Co-processing of Copper and Nickel Ores from Noril’sk Deposits and the Apatites from Maymecha-Kotuy Province

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Abstract

The processes involved in treatment and processing of copper and nickel ores with the use of phosphoric acid solutions are investigated, as well as processes of precipitation of platinum metals with thioacetamide and sorption of nickel and cobalt from phosphoric solutions. A technology is proposed for co-processing of copper and nickel ores from Noril’sk deposits and the apatites from Maymecha-Kotuy province. Advantages of this technology are: isolation of all valuable components from raw material in the form of high-quality primary concentrates, decrease in the amount of recycling products due to simplification of the technology, high coefficient of multipurpose utilization of raw material, which provides manufacture of additional products, absence of the necessity for expenses to build tailing and cake dumps, sulphur utilization in Clause process, which provides a decrease in environmental hazard, simplicity of instrumentation, simultaneous production of phosphoric fertilizers for the needs of agriculture in Siberia.

INTRODUCTION

At present, the Norilsk Mining and Smelting Plant (NMSP) proceeds rich copper-nickel ores which are sharply different from impregnation ore both in chemical and in mineralogical composition. Meanwhile, physical enrichment processes and metallurgical processes which take only poor account of the specific features of the composition of lode roes are traditionally conserved in the technology of lode ore processing. Because of this, the efficiency of ore processing is rather low. For instance, only 13 elements of 18–20 useful ones are extracted to one extent or another from ores into commercial products. The recovery of many metals is at a low level, %: Os 5, Ir 10, Ag 30–40, Ru 20, S 2, Se 20, Te 10, Pt, Pd, Rh 60–80, Co 40, Ni 75, Cu 80. Many valuable and rare metals are not extracted at all; these include Re, In, Bi, etc. The major fraction of losses of nonferrous and precious metals is connected with traditional processes. Hence, an increase in the efficiency is to be expected with a technology which should take into account new properties of raw material and solve the problem of more complete extraction of all the useful components of the raw material. A complete absence of the emission of wastes into the environment or its reduction to a minimum is an obligatory requirement to the new technology.

Substantial reserves of apatites are present in the Taymyr Peninsula. At the same time, the region and the country suffer deficit of phosphoric fertilizers, since the productivity of Siberian fields is low because of the lack of mineral fertilizers. Siberia should have its own production of mineral fertilizers, in particular phosphate ones. Raw resources for this purpose are available; it is the apatites of Taymyr.
Starting from the principle of complex utilization of the mineral raw materials of the Noril’sk region as a whole, one can jointly solve two autonomous problems of the development of the productive forces of the Krasnoyarsk Territory:

1) an increase in production volume and improvement of technical and economic parameters of the processing of pyrrhotine-containing copper and nickel ores of the Noril’sk region;

2) establishment of the Siberian large-scale production of phosphorus-containing fertilizers in order to provide dynamic increase in the productivity of agriculture in Siberia.

Complex solution of these problems can be provided by decomposition and enrichment of the ores of nonferrous metals in phosphate media (ROFOSS process) with the removal of phosphorus at the end of the process into the commercial calcium phosphate [1].

Massive ores of the Talnakh and Oktyabr’sk deposits are distinguished by low gob content. This is so if pyrrhotine, with its content up to 60–80 %, is considered as valuable component, too. In practice, according to the known technology, ore is separated by means of physical enrichment into several primary concentrates, %: copper (Cu 27.7, Ni 1.27), nickel rich (Cu 11.75, Ni 4.53), base nickel (Cu 0.31, Ni 0.37), pyrrhotine (Cu 0.52, Ni 1.95). Total amount of metals extracted into these concentrates is, %: copper 92.3, nickel 82.3, platinum metals 85.

A clear separation of minerals is absent from this technology. Each of the resulting primary concentrates contains all minerals of the ore; only their quantitative ratio is varied. For example, only 50 % of pyrrhotine is isolated into the pyrrhotine concentrate, capturing 15 % of pentlandite, 20 % of magnetite, 13 % of rock-formers, more than 8 % of platinum metals.

