(51) International Patent Classification: Not classified

(21) International Application Number: PCT/IB2013/002570

(22) International Filing Date: 8 August 2013 (08.08.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 2012134684 14 August 2012 (14.08.2012) RU

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Published: — without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: METHOD FOR EXTRACTING NOBLE AND NON-FERROUS METALS FROM REFRACTORY RAW MATERIALS

(57) Abstract: A method for extracting noble and non-ferrous metals from refractory raw materials includes a first stage electric treatment of ground pulp in a chloride solution and a subsequent second stage of extracting commercial metals, carried out in one reactor or using electrolyzers with graphite anodes and steel cathodes. The reactor is fed with pulp having an S:L ratio of 1:(1-20) in a solution with a chloride concentration of 60-180 g/L, being acidified to pH=0.2-1.0, it's agitated, the volume current density is set to 1000-10000 A/m² and the electrolyser's voltage to 2-5 V, then maintained constant. The first stage terminates by a transition of electric current through a maximum and changing pH to 1-2. At the second stage, the cathode current density is set to 50-200 A/m², until pH reaches 3-7. Cathode deposits of both stages are combined for further processing.

FIG. 1
METHOD FOR EXTRACTING NOBLE AND NON-FERROUS METALS
FROM REFRACTORY RAW MATERIALS

FIELD OF THE INVENTION

The invention relates to metallurgy of noble metals, namely, to hydrometallurgical methods for processing refractory gold-containing and silver-containing concentrates and ores.

BACKGROUND OF THE INVENTION

Metal extraction from refractory gold-containing ores, where noble metals are concentrated in sulphide minerals in the form of an isomorphous admixture or as a solid solution and are not accessible for direct cyanidation is known to present substantial technical difficulties. Globally, the most widespread process involves multiple stages, including oxidizing roasting in an oven, cyanidation of the roasted product to produce gold-containing solutions, extraction of gold from these solutions using sorption, cementation or electrolysis. A refractory ore hydrochlorination process is also known, which can solve the problem of comprehensive extraction of valuable components due to the high chemical activity of chlorine with respect to gold and lower activity with respect to gangue components.

A version of the hydrochlorination process, called electrochlorination, involves direct electrochemical treatment of refractory ores using chlorine, which is released during the electrolysis of solutions of alkaline metal chlorides. Thus, patent (US351576, Cassel, 26.10.1886) describes a method of extracting gold from ores using an electrochemical cell. The anode and cathode compartments of the latter are separated by a porous asbestos septum and, essentially, form a diaphragm electrolyser. The anode compartment generates chlorine, which interacts with ore under vigorous agitation, and the cathode separates gold from the solution filtered by the septum. Invention (GB190920471 (A), Cobb, 07.09.1909) suggests that ore in the form of pulp with particle size 60 mesh with added sodium chloride solution
(5g/L) be treated using electrolysis in an undivided electrolyser with lead electrodes. Gold plates out on the cathode, while silver chloride is precipitated and can be removed by electrolysis or using any other known process. Invention (US3957603, Rhodes, 18.05.1976) describes a method of electrochlorination for extracting gold from refractory ores, which involves preparing pulp from ground gold ore with water and sodium chloride in the first vessel and placing an anode in the said first vessel. The cathode is placed in the second vessel equipped with a porous membrane to make electric current pass through the membrane. Chlorine generated at the anode interacts with pulp and makes gold dissolve in the form of auric chloride.

Invention (WO8706274 (A1), Kelsall, 22.10.1987) describes a method and apparatus for extracting gold using chlorine and chloride solutions from scrap material, ore or other material, where the oxidizer is also electrochemically generated in the anode compartment of an electrochemical cell. The oxidizer reacts with the said raw material and provides the formation of soluble compounds, which are converted to gold in the cathode compartment of the cell. There are descriptions of other methods of electrochemical chlorination for the oxidation of refractory gold ore and release of metals from refractory sulphide raw materials to the solution. To isolate the metals themselves either sorption or other well-known technologies not associated with previous electrochlorination are recommended, for example, electrolysis of gold from pulp. (See “Chloride metallurgy of gold”, Zyryanov M.N., Leonov S.B., Moscow, “SP Internet Engineering”, 1997, pp. 263–267 [in Russian]). In these experiments, gold electrolysis from pulp with a particle size of 0.15 mm was carried out on lead or graphite electrodes at a current density of 50–100A/m² with a degree of extraction 98–99%.

