

Development of an Innovative Technology for the Complex Extraction of Nickel and Cobalt from Iron-Silicate Ores

Kenzhegali M. Smailov, Yeldar Nuruly, and Uldana Zh. Beisenbiyeva

ABSTRACT

This article studies the development of a new hydrometallurgical technology for the complex extraction of nickel and cobalt from iron-silicate ores. As a result the following algorithm of actions for obtaining high percent of extraction (for nickel 97,0 %, for cobalt 92,8 %) is offered: Crushed ore from the Batamshy deposit (-200 mesh) is treated with dissolving reagents to transfer cobalt and nickel from the solid phase into solution with subsequent filtration and washing, where 1.0% to 7.5% (by mass) calcium hypochlorite and 3.0% to 6.0% (by mass) ammonium fluoride in 10% technical hydrochloric acid solution (by volume) are used as dissolving reagents. Dissolution is carried out at room temperature for 120 minutes at a ratio of Solid to Liquid 1:10 (S:L = 1:10) and under constant stirring by horizontal-circular rotation of 100 revolutions/minute. The implementation of the method makes it possible to significantly increase the degree of extraction, simplify the technological process and avoid complications in operation hardware design.

Keywords: Complex Extraction, Hydrometallurgical Method, Iron-Silicate Ores, Nickel and Cobalt Minerals.

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K. M. Smailov

Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, Almaty, Kazakhstan.

(e-mail: k.smailov@satbayev.university)

Y. Nuruly*

Al-Farabi Kazakh National University NJSC, Almaty, Kazakhstan.

(e-mail: yeldar.nuruly@kaznu.edu.kz)

U. Z. Beisenbiyeva

Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, Almaty, Kazakhstan.

(e-mail: dana_91_21@mail.ru)

*Corresponding Author

I. INTRODUCTION

It is well known that when choosing efficient solvents for dissolving nickel-cobalt-containing raw materials, the forms of nickel and cobalt compounds in ores and products of their processing should be taken into account. The degree of nickel and cobalt extraction depends on the mineralogical composition of the object under study. Geologists and metallurgists in their time studied in detail the ores of Batamshy deposit (Aktobe region, Kazakhstan) by various physical and chemical methods [1].

The nickel-cobalt-containing ores of the Batamshy deposit were taken as the object of study. First, the material composition of cobalt and nickel in ores of this deposit was presented. Then degrees of extraction of cobalt and nickel from iron-silicate ore were studied.

The Batamshy deposit was discovered in 1933 while searching for silicate nickel deposits. It is located 2 km to the south of the town of Batamshy, Aktobe region. The deposit is located in the middle part of the Kempirsay massif of hyperbasites in the zone of its eastern contact with the host gabbro-amphibolites, in the area of sublatitudinal dikes gabbro-diabase [1].

The mineralization is localized in the weathering crust of serpentinites, which compose the watershed elevation. The weathering crust consists of three zones (from bottom to top): leached nontronitized serpentinites, nontronitic clays, ochres and ochric-nontronitic rocks. The total eluvium thickness averages 50 m. Industrial cobalt-nickel mineralization is observed within all zones.

The deposit has two deposits, which unite 7 ore bodies, 6 of which have been developed by YuzhUralNickel by now. The horizontally occurring ore bodies have a plate-like shape with an undulating roof and an uneven base, complicated by pocket-like depressions.

The length of ore bodies is 225-1900 m, width is 15-150 m, thickness is 1-29.6 m, and average is 4.8 m. Depth of occurrence of the roof of ore bodies varies from 0.3 to 45 m. From the surface, they are covered by a cover of Neogene-Quaternary sediments. The ratio of lithologic types of ores is as follows: ocher and ochered nontronites – 10.9%, nontronitic clays – 38.8%, nontronitized serpentinites – 36.6%, leached serpentinites – 13.7%.

The main ore minerals are nontronite and garnierite, secondary minerals are kerolite, nickel-bearing chlorite, and asbolane. Nontronite is present in all types of ores up to 80% in the form of clumps of waxy yellow-green color with a greasy sheen. Garnierite occurs as dense matte green crusts and thin branching

veins [1].

