diffused through the cathodic cloths 10 in the direction of the arrows f2 to the anolyte 3, the remaining catholyte fraction being reheat to 14 and returned to the electrolyte reservoir 8 by an intermediate reheating in 14 at the rate of 0.66 gallon/hr. per amp/hr. The catholyte is heated at a temperature of about 50° C. to 60° C. (122° F. to 140° F.) for example in a steam-heated graphite-type heat transfer device. The 50 to 60° C. (122° F. to 140° F.) temperature of the catholyte is one of the factors ensuring a proper deposit of nickel on the cathode.

The anolyte 3 is taken from the electrolytic cells and delivered to the purifying system at the above-mentioned rate of 4.8 cu. in./hr. per amp/hr.

A cascade set of purifying cells operating continuously provides for purifying iron at 15 (by means of chlorin 16 and hydrite of nickel 17) and cobalt at 18 (by means of chlorine 16 and hydrite of lime 19) in the anolyte 3 issuing from the electrolytic cells, the filtration requires three filter presses having a useful surface of 750 sq. ft. each, one filter press commencing the filling, the second being unclogged and the third completing the purifying.

The purified anolyte 5 is fed at 9 to the catholyte circuit and the resulting mixture 12 is reintroduced with an hourly output of 0.682 gallon per amp/hr. into the cathodic cells 7 from which it flows by gravity from one to the other end of the cathodic boxes. The above-mentioned fraction of 4.8 cu. in./hr. per amp/hr. flows through the pervious cloths 7 to the anolyte and the remaining fraction 8 of the catholyte is fed to a circuit from which it is pumped for reheating and eventually recycled.

By way of example, given a catholyte output of 320,000 gallons per hour and an average temperature difference of 5° C. (9° F.), the recirculation circuit comprises a 3,500 cu. ft. (26,400 gallon) storage vat, three pumps having a capacity of 105,000 gal./hr. each, and a reheated catholyte stocking vat having a capacity of 3,500 cu. ft. (26,400 gallons).

The anode slimes accumulate in the bottom of cell 11. They are removed periodically during the idle time period of the cell and collected at 21. The anode washes at the end of the electrolytic process are collected at 22.

The electrolytic nickel is deposited on 0.25" stainless steel cathodic plates. After height to ten days deposit under a current density of 3,000 amps/sq. ft. the cathodic plates coated on each face with a layer of electrolytic nickel having a thickness ranging from 0.5" to 0.053", and extracted from the bath at 23, snared and washed at 24; the nickel plates are separated from their supporting plates at 25, renannealed in neutral atmosphere to degasify same at 26, and cut to standard dimensions at 27 to yield the final product 28.

Although this invention has been described with reference to favorable and/or optimum conditions, it will be readily understood by anybody conversant with the art that variations or modifications may be contemplated without departing from the spirit and scope of the invention. Such variations and modifications are considered as forming an integral part of the invention as set forth in the appended claims.

What I claim is:

1. A method of producing high-purity nickel by electrolytic refining which comprises the steps of corrodng ferronickel anodes in an aqueous nickel-chloride electrolyte contained in the anodic compartment of a divided electrolytic cell for producing a high-nickel impure anolyte containing impurities, and applying a chemical treatment to said impure anolyte to convert into a purified nickel electrolyte cell with a view to form a purified electrolyte cell as a catholyte into the cathodic compartment of said electrolytic cell, said cathodic compartment comprising walls of pervious cloths, electrodeposition the nickel from said catholyte on the cathode, and causing said nickel-impovery catholyte to pass into said anodic compartment by diffusion through said pervious cloths, the improvements consisting in that said ferronickel anodes have a nickel content greater than 80% by weight, that said nickel-chloride anolyte contains per liter about 70 to 85 grams of nickel ions, about 30 to 60 grams of calcium ions, and about 15 to 20 grams of sodium ions, the anions of said anolyte consisting essentially of chloride ions, that said anolyte has a pH value of about 4 and a temperature ranging from 45 to 60° C. (113° F. to 140° F.), and that said catholyte has the same nickel, calcium, sodium and chloride ion contents as said anolyte, a pH value ranging from 4 to 5 and a temperature ranging from 50° C. to 60° C. (122° F. to 140° F.).

2. An improved method as set forth in claim 1, wherein said electrolytic cell comprises a plurality of anodes and a plurality of cathodes disposed in as many cathodic compartments.

3. An improved method as set forth in claim 1, wherein the chemical treatment of said impure anolyte comprises the steps of precipitating the iron, copper and arsenic at a pH value ranging from 1.8 to 3.5 by chlorine peroxidation in the presence of a basic nickel compound, precipitating the cobalt at a pH value ranging from 3.5 to 4.5 by using chlorine and milk of lime, and separating the precipitates by filtration, the filtrate being used as a catholyte and having a pH value ranging from 4 to 5 and a nickel content of about 70 to 85 grams per liter.