Invention (EP0115500 (A), EVERETT, DEXTEC METALLURG, 15.08.1984) describes a method of extracting silver and gold from ores and concentrates with the use of electrochlorination. The method involves preparing a mixture of ore or concentrate (pulp 300 g/L) and a strong electrolyte - NaCl (250 g/L). The mixture is kept at the electrolyte boiling temperature, at which silver and gold become dissolved, the pH varies between 3.0 and 8.0. The redox potential is maintained at 750–850 mV. The metal is produced at the cathode and can be separated mechanically. This method also employs a diaphragm electrolyser; chlorine
is fed in the gaseous form or in a hypochlorite. The electrode system works only to precipitate the metals from the solution. Complete precipitation at the cathode is not guaranteed, as the diaphragm hinders the process.

At the same time electrochlorination in pulp and recovery of precious metals in a unified technological cycle using electrolyzers of the same type appears promising.

SUMMARY OF THE INVENTION

This invention relates to an improvement of a method for extracting gold and other noble metals from refractory raw materials without preparatory sulphide oxidation operations, where both processes, i.e. electrochlorination and the preparation of high-quality precipitates of gold and other valuable metals, are carried out in one reactor practically simultaneously. Besides, the invention can be used for a wide range of ores and materials, including natural sorbents, since at the recommended process temperatures, sorption from the solutions utilized is completely suppressed.

The inventive method for extracting noble and non-ferrous metals from refractory raw materials includes the stage of electric treatment of ground raw material pulp in a chloride solution and the subsequent stage of isolation of commercial metals, where both stages are carried out in one reactor using at least one undivided electrolyser. The material fed to the electric treatment stage is ground raw material pulp with the S:L ratio of 1:(1–20) in a chloride solution with the chlorine concentration of 60–180 g/L, which is acidified to the pH of 0.2–1.0. At the beginning of the electric treatment stage under pulp agitation, the volume current density is set at 1000–10 000 A/m\(^2\) at the electrolyser voltage of 2–5 V, which is maintained constant. The end of the pulp electric treatment process is determined by the transition of the current vs. time curve through a maximum and subsequent pH change to 1–2. The processed pulp is fed to the metal extraction stage; for this, cathode current density in the electrolyser is set in the range of 50–200 A/m\(^2\). The extraction stage is considered complete when pH reaches 3–7. After this the cathode deposits of both stages are combined and sent for further processing commercial metals using known methods.

Refractory raw material is an ore, gravity concentrate or flotation concentrate of pyrite or arsenopyrite ores with the sulphide content of 20–80% by weight. The particle size of the ground raw material shall not exceed 0.15 mm.
The reactor may contain segregate electrolyzers for the pulp electric treatment stage and product extraction stage equipped with facilities for agitating the pulp and removable cathodes. The reactor may contain an electrolyzer with a selector to switch between the pulp electric treatment stage and metal extraction stage modes. The chloride solution can be selected from the group of chloride solutions containing the chlorides NaCl, KCl, CaCl₂ and MgCl₂. The electric treatment stage is carried out at temperatures above 60°C, predominantly in the range 60–90°C, and the commercial method extraction stage is carried out at temperatures in the range 20–50°C. Cathode deposits can be separated from cathodes mechanically. In an undivided electrolyser steel cathodes and anodes made of graphite or of a material based on ruthenium oxide and titanium can be used.

The technical result is the possibility to concurrent extraction of commercial metals in the process of ore material electrochlorination with subsequent additional recovery of the desired materials at the same cathodes of the reactor based on undivided electrolyzers of the same type.

