United States Patent Office 2,839,461 Patented June 17, 1958

2,839,461

ELECTROLYTIC RECOVERY OF NICKEL

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No Drawing. Application February 1, 1954
Serial No. 407,585

Claims priority, application Canada October 29, 1953

11 Claims. (Cl. 204—113)

The present invention relates to the production of high purity nickel and elemental sulfur from nickel matte and, more particularly, to a process for electrolytically producing high purity nickel cathodes and elemental sulfur from nickel matte anodes.

It is well known that the conventional recovery of nickel from sulfide ores usually involves the processing of nickel matte, as by roasting, to nickel oxide followed by high temperature reduction, e. g., at about 2800° F., to the impure metal which is then cast into impure nickel anodes and finally electrolytically refined to nickel of high purity. These high temperature operations for reducing nickel matte to metallic nickel anodes are costly, cumbersome, and time consuming. In addition, metal values are lost through dust and slags. The sulfur initially in the nickel matte is exhausted as gas of relatively low value when the matte is sintered to oxide. Although attempts were made to overcome the foregoing difficulties and other disadvantages, none, as far as we are aware, was entirely successful when carried into practice commercially.

It has now been discovered that high purity nickel and elemental sulfur can be produced in a special way through the direct electrolysis of sound nickel matte anodes.

It is an object of the present invention to provide a process for electrolytically producing high purity nickel from sound nickel matte anodes.

Another object of the invention is to provide a process for electrolytically producing nickel and concomitantly recovering elemental sulfur.

The invention also contemplates providing a process for anodically corroding sound nickel matte anodes to recover high purity nickel and elemental sulfur.

The invention further contemplates providing a process for electrolytically concentrating the precious metals found in nickel matte.

A still further object of the invention is to provide an improved aqueous electrolyte for use in the anodic corrosion of nickel matte anodes.

It is another object of the invention to provide a process for preparing improved nickel matte anodes for use in the process contemplated by the present invention.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention contemplates a process for electrolytically recovering nickel and sulfur from nickel matte (nickel sulfide) comprising anodically corroding sound, impure nickel matte anodes in the anode compartment of a divided cell containing an aqueous sulfate-chloride electrolyte to form an impure nickel-rich anolyte which may contain iron, arsenic, lead, copper, cobalt, etc., and to form an anode sludge mainly comprised of elemental sulfur and including therein substantially all the precious metals, the selenium and the tellurium originally in said impure anode. The impure nickel-rich anolyte is treated to remove substantially all the iron, arsenic, lead and copper and, if desired, also the cobalt, thus providing a purified electrolyte which is then used as the catholyte. Nickel is electrodeposited in the cathode compartment of the cell from the catholyte and thereafter the impoverished catholyte is preferably recycled to the anode compartment. The crude elemental sulfur is recovered as anode sludge which is treated to separate the sulfur from the metal values, especially the precious metals.

The matte anodes utilized in the present invention may be produced from nickel matte, nickel sulfide precipitates, or other source of nickel sulfide. Sound nickel matte anodes can be prepared by melting nickel sulfide in a furnace, skimming off any dross or slag formed, and then pouring the molten matte into molds of suitable size and configuration. The nickel matte anodes, if allowed to cool in the air, are brittle and highly stressed and crack spontaneously. Such cracking can be eliminated for all practical purposes by slow cooling of the anodes at least through the temperature range of about 975° F. down to about 400° F. to 500° F., particularly in the upper part of this range in which polymorphic transformations occur. At temperatures in excess of about 975° F., the anodes are strong and will withstand rough handling. Suitable anodes have been prepared by a process comprising melting nickel sulfide at about 1700° F., casting the molten nickel sulfide into open horizontal cast iron anode molds, and cooling the thus-formed anodes to a temperature of between about 1000° F. and 1100° F. in the mold. The matte anodes were then removed from the mold and passed through a furnace in which they were gradually cooled from about 975° F. to about 800° F. at the rate of about 20° F. per hour, then to about 400° F. at a rate not exceeding 150° F. per hour and then air cooled. Alternatively, the anodes may be cooled at the foregoing rates in annealing boxes. After cooling, the matte anodes still are relatively fragile and require more careful handling than metal anodes to prevent breakage. To facilitate handling of the anodes and more particularly collection of the voluminous sludge which forms during anode corrosion, the cooled anode is suspended within a wooden frame. However, it has also been found satisfactory to place the anodes in loosely woven bags of a material resistant to the action of the anolyte at a pH as low as 1.8.