There is no technology of efficient processing of the base nickel and magnetite concentrates. A large amount (more than 50 % of the ore mass) of pyrrhotine concentrate enters the treatment according to the oxidative autoclave technology at the Nadezhdinsk nickel plant [2]. So, the basic technology for the processing of sulphide copper and nickel pyrrhotine-containing ores of the Noril’sk industrial region is the technology involving ore enrichment by physical methods resulting in copper and nickel concentrates, magnetite and pyrrhotine concentrates; autoclave oxidation of the pyrrhotine concentrate resulting in the pulp containing sulphur, sulphides of nonferrous and precious metals, and iron hydroxide; precipitation of the sulphides of nonferrous metals, flotation separation in the pulp resulting in the dump ferriferous cake and the pulp of sulphur-sulphide concentrate; sulphuric floatation leading to sulphur and the sulphide copper-nickel concentrate.

It is necessary to isolate copper, nickel, cobalt and precious metals from all the five concentrates; sulphur is partially extracted only from the pyrrhotine concentrate; iron which accounts for 35–45 % of the ore mass goes directly to the tailing. The coefficient of useful consumption of the resource does not exceed 55 %. High level of specific expenses is connected with high inputs of enrichment process and small separation coefficients, which creates large amount of recirculated middlings at all repartition stages.

The major disadvantage of the autoclave oxidative technology is that a large amount of the tailing product (iron hydroxide) is formed at the head of the process, during the operation which is not accompanied by separation effects. A large-scale operation of the autoclave oxidation is goalless with respect to the separation aspect.

In the physicochemical sense, the oxidized pulp with high oxidizing potential is a powerful chemical power reservoir in which the accumulated free energy hinders reduction with iron pellets, sulphide precipitation and possibly floatation, since sulphide particles are screened by oxide films.

In sulphate media, the hydrolysis of platinum metals, especially rhodium, iridium, ruthenium, occurs simpler than in chloride media, at low pH. Hence, hydrolysis of iron and platinum metals is parallel in time; the quantitatively prevailing iron hydroxide captures platinum satellites and retains them. Small particles of melted sulphur are also able to capture nonferrous and precious metals, which are lost with floatation tails. In addition, sulphur dioxide emission into the atmosphere and re-
jection of ferriferous cake into the tundra exceed half of the mass of the mined ore.

The acidic methods of non-oxidative decomposition of mattes are chemically more logical, because they allow one to separate the matte into three phases at the head of the technological scheme.

In 1973, K. K. Beloglazov proposed a technology for pyrrhotine-containing ores [3], which has some advantages over the basic technology; however, it can be realized only with wide application of the autoclave technique. The technology includes smelting of the ore to obtain matte, the decomposition of matte in autoclaves with sulphuric acid, with sulphur isolation in the form of hydrogen sulphide, isolation of copper, nickel, cobalt and precious metals into the sulphide residue, autoclave oxidation of the sulphide residue in sulphuric acid, with the transfer of nickel, cobalt and iron into solution; autoclave precipitation of nickel and cobalt by hydrogen from solutions, high-temperature hydrolysis of iron (III) sulphate in autoclave, the autoclave reduction of iron with hydrogen from hydroxide. No autoclaves of the necessary productivity and durability have been designed for the volume of production required for the NSMP. The complexity of apparatus implementation makes the technology proposed by K. K. Beloglazov difficult for realization and too high-input. This technology was not accepted for designing and realizing, though it was considered as an alternative to the autoclave oxidative technology.

The Nadezhinsk technology of pyrrhotine concentrate processing, which has been introduced and has no analogs in the world experience, does not solve all problems of technical progress at the NSMP. At present, it restrains the quantitative growth of metal production. In order to provide the most rational and complex consumption of ore raw material in future, the NSMP should develop not as narrowly specialized plant of nonferrous metallurgy but as a link of the spacious territorial and industrial complex embracing also other minerals of the Taymyr.

The present work is aimed at the development of simpler and ecologically safer technology than the existing one, which would allow one to increase the complex character of using mineral resources of the Noril’sk region. The proposed measures (phosphate technology) are aimed at an increase in the efficiency of the program of development of productive forces of Siberia.