BRIEF DESCRIPTION OF THE DRAWINGS

The inventive method is illustrated in the drawings, wherein:

Fig. 1 shows a flow chart of the inventive method;

Fig. 2 shows a waveform for dependence of current volume density \( I (A/m^3) \) and pH upon time in an electrolyser at an electric treatment stage of the inventive method;

Fig. 3 shows a waveform for dependence of cathode current density \( I_C (A/m^2) \) and pH upon time at an extraction stage of the inventive method.

DETAIL DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

While the invention may be susceptible to embodiment in different forms, there are described in detail herein below, specific embodiments of the present invention, with the understanding that the instant disclosure is to be considered an exemplification of the principles of the invention, and is not intended to limit the invention to that as described herein.
The inventive method claimed involves carrying out two stages of refractory material pulp treatment with a direct electric current in an undivided electrolyser with various treatment modes and reaction conditions.

A first stage of the inventive method is intended to oxidise sulphides as completely and quickly as possible. This is favoured by vigorous agitation, acidic medium, heating and high current values. Gold is liberated and passes into the solution under the action of chlorine as an oxidiser and chloride ion as a complexing agent.

In this process, electric current acts as a reagent, a source of chlorine. It must be passed in the amount sufficient for oxidising sulphides. Therefore, each type of raw material will have an individual specific electric power consumption, which is determined by sulphide content. But arbitrary electric power cannot be supplied. If the power is too low, the process will be unnecessarily protracted. If the power is too high, excess unreacted chlorine will escape into the gas phase and become useless. This means that there is an optimum value, which must be relative to the volume (V) of the reaction mass, i.e., expressed in A/m³, which is done in the claimed invention.

The rate of the chemical oxidation reaction can be increased by heating the reaction mass and by creating an acidic medium, where the oxidative potential of chlorine increases. We have established the range where further decrease in pH values below 0.2 does not increase the initial rate of the reaction, whereas pH increase above 1.0 decreases it.

As for the first stage temperature, higher temperature, while significantly reducing the overall process time, generally does not affect the end results of the subsequent gold recovery stage, and its optimum value must be determined on the basis of economic considerations. However, a very important point must be taken into account when selecting the temperature. If the source material contains chemically stable natural sorbents (coal, shungite, graphite), which are not degraded by the process, the temperature must be kept at or above 60°C, which allows to completely suppress secondary sorption of gold by these sorbents and avoid additional losses.

Pulp dilution. Undoubtedly, higher pulp dilution to S:L (ton : m³) = 1: (1–20) reduces the overall process time, since there is less solid material, while the volume current density per unit volume of the reaction mass remains unchanged; however, this does not lead to a
noticeable increase in gold recovery factor nor to a reduction in specific electric power consumption. Thus, the optimum parameters should be selected based on economic considerations.

Reagent concentration (60–180 g/L in terms of the chloride ion). The upper limit is selected based on the reasoning that above it lies the range of saturated solutions, in which the solubility of gases is severely reduced. Given the fact that the process involves chlorine in the atomic and molecular form, reduction of its solubility begins to hamper the process. The lower limit is based on the fact that further reduction decreases gold recovery while having no effect on the completeness on sulphide oxidation.

A second stage of the inventive method is recovery of commercial metals. At this stage, once sulphides are almost completely oxidised, generating large amounts of chlorine is not required. It is only necessary to maintain a working concentration, which will allow to complete the process of gold dissolution and will not interfere with gold deposition on the cathodes. Pulp temperature is not crucial, since gold dissolution occurs at a rather high rate even at room temperature. However, if natural sorbents are present, the temperature at this stage must also be maintained at or above 60°C. The transition of current load through a maximum $I_{\text{max}}$ indicates that the majority of sulphides have been oxidised, and pH increase to 1–2 (pH$_1$) marks the point of complete termination of the process, because at this point acidic reaction products cease to form.