The nickel matte anodes are comprised largely of nickel and sulfur (between about 20% and 32% sulfur), the sulfur content increasing with increasing copper content, and may contain, in addition to the copper mentioned, small amounts, e. g., up to about 5%, of such other materials as iron, arsenic, lead, cobalt, precious metals, selenides and tellurides. The nickel sulfide present in the anode is mainly in the form of Ni_3S_2.

Nickel to sulfur ratios approximating that satisfied by the formula Ni_3S_2, e. g., matte anodes containing about 27% sulfur and the balance essentially nickel, have been found most satisfactory in the present process. It is believed that the mechanism involved in the anodic corrosion of the nickel matte anodes in the process contemplated by the present invention is as follows:

$$Ni_3S_2 - 6e \rightarrow 3Ni^{++} + 2S \text{ (elemental sulfur)}$$

Experimental evidence on the nickel-sulfur system indicates that on solidification a metallic phase separates as "islands" in a nickel sulfide matrix as the sulfur content is decreased below about 25%, as shown by the increase in magnetic permeability and by microscopic examination. The metallic phase, of course, increases as the sulfur content decreases. When a mixture of a nickel sulfide phase with a substantial amount of a metallic phase is anodically corroded, the metallic phase dissolves selectively leaving uncorroded sulfide fragments. When the sulfur content of the nickel matte anode is about 20% to about 25%

(about 75% to about 95% nickel sulfide), corrosion of the sulfide phase is not substantially hindered. However, as the sulfur content drops below about 20%, selective dissolution of the metallic phase makes it difficult to corrode the sulfide phase uniformly. As a result, the proportion of the non-corroded sulfide rapidly increases with decreasing sulfur content.

The nickel matte anodes may contain copper in amounts up to about 30%, although preferably the copper content of the matte anodes should not exceed about 20%. Secondary nickel matte anodes, described hereinafter, may contain about 30% of copper. In the normal course of the nickel matte production, nickel and copper apparently occur as Ni_3S_2 and Cu_2S. If sulfur in excess of that necessary to form Ni_3S_2 and Cu_2S is present, it apparently unites with the copper to form what appears to be CuS rather than Cu_2S. It has been found that for optimum results sufficient sulfur should be present in the nickel matte anodes so that substantially all the copper is present as CuS. This is explained by the fact that in the sulfate-chloride electrolytes contemplated, the anode potential required to corrode Cu_2S is less than that required to corrode Ni_3S_2, while that required to corrode CuS is of the same order as that required to corrode Ni_3S_2. Thus, when a nickel matte anode containing copper in the form of Cu_2S is anodically corroded, the cuprous sulfide is selectively dissolved leaving uncorroded nickel sulfide. The deleterious effect caused by the selective dissolution of the Cu_2S is not apparent until the copper content is at least 5% and is not serious until the copper content is about 10%. When more than about 5% of copper is present in the nickel matte anode, the minimum sulfur content (20%) of the matte anode should be raised about 1% for each 2% of copper present in excess of 5%. Thus, a nickel matte anode containing 20% copper should contain at least about 28% of sulfur. Although the copper sulfides discussed hereinbefore have been referred to as CuS and Cu_2S, respectively, it is not intended to indicate that these copper sulfide compounds are actually present but that the proportioning of the elements approximates that expressed by the aforementioned formulas.