4. A method as set forth in claim 1, wherein the original cathode consists of a stainless steel mother plate, the electrodeposition of nickel forming on each face of said mother plate a commercial nickel cathode having a thickness of 0.5" to 0.053", which is separated from the mother plate upon completion of the electrolysis.

5. A method as set forth in claim 1, wherein said original cathode is a nickel mother sheet having a thickness of about 0.02" to 0.044", obtained by electrodeposition nickel on a stainless steel mother plate and separating the deposited nickel sheets when their thickness attains from 0.02" to 0.044", said sheets being used as mother sheets for producing commercial nickel cathodes of a thickness of about 0.35" to 0.47" incorporating the mother sheet constituting the intermediate portion of said commercial cathode.

6. A method as set forth in claim 1, wherein the surface area of the anode and cathode electrodes used ranges from 2.15 to 13 sq. ft.

7. In a method of producing high-purity nickel by electrolytic refining which comprises the steps of corroding ferronickel anodes in an aqueous nickel-chloride electrolyte contained in the anodic compartment of a divided electrolytic cell for producing a high-nickel impure anolyte containing impurities, and applying a chemical treatment to said impure anolyte outside said electrolytic cell with a view to form a purified electrolyte cell as a catholyte into the cathodic compartment of said electrolytic cell, said cathodic compartment comprising walls of pervious cloths.
cloths, electrodepositing the nickel from said catholyte onto the cathode, and causing said nickel-impoverished catholyte to pass into said anodic compartment by diffusion through said porous cloths, the improvements consisting in that said ferronickel anodes have a nickel content greater than 80% by weight, that said nickel-chloride anolyte contains per liter about 70 to 85 grams of nickel ions, about 30 to 60 grams of calcium ions and about 15 to 20 grams of sodium ions, the anions of said anolyte consisting essentially of chloride ions, that said anolyte has a pH value of about 4 and a temperature ranging from 45°F to 60°C (113°F to 140°F), and that said catholyte has the same nickel, calcium, sodium and chloride ion contents as said anolyte, a pH value ranging from 4 to 5 and a temperature ranging from 50°C to 60°C (122°F to 140°F), that said catholyte is recycled in said cathodic compartment whereby it will sweep the cathode faces, is reheated during its recycling to a temperature ranging from 50°F to 60°F (122°F to 140°F) and electrolyzed in said cathodic compartment with a current density ranging from about 1,500 to about 4,500 amps/sq. ft.

8. An improved method as set forth in claim 7, wherein said current density is of 3,000 amps/sq. ft. and the catholyte circulation output is at least 0.66 to 0.8 gallon/hr. per amp/hr.

9. An improved method as set forth in claim 8, wherein said electrolytic cell comprises a plurality of anodes and a plurality of cathodes disposed in as many cathodic compartments.

10. An improved method as set forth in claim 8, wherein said chemical treatment of the impure anolyte comprises the steps of precipitating the iron, copper and arsenic at a pH value of 1.8 to 3.5 by chlorine peroxidation in the presence of a nickel basic compound, precipitating the cobalt at a pH value of 3.5 to 4.5 by using chlorine and milk of lime, and separating the precipitates by filtration, the filtrate being used as a catholyte having a pH value ranging from 4 to 5 and a nickel content of about 70 to 85 grams per liter.

11. An improved method as set forth in claim 7, wherein said electrolytic cell comprises a plurality of anodes and a plurality of cathodes disposed in as many cathodic compartments.

12. An improved method as set forth in claim 7, wherein the chemical treatment of said impure anolyte comprises the steps of precipitating the iron, copper and arsenic at a pH value of 1.8 to 3.5 by chlorine peroxidation in the presence of a basic nickel compound, precipitating the cobalt at a pH value of 3.5 to 4.5 by using chlorine and milk of lime, and separating the precipitates by filtration, the filtrate being used as a catholyte having a pH value ranging from 4 to 5 and a nickel content of about 70 to 85 grams per liter.

13. A method as set forth in claim 7, wherein the original cathode consists of a stainless steel mother plate, the electrodeposition of nickel forming on each face of said mother plate a commercial nickel cathode having a thickness of ¼" to ¾", which is separated from the mother plate upon completion of the electrolysis.

14. A method as set forth in claim 7, wherein said original cathode is a nickel mother sheet having a thickness of about 0.02" to 0.04", obtained by electrodepositing nickel on a stainless steel mother plate and separating the deposited nickel on a stainless steel mother plate and separating the deposited nickel sheets when their thickness attains from 0.02" to 0.04", said sheets being used as mother sheets for producing commercial nickel cathodes of a thickness of about 0.35" to 0.47" incorporating the mother sheet constituting the intermediate portion of said commercial cathode.

15. A method as set forth in claim 7, wherein the surface area of the anode and cathode electrodes used ranges from 2.15 to 13 sq. ft.

16. An aqueous catholyte for producing high-purity electrolytic nickel, containing about 70 to 85 grams of nickel ions, about 30 to 60 grams of calcium ions and about 15 to 20 grams of sodium ions per liter, the anions of said catholyte consisting essentially of chloride ions, said catholyte having a pH value ranging from 4 to 5.

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