Then the current load $I_C$ must be set to bring cathode current density to 50–200 A/m$^2$. In pH$_1$ range iron salts begin to hydrolyse and yield hydrate precipitates. At this point gold must be recovered as completely as possible to avoid its capture by the forming precipitate. This is achieved by significantly reducing current load and slowing the pulp neutralisation process, which prevents the precipitate from forming. Reduction processes at the cathode are carried out until pH reaches 3–7 (pH$_2$). At this point precipitation of gold with other elements at the cathode is brought to a completion, whereas iron and arsenic are almost completely precipitated. The metal is deposited on a cathode in the form of a tight precipitate. As it accumulates, the cathode is removed and replaced with a new one, while the deposit is removed either mechanically or chemically. Then the gold-containing deposit is processed using known methods to produce metallic gold. After the extraction process is complete, the
pulp is filtered, the solid residue is washed and sent to a tailings storage facility, and the solution obtained is corrected and sent to the process input for reuse.

Fig. 1 shows the method flow chart. The refractory raw material (ore, flotation concentrate, gravity concentrate) is fed to the grinding stage (if necessary). Then the raw material with particle size not more than 0.15 mm is sent to the pulp preparation stage. Pulp is prepared with the S:L ratio (ton:m³) of 1:1–20 in a chloride solution with the chlorine concentration of 60–180 g/L. Chlorides of alkaline metals NaCl, KCl, CaCl₂, MgCl₂ and mixtures thereof are used as chlorides. Pulp is acidified to the pH of 0.2–1.0; hydrochloric acid can be used as an acidity regulator.

The pulp thus prepared is added to a reactor, which constitutes one or more undivided electrolyzers having means for regulating the current and means for controlling pulp acidity and temperature. The reactor is equipped with means for vigorously agitating the pulp in the process of electric treatment. At the beginning of the electric treatment stage under pulp agitation, the volume current density is set at 1000–10 000 A/m³ at the electrolyser voltage of 2–5 V, which is maintained constant. As current is passed through the solution of sodium chloride or other chlorides, the electrochemical process results in the liberation of chlorine, which, acting as a strong oxidiser, breaks down sulphide minerals and dissolves their component, including the commercial metals present in the sulphides. The process of pulp electric treatment is accompanied with commercial metal deposition on metallic electrodes (cathodes). The termination of the pulp electric treatment process is determined using two signs: the transition of the current vs. time curve through a maximum (Iₘₐₓ) and subsequent pH change to 1–2.

Then additional extraction of the commercial material is performed. For this, cathode current density Iₐ in the electrolyser is set in the range of 50–200 A/m² (see Fig. 3). The extraction stage is considered complete when pH reaches 3–7 (pH₂). After this the cathode deposits of both stages are combined and sent for extracting commercial metals using known methods (see Fig. 3).

The reactor can be implemented in the form of a plurality of separately controlled electrolyzers for the pulp electric treatment stage and commercial product extraction stage, equipped with facilities for agitating the pulp and removable cathodes, or as a single
electrolyser with a selector to switch between the pulp electric treatment mode and the commercial product extraction mode. As the commercial metal deposits are accumulated, the cathodes are removed from the reactor at regular intervals. The deposits are separated mechanically or chemically. The cleaned cathodes are reused. The undivided electrolyser can have steel cathodes and anodes made of graphite or of a material based on ruthenium oxide and titanium oxide. Such electrodes are known to be used in the chlorine industry and enable to considerably reduce electric power consumption for electrolysis.

Carrying out the process in solution ensures the absence of gaseous emissions, while the small amounts of chlorine released from the solution can be removed by a ventilation system and returned into the process. Solid waste that is sent to the tailings storage facility contains harmful substances in poorly soluble form. In particular, arsenic is present as iron arsenate, which is similar to the natural mineral scorodite.

The achievement of the technical result was demonstrated in the following laboratory experiments in gold and silver recovery from flotation and gravity concentrates using undivided electrolyser prototypes; the numerical values of current density and pH for each experiment are given in the Table.

Experiment 1. The process was performed in a glass vessel with the capacity of 0.8 dm³. Agitation was performed using a magnetic stirrer with a hot top. Reduction in pulp volume was compensated by adding distilled water.