Anode corrosion of sound nickel matte anodes (in accordance with the invention) is smooth and uniform and is superior in this respect to conventional metal anodes. This factor together with the uniform anode weight obtainable and the use of the anode frame or bag to hold the sludge permits almost complete corrosion of the anodes and requires the return of only about 10% of the original anode weight as scrap for remelting. This is in contrast to the usual 20% anode scrap returned when using conventional metallic nickel anodes. The anode sludge, which is largely elemental sulfur, is granular, porous and clings to the uncorroded portion of the matte anode. This enables substantially complete retention of the sludge within the anode frame. During the course of the anodic corrosion, the volume of the original anode material is approximately doubled, i. e., the anode sludge occupies twice the volume initially occupied by the matte anode. The wooden frame employed to hold the matte anode has two substantially parallel faces which are fitted with acid-resistant cord running vertically over each face and spaced a number of inches apart, e. g., about 2 inches apart. The thickness of the frame, i. e., the distance between the two corded faces, is made twice the anode thickness to allow for swelling during anode corrosion. Similar allowance for increase in volume is made if an anode bag is used instead of the anode frame.

In accordance with the invention, sound nickel matte anodes are anodically corroded in the anode compartment of a divided cell in an aqueous nickel-containing sulfate-chloride electrolyte to produce an impure nickel-rich anolyte. The impure aqueous anolyte which is produced has a pH of between about 1.8 and 2.4 and contains from about 40 to 70 and preferably from about 40 to 60 g. p. l. (grams per liter) of nickel, from about 12 to 30 g. p. l. of sodium, from about 20 to 55 and preferably from about 30 to 50 g. p. l. of chloride radical, from about 65 to 115 g. p. l. of sulfate radical, from about 10 to 25 and preferably from about 15 to 25 g. p. l. of boric acid, up to about 0.5 and preferably not more than about 0.1 g. p. l. of iron, up to about 3 and preferably not more than about 2 g. p. l. of copper, up to about 0.05 g. p. l. of arsenic, up to about 0.002 g. p. l. of lead, up to about 0.25 g. p. l. of cobalt, and up to about 0.6 g. p. l. of calcium. The impure anolyte is treated with a basic material and preferably a basic nickel material, such as nickelous hydroxide, nickel carbonate, etc., to raise the pH to from about 3.7 to 4.3. The impure electrolyte is then treated to remove substantially all the iron, copper, arsenic, lead and cobalt to yield a purified aqueous electrolyte which becomes the catholyte. The electrolyte purification system is substantially that detailed in U. S. Patent No. 2,394,874 wherein a process is disclosed for removing substantially all the iron, copper, arsenic, lead and cobalt present in the impure nickel-containing anolyte to yield a substantially pure catholyte from which a nickel cathode containing at least 99.88% nickel, up to 0.1% cobalt, up to 0.01% iron, up to 0.002% arsenic, up to 0.002% lead and up to 0.01% copper is electrodeposited. The catholyte, i. e., the purified aqueous sulfate-chloride electrolyte, has a pH between about 4 and 5 and preferably about 4 and contains not more than about 0.002 g. p. l. of iron, not more than about 0.001 g. p. l. of copper, not more than about 0.0005 g. p. l. of arsenic, and not more than about 0.0005 g. p. l. of lead. The catholyte may be saturated with respect to calcium ions. Thus, it may contain up to about 0.6 g. p. l. of calcium without affecting the operating characteristics of said process. The concentrations of nickel, of chloride and of sulfate radical fall within substantially the same ranges as set forth hereinbefore for the impure anolyte. The catholyte is electrolyzed at a temperature between 100° F. and 160° F. and preferably between about 135° F. and 145° F. by passing an electric current at a current density of between about 5 to about 25 and preferably between about 10 to about 15 amperes per square foot through said catholyte between an anode and a cathode to electrodeposit nickel cathodes. During electrolysis, a potential between about 2 volts and about 4 volts is maintained between the anode and cathode.