II. LITERATURE REVIEW

Hydrometallurgical methods of nickel and cobalt extraction began to be used in industry in the late forties [2],[3]. Currently, they are used to process oxidized and sulfide cobalt-nickel-containing materials using sulfuric acid, hydrochloric acid, and ammonia solutions [4],[5]. Ammonia solutions are most widely used due to their good selectivity, ability to form well-soluble nickel and cobalt compounds, low aggressiveness, and easy regeneration [6]-[8].

A review of the literature data has shown that cobalt and nickel extraction technologies have a number of serious drawbacks. Mainly the extraction of cobalt and nickel from cobalt-nickel-containing ores and concentrates is carried out at high temperatures, according to a complex scheme very unprofitable both economically and ecologically.

It follows that the intensification of dissolution processes and more complete extraction of valuable metals from ores with low content of valuable components, as well as increasing demands on the quality of the resulting product, make it necessary to find effective methods, beneficial both economically and environmentally, in the processing of minerals.

Moreover, a patent search similar to our proposed technology also revealed some shortcomings in the extraction of nickel and cobalt metals, the results of which are presented below in Table I as a comparative analysis.

TABLE I: COMPARATIVE ANALYSIS OF INVENTIONS SIMILAR TO THE PROPOSED TECHNOLOGY

No.	Name of invention	Background data on the invention	Technology description	Disadvantages of technology
1	Direct atmospheric leaching of highly-serpentinized saprolitic nickel laterite ores with sulphuric acid [2]	U.S. Patent No. 6379637 B1, IPC C22B 23/00, published April 30, 2002	A method for extracting nickel and cobalt by sulfuric acid leaching at atmospheric pressure of nickel laterite ores with high serpentine content, involving leaching of the highly serpentinized saprolite portion of the nickel laterite ore profile in strong sulfuric acid solutions at atmospheric pressure and temperatures of 80°C to 100°C, essentially autogenous, with recovery of at least 90 % of the nickel contained therein and a significant fraction of the cobalt after a leaching reaction time of about one hour or less. Seven ore samples with 1.92-3.34 % nickel and 0.02-0.18 % cobalt was tested	The leaching process takes place at temperatures ranging from 80 to 100°C, which must be maintained at all times, accordingly, leads to significant energy costs, and is also characterized by a wide range of variations in nickel extraction from various ore samples. In addition, the impossibility of extraction by sulfuric acid of metals that are in closed silicates, the difficulty of extraction of metals from solutions due to the formation of gelled silicic acid during leaching by mineral acids
2	Method for processing cobalt-containing products [3]	Patent of the Republic of Kazakhstan No. 20321, IPC C22B 3/14, C22B 23/00, published August 16, 2010	Method of processing cobalt-containing products, which refers to hydrometallurgy, and can be used for processing of cobalt- and nickel-containing concentrates and cinders, where the result is the processing of cobalt- and nickel-containing solutions by ammonia method, separation of cobalt and nickel and getting cobalt oxide, which is achieved by the fact that in the known method of processing cobalt-containing products, which includes roasting, leaching, separation and extraction of components. According to this method, the concentrate was subjected to roasting for 2-4 hours at a temperature of 600-800°C. After roasting, the pyrite slag was subjected to granulation and sulfation roasting. At 650°C the extraction of cobalt was 87.1 %. After sulphate firing the pellets were leached with water. The extraction rate of cobalt, in this case, was 80.26 % of nickel – 49.56 %. Ammonia solutions have the ability to form well soluble stable compounds of nickel and cobalt like $Ni(NH_3)_5CO_3$ and $Co(NH_3)_5CO_3$	Ammonia leaching is not a universal process for all types of cobalt-nickel-containing ores, since they leach poorly, which is explained by their low recoverability. Moreover, the use of roasting at the beginning of the process is very energy intensive. Also, the method is characterized by insufficiently high recovery rates of cobalt and nickel
3	Method for processing oxidized nickelcobalt ore [4]	Patent of the Russian Federation No. 02245933, IPC C22B 23/00, published February 10, 2005	Method for processing oxidized nickel-cobalt ore and includes pelletizing ores with sulfuric acid in stoichiometric amounts. The pellets are calcined at 650-700°C for 2.5-3.0 hours followed by water leaching. Grinding pellets are calcined to the content of soluble iron in the range of 1.0-3.9%. Pellets are sulfatized before calcination at 200-250°C for 1 hour	The disadvantage of the method is the multistage process of extraction