The electrode cell consisted of two graphite anodes and one replaceable cathode of stainless steel on a nonconductive suspension installed between the anodes, 20 mm away. The electrodes were rectangular and had the dimensions of 55 × 120 (mm). The cell was immersed into the pulp 80–90 mm deep. The cell was powered by a DC power supply, which could stabilise the current or the voltage. As the deposit accumulated, the cathode was replaced with a new one, and the removed cathode was washed, dried, and the deposit was removed mechanically using a scraper.

Raw material and preparation thereof. The refractory raw material subject to processing is a flotation concentrate with particle size of 0.15 mm containing pyrite 58.8%, arsenopyrite 22.2%, gold 15.1 g/t, and silver 95.0 g/t. 0.5 dm³ of a sodium chloride solution
with the chloride ion concentration of 120 g/L was added to 100 g of the raw material. The pulp was acidified with hydrochloric acid to pH 0.70 and heated to 75°C under agitation.

Electric treatment stage. The electrode cell was immersed into the pulp and energised; stabilised voltage was set at 2.5 V. The total pulp volume was 0.53 dm³, the cathode working area was 0.9 dm². Under these conditions the electric treatment was carried out for 168 hours. The current volume density at the start of the experiment was set at 7000 A/m³ and then increased to 9800 A/m³; in 168 h it decreased to 6200 A/m³. During the process, pH dropped to 0.28 and then grew to 1.32.

Metal extraction stage. After 168 hours heating was turned off, and the cell was powered with 1.8 A current in the current stabilisation mode. The resulting current volume density of 3600 A/m³ corresponds to the cathode current density of 200 A/m², which is recommended for this stage. The experiment proceeded in this mode for another 20 hours. During this time, pH increased to 6.11, and the metal extraction stage was considered complete.

At the end of the experiment the processed pulp was filtered, the solid residue (tailings) was washed, dried and weighed. The tailings mass was 82.4 g, gold content was 0.78 g/t, silver content was 0.4 g/t. The mass of the cathode deposits collected was 23.5 g. The content of gold is 61.4 g/t, the content of silver is 344 g/t. Solution analysis showed gold concentration to be 0.01 mg/L, and silver concentration, 1.37 mg/L. Thus, gold was distributed across the products as follows: cathode deposits: 95.5%; tailings: 4.2%; solution: 0.3%. Silver: cathode deposits: 92.5%; tailings: 0.3%; solution: 7.2%.

Experiment 2. The process was performed in a glass vessel with the capacity of 1.2 dm³. Agitation was performed using a magnetic stirrer. The electrode cell design and power supply are similar to those in Experiment 1. The cell was immersed into the pulp 80–90 mm deep.

Raw material and preparation thereof. The refractory raw material subject to processing is a gravity concentrate with particle size of 0.15 mm containing pyrite 39.9%, arsenopyrite 17.4%, and gold 50.1 g/t. 0.8 dm³ of a sodium chloride solution with the chloride ion concentration of 120 g/L was added to 100 g of the raw material. The pulp was acidified with hydrochloric acid to pH 0.43 under agitation.
Electric treatment stage. The electrode cell was immersed into the pulp and energised; stabilised voltage was set at 2.5 V. The pulp was not heated; during the experiment, the temperature varied in the range of 20–27°C. The total pulp volume was 0.83 dm³, the cathode working area was 0.9 dm². The experiment proceeded under these conditions for 72 hours. The current volume density at the start of the experiment was set at 1125 A/m³ and then increased to 5000 A/m³; in 72 h it decreased to 4500 A/m³. During the process, pH dropped from 0.43 to 0.02 and then grew to 1.82.

Metal extraction stage. Cathode current density was set constant at 70 A/m². Electrolysis was carried out in this mode for another 21 hours. During this time, pH increased to 6.14, whereupon the metal extraction stage was considered complete.

At the end of the experiment the processed pulp was filtered, the solid residue (tailings) was washed, dried and weighed. Tailings weight was 48.3 g. Gold content was 4.4 g/t. The weight of the cathode deposits collected was 33.9 g. Gold content was 104.8 g/t. Solution analysis showed gold concentration to be 0.02 mg/L. Additional analysis of graphite electrodes demonstrated them to contain 8.7 g/t of sorbed gold.