In practice, only about 25% of the nickel content of the purified nickel-rich catholyte is removed during the electrodeposition of nickel in the cathode compartment. The catholyte depleted in nickel content then flows through the cathode diaphragm to the anode compartment where it is replenished in nickel and impurities content before flowing out of the cell as impure anolyte.

When anodically corroding nickel matte anodes in an aqueous sulfate-chloride electrolyte within the scope of the invention, the anode current efficiency with respect to nickel is about 96% while the cathode current efficiency is about 99.5%. Thus, when the process is operated continuously, a nickel deficiency arises in the electrolyte which is manifested by an equivalent increase in acid content. The operating characteristics of the system are such that the pH of the anolyte flowing from the electrolytic cells is between about 1.8 and 2.1. Since the increase in acidity is equivalent to the nickel deficiency, the low pH as well as the nickel deficiency in the system are corrected simultaneously by the addition of a basic nickel salt prior to the first step in the electrolyte purification treatment, which requires a pH of about 3.7 to about 4.3.

If electrolyte composition is not maintained within the limits specified hereinbefore, particularly with respect to the chloride and sulfate content thereof, the electrolysis is adversely affected. Utilization of electrolyte compositions outside of the range specified decreases the anode efficiency. This is of great practical importance since cost of basic nickel salts is a major factor in determining the economy of the operation and since even a small de-

crease in the anode efficiency with constant cathode efficiency sharply increases the quantity of such basic salts to be added. For example, the cost of basic nickel salts added to an electrolyte not having a composition in accordance with the invention, operating at an anode efficiency of 94% and having a pH of about 1.5 was 50% higher than the cost of that added to an electrolyte operating at an anode efficiency of 96% and having a pH of about 2.1. In addition, life of cathode diaphragms and tank linings is much shorter at pH 1.5 than at pH 2.1.

The differences in the results attained in the process by varying the chloride and sulfate contents of a sulfate-chloride electrolyte are brought out in Table I.

Table I

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Composition: gm./liter—						
Cl^-	0	20	40	100	85	30
$SO_4^=$	100	100	100	100	0	80
Ni^{++}	50	50	50	50	50	50
H_3BO_4	20	20	20	20	20	20
Anolyte pH	1.3	1.9	1.9	1.6	1.5	2.1
Anode Eff., Percent	75	95	95	94	94	96
Anode Sludge, S content, Percent	80	96	98	92	94	96
Cell Voltage	2.4	2.3	2.1	2.0	2.1	2.1
Anode C. D., a. s. f.	15	15	15	15	15	15
Temperature, ° F	140	140	140	140	140	140

After a nickel matte anode has been completely corroded, there is usually about 10% anode scrap, i. e., about 10% nickel matte in the anode sludge. The anode sludge, excluding the anode scrap contained therein, contains about 97% elemental sulfur, about 1.25% nickel, about 0.3% copper, about 0.2% selenium, about 0.02% tellurium, about 0.01% precious metals, about 0.6% iron, and about 0.7% sulfide sulfur. The sludge can be removed from the anode frame, dried and treated for the recovery of elemental sulfur of commercial purity, the precious metals, and the base metals.

Sulfur purification and recovery may be carried out by known means, such as by distillation. The residue containing the precious metals, now concentrated to about 100 times the initial concentration of the precious metals in the initial matte anode, can be mixed with a precious metals concentrate produced in accordance with the teachings of U. S. Patent No. 2,425,760. Sufficient elemental sulfur in the form of primary anode sludge can then be added to bring the sulfur content of the mixture to between about 27% and 30%. This mixture is then melted and cast into secondary matte anodes containing between about 45% and 55% nickel, about 15% to 20% copper, about 2% to 3% iron, about 27% to 30% sulfur and about 0.2% to 0.4% precious metals. The secondary anodes are heat treated, assembled in the anode frame, and electrolyzed in a manner and under conditions substantially the same as those detailed herein for nickel matte anodes. The products of this electrolysis of the secondary matte anodes are electrolytic nickel and an anode sludge containing about 90% elemental sulfur and the precious metals. Sulfur is recovered from this sludge by distillation as from the primary anode sludge. The residue containing large amounts of precious metals, e. g., about 2000 ounces per ton, together with base metal sulfides, selenium, tellurium, etc., is processed for the recovery of the precious metals. The precious metals may be recovered by roasting the residue between about 800° F. and 1000° F. to sulfate the base metals and to produce a calcine. The calcine is leached with a weak sulfuric acid solution to dissolve the base metals. The leach residue containing the precious metals is processed by known means for the separation of the various noble metals.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative example is given:

Finely divided nickel sulfide concentrates containing about 70% to 72% nickel, about 21% to 25% sulfur, about 2% to 3% copper, about 0.5% to 1% cobalt, up to about 1% iron, and small amounts of lead, arsenic, precious metals, etc., were melted in a furnace at about 1700° F. After the matte was completely molten, the dross and slag were skimmed off and the matte poured into open horizontal cast iron molds. The molds were provided with two steel anode suspension straps about one and one-half inches wide by one-quarter inch thick centered and spaced about 14 inches apart so that when the nickel sulfide was cast around the straps they projected about two inches into the body of the anode. Anode dimensions were about 45 inches by 29½ inches by 1½ inches. After casting, the anodes were allowed to cool to between 1000° F. and 1100° F. in the mold. They were then removed from the mold and passed through a tunnel furnace during which they were gradually cooled to within the range of about 400° F. to 500° F. over a period of twenty hours. After removal from the tunnel furnace, the anodes were air cooled to atmospheric temperatures. The resultant nickel matte anodes were placed in wooden frames having two parallel faces with acid-resistant cords running vertically over each face and spaced about 2 inches apart. The distance between the two faces of the frame was about twice the anode thickness, i. e., about 3 inches. The framed matte anode was placed in the anode compartment of a compartmented cell and anodically corroded in an aqueous sulfate-chloride electrolyte to yield a nickel-rich impure aqueous anolye having a pH of about 1.9 and containing about 54 g. p. l. of nickel, about 28 g. p. l. of sodium, about 46 g. p. l. of chloride radical, about 87 g. p. l. of sulfate radical, about 18 g. p. l. of boric acid, about 0.07 g. p. l. of iron, about 0.012 g. p. l. of lead and arsenic, about 0.36 g. p. l. of copper, and about 0.1 g. p. l. of cobalt and to yield an anode sludge largely retained in the wooden frame comprising 97% elemental sulfur, 0.01% precious metals, 2.8% loose uncorroded sulfides and 0.2% of selenium and tellurium. The impure nickel-rich anolyte was withdrawn and the pH raised to about 4 by the addition of nickel hydroxide. It was then purified in accordance with the procedure set forth in U. S. Patent No. 2,394,874 to yield a purified nickel-rich catholyte having a pH of about 4 and containing about 55 g. p. l. of nickel, about 28 g. p. l. of sodium, about 46 g. p. l. of chloride radical, about 87 g. p. l. of sulfate radical, and about 18 g. p. l. of boric acid. The catholyte was electrolyzed in the cathode compartment of the compartmented cell at a temperature of about 140° F. by passing about 6300 amperes at an impressed voltage of 2.5 from the anode to the cathode to deposit commercially pure nickel on the cathode. The anode frame was removed from the electrorefining tanks and the sludge sluiced off. The sludge slurry was filtered to recover the solids which were dried and treated for recovery of elemental sulfur of commercial purity and for recovery of base metals and precious metals. This was done by distilling the sulfur off at about 850° F. and casting the liquid sulfur distillate into molds to produce elemental sulfur of commercial purity. The residue containing the precious metals, now concentrated to about 100 times the initial anode concentration, was mixed with other precious metal concentrates obtained from a smelter and sufficient elemental sulfur was added to bring the sulfur content of the mixture to about 27% to 30%. This mixture containing about 50% nickel, about 16% copper, about 27% sulfur, and about 0.25% precious metals was then melted and cast into molds to form secondary nickel matte anodes which were then electrolyzed in the same manner as were the primary nickel matte anodes described hereinbefore to produce electrolytic nickel and an anode sludge containing the precious metals and about