DESCRIPTION OF THE PROPOSED TECHNOLOGY

In order to justify the outlooks of processing of the Taymyr apatites, we mastered the major items of the phosphate technology of primary processing of pyrrhotine-containing ores of nonferrous metals both theoretically and experimentally (at the laboratory level) (Fig. 1). The obtained results are the initial statements of the complex.

1. The production of phosphoric acid should be created on the basis of the Maymecha-Kotuy apatites according to the known technologies.

2. In the non-oxidative process, mattes (which are products of ore smelting) are decomposed with phosphoric acid [4]. As a result of one operation of this type, efficient separation of the components of raw material is achieved:
   - sulphur is emitted into the gas phase in the form of hydrogen sulphide; the fraction of this sulphur is equivalent to the iron, nickel and cobalt content (more than 70 % of total content);
   - iron (more than 98 %), nickel and cobalt (more than 80 %) pass into solution;
   - in the non-decomposed residue, metals are concentrated: copper (100 %), all precious and rare metals (more than 98 %), the remaining nickel and cobalt (15-20 %); the yield of non-decomposed residue is up to 20 %, copper content in it is 55 %.

3. Nickel and cobalt are quantitatively recovered from iron phosphate solutions, for example by sorption-desorption.

4. Tailing solutions containing free phosphoric acid and iron are neutralized by lime. Mainly iron phosphates are thus deposited. The recovery of iron is 94 %, phosphorus pentoxide 23 %. The filtrate after iron separation is a diluted solution of phosphoric acid. Iron phosphate can be processed according to the known method to obtain ferrophosphorus and phosphorus pen-
toxide. The latter is directed to strengthen the solution of phosphoric acid.

5. Any part of the filtrate from the first stage of neutralization can be admitted to the second stage of neutralization, in which almost pure calcium phosphates are precipitated. The final filtrate is almost completely demineralized water suitable for recycling; calcium phosphate is a fertilizer; ferrophosphorus is a useful product; slag can be used in cement production. Versions of transfer phosphate solutions (partially or fully) to central and southern regions of the Krasnoyarsk Territory should be economically examined for profitability.

The use of phosphate technology and production of phosphorus-containing compounds in the described territorial industrial intersec-

toral complex will lead to an increase in the efficiency in mineral raw consumption. The advantages of this technology are as follows.

1. Ores of different deposits can be processed without a cumbersome stage of physical enrichment; a single technology can be applied.

2. All valuable components of the raw material are separated into the primary concentrates or into commercial products of high quality, namely:
   - copper concentrate in which copper, precious metals and a part of nickel and cobalt are collected;
   - eluate which contains only nickel and cobalt;
   - sulphur in the form of hydrogen sulphide;

Fig. 1. Functional technological diagram of the complex processing of copper and nickel raw material in phosphate systems. ISR – insoluble residue, PM – precious metals.
According to predictive estimates, the profitableness of mining and processing of the apatites from Maymecha-Kotuy province in such a technological complex is provided by the economic effect arising both in the area of production of nonferrous and precious metals as a result of increase in the recovery, complex consumption of raw material, ecological effect and a decrease in expenses, and in the area of agriculture as a result of an increase in the productivity of grain crops under the application of fertilizers.

**PROCESS CONDITIONS**

*Decomposition of matte with phosphoric acid, copper and sulphur isolation*

In the absence of oxidizers, phosphoric acid dissolves iron, nickel and cobalt sulphides replacing hydrogen sulphide and does not dissolve (even at high temperature about 300 °C) sulphides of copper and precious metals (sulphides of hydrogen sulphide group).

For instance, as a result of the decomposition of nickel-pyrrhotine concentrate, 9 % of iron and 55 % of nickel pass into solution; about 70 % of sulphur pass into the gas phase; copper remains quantitatively in the insoluble residue (ISR). However, natural sulphides (pyrrhotine, etc.) are difficult to be treated.