Thus, gold was distributed across the products as follows: cathode deposits: 69.7%; sorbed on anodes: 25.6%; tailings: 4.2%; solution: 0.5%.

Experiment 3. The process was performed in a glass vessel with the capacity of 10 dm³. Agitation was performed using a mechanical stirrer made of rigid PVC plastic.

Electrolysis was carried out using two electrode cells. Each of them was made of two rectangular graphite anodes with the dimensions of 140 × 200 mm and one rectangular cathode of stainless steel with the dimensions of 140 × 200 mm. The distance between the electrodes was 20 mm. The cells were immersed into the pulp ~115 mm deep. The cell was powered by a DC power supply similar to that used in Experiments 1 and 2.

Raw material and preparation thereof. The refractory raw material subject to processing is a flotation concentrate with particle size of 0.15 mm containing pyrite 10.9%, arsenopyrite 9.1%, and gold 12.8 g/t. 6.0 dm³ of a sodium chloride solution with the chloride ion concentration of 120 g/L was added to 1000 g of the raw material. Treatment was carried
out under agitation at the temperature of 25–30°C. Pulp was acidified with hydrochloric acid to pH 0.68.

Electric treatment stage. The electrode cells were energised; stabilised voltage was set at 2.5 V. The total pulp volume was 6.3 dm$^2$, the cathode working area was 6.4 dm$^2$. The experiment proceeded under these conditions for 58 hours. The current volume density at the start of the experiment was set at 1050 A/m$^3$ and then increased to 2500 A/m$^3$; in 58 h it decreased to 1700 A/m$^3$. During the process, pH dropped from 0.68 to 0.45 and then grew to 1.88.

Metal extraction stage. The process was continued in the current stabilisation mode, the cathode current density was set at 65 A/m$^2$ (the volume current density was 690 A/m$^3$). The metal extraction stage continued for another 38 hours. During this time, pH increased from 1.88 to 6.45, whereupon the metal extraction stage was considered complete.

At the end of the experiment the processed pulp was filtered, the solid residue (tailings) was washed, dried and weighed. Tailings weight was 848.4 g. Gold content was 0.11 g/t. The weight of the cathode deposits collected was 77.1 g. Gold content was 95.9 g/t. Solution analysis showed gold concentration to be 0.28 mg/L. Additional analysis of graphite electrodes demonstrated them to contain 0.45 g/t of gold.

Thus, gold was distributed across the products as follows: cathode deposits: 68.4%; sorbed on anodes: 15.1%; tailings: 0.9%; solution: 15.6%.

Experiment 4. The process was performed in a glass vessel with the capacity of 0.8 dm$^3$. Agitation was performed using a magnetic stirrer. The electrode cell was analogous to that used in experiment 1, but the graphite anodes were replaced with oxide ruthenium-titanium anodes of the same size, and steel cathodes were used.

Raw material and preparation thereof. The same concentrate as in experiment 3 was used. A solution of sodium chloride (0.5 dm$^3$) with the concentration of 120 g/L by the chloride ions was added to 100 g of the raw material. The pulp was acidified with hydrochloric acid to pH 0.58.

Electric treatment stage. The electrode cell was immersed into the pulp and energised; stabilised voltage was set at 3.0 V. The total pulp volume was 0.53 dm$^3$, the cathode working area was 0.9 dm$^2$. The experiment proceeded under these conditions for 24 hours. The current
volume density at the start of the experiment was set at 6000 A/m$^3$ and then increased to 9100 A/m$^3$; in 24 h it decreased to 3400 A/m$^3$. During the process, pH dropped from 0.58 to 0.46 and then increased to 1.62.

Metal extraction stage. After 24 h voltage was set constant at 2.5 B. Electrolysis was carried out in this mode for another 18 hours. Cathode current density was set constant at 106 A/m$^2$. During this time, pH increased from 1.62 to 5.84, whereupon the metal extraction stage was considered complete.