90% elemental sulfur. The sulfur was recovered by distillation to leave an enriched residue containing about 2000 ounces per ton of precious metals and also containing base metal sulfides, selenium and tellurium. This residue was roasted at about 1000° F. and then leached with water containing about 1% sulfuric acid to dissolve the base metals. The leach residue, containing about 50% precious metals, was then treated to separate the various precious metals, viz, gold, silver, platinum, palladium, rhodium, iridium and ruthenium.

The present invention is particularly applicable to the treatment of nickel matte produced in accordance with the procedure detailed in U. S. Patent No. 2,419,973, said nickel matte being largely composed of nickel sulfide and including copper sulfide, precious metals, selenium, tellurium, etc. It is apparent that, in addition to the specific application of the present invention herein enumerated, the invention is broadly applicable to the electrolytic recovery of nickel of high purity and elemental sulfur from nickel sulfides.

It is to be observed that the present invention provides for electrolyzing nickel matte anodes in a special electrolyte to yield not only high-purity electronickel but also elemental sulfur and precious metals.

Furthermore, the invention provides a process for electrolytically recovering and concentrating precious metals directly from nickel matte without need for an elaborate prior treatment.

Moreover, the invention provides a process for producing electronickel, elemental sulfur and precious metals in which specially prepared nickel matte anodes are employed.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and various may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A method for producing electrolytic nickel which comprises in combination the steps of anodically corroding by direct electrolytic action at high anode efficiency in the anode compartment of a divided cell a unitary and conductive anode of nickel matte characterized in having a sulfur content of about 20% to about 32% by passing a current through said anode of nickel matte while it is in contact with an aqueous sulfate-chloride anolyte containing from about 65 to about 115 grams per liter of sulfate radical and from about 20 to about 55 grams per liter of chloride radical and maintaining the pH of said anolyte at a pH of about 1.8 to about 2.1, to thereby produce an impure nickel-rich anolyte and an anode sludge comprised mainly of elemental sulfur; removing said impure anolyte from said anode compartment; purifying said impure anolyte; introducing said purified anolyte into the cathode compartment of a divided cell to thereby provide a catholyte; and electrodepositing nickel from said catholyte onto a cathode in said cathode compartment.

2. A method for producing electrolytic nickel which comprises in combination the steps of anodically corroding by direct electrolytic action at high anode efficiency in the anode compartment of a divided cell a unitary and conductive anode of nickel matte characterized in having a sulfur content of at least about 20% by passing a current through said anode of nickel matte while it is in contact with an aqueous sulfate-chloride anolyte containing about 65 to 115 grams per liter of sulfate radical and about 20 to 55 grams per liter of chloride radical and maintaining the pH of said anolyte at a pH of about 1.8 to about 2.4 to thereby produce an impure nickel-rich anolyte and an anode sludge comprised mainly of elemental sulfur; removing said impure anolyte from said anode compartment; purifying said impure anolyte; introducing said purified anolyte into the cathode compartment of a divided cell to thereby provide a catholyte and electrodepositing nickel from said catholyte onto a cathode in said cathode compartment.

3. A method for producing electrolytic nickel which comprises in combination the steps of anodically corroding by direct electrolytic action at high anode efficiency a unitary and conductive anode of nickel matte characterized in having a sulfur content of at least about 20% by passing a current through said anode of nickel matte while it is in contact with an aqueous sulfate-chloride anolyte and maintaining the pH of said anolyte at a pH of about 1.8 to about 2.4 to thereby produce an impure nickel-rich anolyte and an anode sludge comprised mainly of elemental sulfur; removing and purifying said impure anolyte to thereby provide a catholyte; and electrodepositing nickel from said catholyte onto a cathode.