Nickel-pyrrhotine concentrate decomposes at the temperature above 220 °C, rather complete leaching is achieved with the process duration of 2 h; however, even in this case the yield of ISR is 22–29 %. Samples with the monoclinic modification of pyrrhotine are treated even with more difficulties; the yield of ISR is 30–35 %.

It is natural to expect that simple sulphides, for example FeS, will be treated more easily. Experiments confirm this expectation.

Nickel-pyrrhotine concentrate, ore, heavy fraction of ore were smelted to obtain matte at 1250 °C adding 5 % iron to bind the excessive sulphur. This activation of the raw material proves to be very efficient. Decomposition temperature decreases to 110–180 °C, duration decreases to 15–30 min, the degree of
transformation increases. Smelting of the initial raw material of different composition also provides the effect of unification and purification of the raw material due to the formation of slag by rock-forming components. Conditions and results of the decomposition of products with phosphoric acid are shown in Table 1.

**Recovery of platinum metals**

As we have already mentioned, phosphate decomposition of matte is accompanied by the emission of hydrogen sulphide. It is able both to reduce and to precipitate metal ions. Phosphate ion forms stable complexes with iron (III) in solution supporting the lowers redox potential, at which sulphide oxidation processes are excluded in the system. The fact that copper is absent from solutions after the decomposition of matte confirms this statement. Hence, it may be assumed that mineral forms of platinum metals under these conditions would not be oxidized and dissolved under these conditions. However, the processes involved in dissolution and precipitation of platinum metals are not fully understood yet. So far, search for methods to avoid losses of platinum metals, especially iridium, is an urgent problem. So, the possibility of their presence in solutions after the decomposition of raw material can be admitted, along with the necessity of measured against losses.

It is known from analytical and technological experience that the most difficult task is to achieve complete precipitation of iridium. Because of this, one can decide whether measures against losses of platinum metals are sufficient basing on iridium recovery. The experiments described below provide evidence for this statement.

With consumption acceptable for the industrial scale, high extent of iridium recovery is achieved using thiocarbamide. At the stage of matte decomposition, known amounts of platinum metals were added into the system in the form of titrated phosphate solutions; thiocarbamide was added as a precipitating agent. Its consumption was varied from 0 to 20 mg/mg of iridium. After separating sulphide precipitate, platinum metal content of the filtrate was determined using the method of their co-precipitation with thiocarbamide. The copper concentrate was analyzed by the spectral method.

Results of the recovery of platinum metals are shown in Table 2. Experiments show that favourable conditions for separation of platinum metals into the sulphide precipitate are really created during the matte decomposition with phosphoric acid: for instance, even knowingly introduced platinum metals are precipi-

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**Table 1**

Composition of matte, yield and composition of insoluble residue (ISR) of the decomposition of matte and recovery of metals

<table>
<thead>
<tr>
<th>Product</th>
<th>Matte/P₂O₅</th>
<th>Yield of ISR, %</th>
<th>Recovery of S as H₂S, %</th>
<th>Content, %</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matte A</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.65</td>
<td>41.7</td>
</tr>
<tr>
<td>ISR (A)</td>
<td>1 : 10</td>
<td>17.4</td>
<td>84.6</td>
<td>21.0/100</td>
<td>11.61/48.58</td>
</tr>
<tr>
<td>Matte B</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.38</td>
<td>3.81</td>
</tr>
<tr>
<td>ISR (B)</td>
<td>1 : 10</td>
<td>7.1</td>
<td>94.5</td>
<td>57.9/100</td>
<td>4.43/3.3</td>
</tr>
<tr>
<td>Matte (C)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>11.6</td>
<td>33.68</td>
</tr>
<tr>
<td>ISR (C)</td>
<td>1 : 5</td>
<td>21.0</td>
<td>78.5</td>
<td>55.2/100</td>
<td>2.49/14.2</td>
</tr>
<tr>
<td>ISR (C)*</td>
<td>1 : 3</td>
<td>21.76</td>
<td>78.0</td>
<td>53.07/100</td>
<td>3.38/20.0</td>
</tr>
</tbody>
</table>