At the end of the experiment the processed pulp was filtered, the solid residue (tailings) was washed, dried and weighed. Tailings weight was 83.6 g. Gold content was 0.66 g/t. The weight of the cathode deposits collected was 10.3 r. Gold content was 98.5 g/t. Solution analysis showed gold concentration to be 0.26 mg/L.

Thus, gold was distributed across the products as follows: cathode deposits: 84.6%; tailings: 4.6%; solution: 10.8%.

It is noteworthy that the results obtained in case of graphite anodes and oxide ruthenium-titanium anodes substantially did not differ. However, in case of using oxide ruthenium-titanium anodes energy consumption per unit of feedstock was reduced. Besides, gold sorption on the anodes did not occur, in contrast to the case of using graphite anodes.

The described experiments demonstrate that a number of technological problems can be solved in the course of pulp electrolysis: sulfides can be oxidised in an environmentally safe way, the gold contained therein can be dissolved, gold can be extracted directly from the pulp without filtering and concentration using sorbents, and a product suitable for directly recovering metallic gold can be obtained at the cathodes.

**INDUSTRIAL APPLICABILITY**

The method can be implemented using equipment for grinding raw materials and preparing solutions and pulp that is known in hydrometallurgy technology, electrolyzers of known designs, as well as means for controlling and adjusting the key process parameters.
## TABLE

**METHOD IMPLEMENTATION MODES FOR THE DESCRIBED EXPERIMENTS**

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CLAIMS

1. The method for extracting noble and non-ferrous metals from refractory raw materials includes the stage of electric treatment of ground raw material pulp in a chloride solution and the subsequent stage of extraction of commercial metals, where:

   both stages are carried out in a reactor using at least one undivided electrolyser having two electrodes: a cathode and an anode;

   the material fed to the electric treatment stage is ground raw material pulp with the S:L ratio of 1:1–20 in a chloride solution with the chlorine concentration of 60–180 g/L, which is acidified to pH in the range of 0.2–1.0;

   at the beginning of the electric treatment stage under pulp agitation, the volume current density is set at 1000–10 000 A/m³ at the electrolyser voltage of 2–5 V, which is maintained constant;

   time dependencies of current and pH are recorded, the termination of the electric treatment stage is determined by the transition of the current vs. time curve through a maximum and subsequent pH change to 1–2;

   then the processed pulp is fed to the metal extraction stage; for this, cathode current density in the electrolyser is set in the range of 50–200 A/m²;

   the extraction stage is considered complete when pH reaches 3–7, whereupon the cathode deposits of both stages are combined and sent for further processing commercial metals.

2. Method according to claim 1, wherein the refractory raw material is an ore and/or gravity concentrate and/or flotation concentrate of pyrite and/or arsenopyrite ores with the sulphide content of 20–80% by weight.

3. Method according to claim 1, wherein the particle size of the ground raw material shall not exceed 0.15 mm.
4. Method according to claim 1, wherein the undivided electrolyser has metallic cathodes and anodes made of graphite or of a material based on oxides of ruthenium and titanium.

5. Method according to claim 1, wherein the reactor contains independent electrolyzers for the pulp electric treatment stage and the metal extraction stage, the electrolyzers are equipped with means for pulp stirring and with dismountable cathodes.

6. Method according to claim 1, wherein the reactor contains an electrolyser with dismountable cathodes and a selector to switch between the pulp electric treatment stage and the metals extraction stage.

7. Method according to claim 1, wherein the chloride solution is selected from the group of chloride solutions containing NaCl, KCl, CaCl₂ and MgCl₂.

8. Method according to claim 1, wherein pulp is acidified with hydrochloric acid.

9. Method according to claim 1, wherein the electric treatment stage is carried out at temperatures above 60°C, predominantly in the range 60–90°C, and the extraction stage is carried out at temperatures in the range 20–50°C.

10. Method according to claim 1, wherein for refractory raw material containing natural sorbents the above stages of the process are carried out at temperatures above 60°C, predominantly in the range 60–90°C.

11. Method according to claim 1, wherein cathode deposits are separated mechanically or chemically.
FIG. 1