4. A method for producing electrolytic nickel which comprises the steps of anodically corroding by direct electrolytic action at high anode efficiency in the anode compartment of a divided cell a unitary and conductive anode of nickel matte comprised mainly of nickel sulfide and up to about 30% copper and characterized in having a weight percent sulfur content of not less than 20 plus half the weight percent copper content of the matte in excess of 5 by passing current through said anode of nickel matte while it is in contact with an aqueous sulfate-chloride anolyte and maintaining the pH of said anolyte at a pH of about 1.8 to about 2.4 to thereby produce an impure nickel-rich anolyte and an anode sludge comprised mainly of elemental sulfur; removing said impure anolyte from said anode compartment; purifying said impure anolyte; introducing said purified anolyte into the cathode compartment of a divided cell to thereby provide a catholyte and electrodepositing nickel from said catholyte onto a cathode in said cathode compartment.

5. A method for producing electrolytic nickel which comprises the steps of anodically corroding by direct electrolytic action at high anode efficiency in the anode compartment of a divided cell a unitary and conductive anode of nickel matte comprised mainly of nickel sulfide and up to about 20% copper and characterized in having a weight percent sulfur content of not less than 20 plus half the weight percent copper content of the matte in excess of 5 by passing a current through said anode of nickel matte while it is in contact with an aqueous sulfate chloride anolyte containing about 65 to about 115 grams per liter of sulfate radical and about 20 to 55 grams per liter of chloride radical and maintaining the pH of said anolyte at a pH of about 1.8 to about 2.1 to thereby produce an impure nickel-rich anolyte and an anode sludge comprised mainly of elemental sulfur; removing said impure anolyte from said anode compartment; purifying said impure anolyte; introducing said purified anolyte into the cathode compartment of a divided cell to thereby provide a catholyte and electrodepositing nickel from said catholyte onto a cathode in said cathode compartment.

6. A method for producing sulfur which comprises anodically corroding by direct electrolytic action at high anode efficiency a unitary and conductive anode of nickel matte comprised mainly of nickel sulfide and up to about 30% copper and characterized in having a weight percent sulfur content of not less than 20 plus half the weight percent copper content of the matte in excess of 5 by passing a current through said anode of nickel matte while it is in contact with an aqueous sulfate-chloride anolyte and maintaining the pH of said anolyte at a pH of about 1.8 to about 2.4 to thereby produce an anode sludge comprised mainly of elemental sulfur.

7. A method as in claim 6 in which said aqueous

sulfate-chloride anolyte contains from about 65 to about 115 grams per liter of sulfate radical and about 20 to about 55 grams per liter of chloride radical.

8. A method for producing sulfur which comprises anodically corroding by direct electrolytic action a unitary and conductive anode of nickel matte characterized in having a sulfur content of at least about 20% by passing a current through said anode of nickel matte while it is in contact with an aqueous sulfate-chloride anolyte and maintaining the pH of said anolyte at a pH of 1.8 to about 2.4 to thereby provide a sludge comprised mainly of elemental sulfur and containing at least one element selected from the group consisting of selenium, tellurium and precious metals, and subjecting the sludge to further treatment to separate elemental sulfur by distillation.

9. A method as in claim 8 wherein the sludge subjected to distillation is comprised mainly of elemental sulfur and contains selenium.

10. A method as in claim 8 wherein the anolyte contains from about 65 to about 115 grams per liter of sulfate radical and from about 20 to about 55 grams per liter of chloride radical.

11. A method as in claim 10 wherein the sludge subjected to distillation contains a small amount of selenium and the balance is mainly elemental sulfur.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,839,461 June 17, 1958

Louis Secondo Renzoni et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 31, for "anolye" read -- anolyte --; column 7, line 9, for "viz," read -- viz., --; line 16, for "selenium, tellurium" read -- selenides, tellurides --; line 35, for "various" read -- variations --; column 8, line 17, for "remoxing" read -- removing --.

Signed and sealed this 2nd day of December 1958.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

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Commissioner of Patents