*Note. Experimental conditions: temperature: 110–180 °C; time: 15–30 min; an open-type apparatus; mixing rate, 200 rpm. A – matte from refining of the nickel-pyrrhotine concentrate, B – matte from refining of the Talnakh ore; C – matte from refining of the heavy fraction of the Talnakh ore. ISR (C): a mean of 8 experiments; ISR (C)*: a mean of 6 experiments.*
Recovery of platinum metals into the sulphide precipitate and the consumption of thiocarbamide in the decomposition of matte with phosphoric acid

<table>
<thead>
<tr>
<th>Number of experiments</th>
<th>Remaining in solution, mg/isolated with sulphide precipitate, %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>Pd</td>
</tr>
<tr>
<td>5</td>
<td>0.06/98.8</td>
<td>0.0/100</td>
</tr>
<tr>
<td>2</td>
<td>0.0/100</td>
<td>0.0/100</td>
</tr>
<tr>
<td>10</td>
<td>0.0/100</td>
<td>0.0/100</td>
</tr>
<tr>
<td>20</td>
<td>0.0/100</td>
<td>0.0/100</td>
</tr>
<tr>
<td>20</td>
<td>0.0/100</td>
<td>0.0/100</td>
</tr>
</tbody>
</table>

Note. Experimental conditions: platinum metals in solution: 5 mg each; total concentration: 25 mg/l.

Non-oxidative decomposition is demonstrated to give a clearly exhibited separation effect. Sulphur is separated in the form of gaseous product, copper and precious metals go into the insoluble precipitate; nickel, cobalt and iron enter the solution.

Recovery of nickel and cobalt from phosphate solution

Relatively small dissociation degree of phosphoric acid \( (K_a(I) = 7.52 \times 10^{-3}; pK_a = 2.21) \) allows performing cation-exchange sorption of nickel and cobalt even from very acidic solution containing 40–45% of free phosphoric acid. Iron (III) is sorbed only slightly under these conditions because it is bound into rather stable complexes with phosphate ion.

The experiments described below verify the sorption recovery of nickel and cobalt from phosphate solutions and their separation from iron by means of selective elution.

Phosphate solution (300 ml) from matte decomposition, diluted with water to the phosphoric acid concentration of 335 g/l, was passed consequently through two columns of 20 mm in diameter, loaded with 10 g of KU-2 × 8 each. The filtration rate was 60 ml/h per 1 g of the resin. Filtrates after the second column were analyzed for nickel and cobalt. The resin was washed with water, nickel and cobalt were collectively elutriated with a 10% solution of sodium nitrite. Eluates from each column were analyzed for nickel, cobalt, and iron. After elution of nickel and cobalt, the resin was recovered with a 45% phosphoric acid.

No cobalt or nickel was detected in filtrates after the second column. Iron was not detected in all eluates in all experiments. It follows from the data shown in Table 3 that nickel and cobalt exhibit almost identical behaviour during sorption and elution: they are quantitatively sorbed from highly acidic phosphate solutions, quantitatively and selectively eluted with the sodium nitrite solution.

Even in the case of rather high iron (III) concentration in the initial solution (22.9 g/l), it is sorbed poorly: with 92–96% sorption extent of nickel and cobalt, sorption of iron (III) is 1–3%; in the case of complete sorption of nickel and cobalt, that of iron is 6%. Under elution of nickel and cobalt with sodium nitrite solution, iron is not eluted; however, it is eluted with 40–45% phosphoric acid during the recovery of the resin. Iron-containing eluate can be brought together with the filtrate.

Thus, the eluate of nickel and cobalt is a 10% concentrate; separate recovery of metals from it can be performed using the known methods.
Utilization of iron and phosphorus

After sorption recovery of nickel and cobalt, the solution remains, which contains iron and the whole phosphorus introduced in the process. By neutralizing the solution with calcium hydroxide, it is possible to precipitate almost the whole iron in the form of phosphate at the first stage and to isolate phosphate ion into the precipitated product. Practical possibility to perform a two-stage neutralization and the facts of separation and isolation of iron (III) and phosphate ion are confirmed by the data of experiments shown in Table 4.

A complex of processes in phosphate systems provides high separation coefficients for valuable components of the ore, i.e., high selectivity and purity of primary concentrates, the processing of which excludes the formation of recycling products and industrial wastes. So, expenses decrease and no hazard is brought to the environment.

Increase in the coefficient of complex usage of the raw material

The ratio of the cost of product to the cost of all useful components per one unit of a resource is known to serve as an economic measure of the complex character of the use of raw material. Complete account of the useful components in the Noril’sk ores allows estimating the cost of the resource at the level of $400/t. The cost of the product manufactured according to the known technology is about $225/t of the resource.

The lode copper and nickel ores can be processed according to the phosphate technology without enrichment by physical methods; therefore, one can exclude losses of valuable components in tailings and in semi-products for which no efficient processing technology exists. The phosphate technology allows obtaining rich concentrates, the processing of which is connected with smaller losses of metals; in addition, the possibility for utilization of iron and sulphur is created. The cost of products manufactured according to the proposed technology can be increased up to $400/t of the resource.
Quality of concentrates

The phosphate technology provides high coefficients of separation and recovery for the main components of the raw material:
- more than 98 % of iron is brought out into the phosphate final solution from which it is utilized at a high recovery extent at the end of the technological process;
- sulphur in amounts equivalent to the amount of iron, nickel and cobalt ions passing into solution is separated in the form of hydrogen sulphide emitted into the gas phase and is processed according to the known technology into the elemental sulphur together with sulphur dioxide emitted during the processing of copper-sulphide concentrate;
- copper, with recovery extent of 100 %, remains in the insoluble residue forming copper concentrate in which copper content is 55–60 %;
- nickel and cobalt with the recovery extent about 85 % form a pure product: eluate from the sorption treatment containing no impurities.

Processing of the concentrates of such a high quality leads to a sharp decrease in the amount of recycling products, the processing of which according to the known technology weighs heavily on the net cost of the product (copper, nickel, cobalt, platinum metals, silver, selenium, sulphur). A decrease in expenses is probabilistically estimated as 50–60 %, which will save $100–120 mln.

Ecological effect

The phosphate technology creates prerequisites for a sharp decrease in the amount of detrimental species such as sulphur and ferriferous cake (Fig. 2) into the environment. In the non-
oxidative decomposition process, sulphur is released in the form of hydrogen sulphide which is a component necessary for the Clause process:

$$2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$$

Calculations show that a decrease in the emission of sulphur and dust with gases into the atmosphere (per the current volume of production) provides the environmental protection effect about 400 mln US dollars. Elimination of the release of ferriferous cakes into the tundra will provide an effect which would be not smaller than that one.

**Production of phosphorus-containing fertilizers**

Autonomous realization of the project of the production of phosphorus-containing fertilizers on the basis of apatite ores of the Maymecha-Kotuy province seems to be a difficult problem, taking into account the negative effect of northern economic factors. The northern factor of increased expenses can be removed due to a part of the economic effect arising in the phosphate technology of the production of nonferrous metals. Satisfaction of the needs of agriculture in Siberia in phosphorus-containing fertilizers means a substantial increase in the productivity of agriculture.

**CONCLUSIONS**

Thus, the technology of nonferrous metals recovery and phosphorus-containing compounds production provides an increased efficiency in the presented interindustry complex. Its constituents are as follows: all the valuable components of the raw material are isolated in the form of high-quality primary concentrates; simplification of technology leads to a decrease in the amount of recycling products, high coefficient of the complex usage of raw material provides manufacture of additional products; the necessity of expenses for creation and utilization of the tailings and cake dumps is eliminated; utilization of sulphur in the Clause process provides a decrease in the hazardous effect on the environment. The national importance of an increase in the productivity of agriculture in the District and in Siberia due to the application of phosphorus-containing fertilizers can be hardly overestimated.

The technology opens wide possibilities for excluding hazardous effect of the expanding human industrial activities on the environment and on humans.

**REFERENCES**

1 Inventor’s certificate 923195 USSR, 1981.