Cont. of Table I

4	Method for extracting nickel and other metals from oxidized ore [5]	Patent of the Russian Federation No. 02245932, IPC C22B 23/00, published February 10, 2005	A method for extracting nickel and other metals from oxidized ore that can be used for the complex extraction of metals when processing oxidized nickel-baltic, laterite, and laterite ores containing nickel, cobalt, and copper, and iron-manganese nickel-containing nodules. This method involves granulation with sulfuric acid, where the granules are sulfated at 250-450°C for 1-2 hours in one or two steps. The sulfates of nickel and other metals are then leached with water, after which the metals are extracted by known methods. This method is the closest analogue to the proposed method	The main disadvantage of the method is that in the dissolution of the above metals is a complex process with the formation of multicomponent media, given that the process takes place at elevated temperatures (within 250-450°C), which also leads to significant energy costs
5	Method for processing oxidized nickelcobalt ore [6]	Patent of the Russian Federation No. 02287597, IPC C22B 23/00, published November 20, 2006	A method of processing oxidized nickel-cobalt ore that most generalizes the features of methods based on sulfurization. This method is chosen as a prototype and includes mixing the ore with sulfuric acid, thermal treatment of the resulting product, transfer into a solution of soluble sulfates and extraction of nickel and cobalt from solutions. The prototype differs in that the ore is mixed with sulfuric acid using a pelletizer, the resulting pellets are sulfated and then calcined in a countercurrent tubular rotary furnace, nickel and cobalt are leached from the calcined pellets with water. From the description of examples of implementation of the prototype method, it follows that the best results are achieved during calcination in the temperature range of 650-750°C for 3.5-4 hours. Under these conditions, a very high extraction of nickel and cobalt in the solution is achieved	The main disadvantage of the prototype is the high cost of thermal treatment of the reaction mixture of ore with sulfuric acid. Given the low content of nickel in oxidized ores (less than 1 %) and the steadily low price of commercial nickel, the use of the prototype method does not provide the necessary profitability
6	Method for processing oxidized nickel-cobalt ore [7]	Patent of the Russian Federation No. 02287597, IPC C22B 23/00, published September 29, 2021	The invention relates to non-ferrous metallurgy and can be used for the extraction of nickel and cobalt from oxidized nickel-cobalt ores. In this method, the ore is mixed with sulfuric acid, the mixture is thermally treated, nickel and cobalt are leached from the thermal treatment product with water, and nickel and cobalt are extracted from the productive solutions. Thermal treatment of the mixture of ore and sulfuric acid is carried out in a microwave oven at a temperature of 200-250 °C for 10-15 minutes in an atmosphere of water vapor. The method makes it possible to reduce the sulfurization time by 10-15 times and the energy consumption by 5-10 times	The treatment process takes place at high temperatures, which leads to additional energy costs.

III. METHODS AND DATA

Ore imaging was performed on a D8 Advance (Bruker), α -Cu, 40 kV tube voltage, 40 mA current. The obtained data of diffractograms and calculations of interplanar distances were processed using EVA software. Sample interpretation and phase search were performed by Search/match using the PDF-2 powder diffractometer database.

The images were also taken with an Axios I kW X-ray (PANalytical) fluorescence wave dispersive spectrometer. The data were processed and transcribed using the SuperQ software (Omnian 37). The error of semi-quantitative analysis was $\pm 20\%$ (relative).

TABLE II: PHASE COMPOSITION OF IRON-SILICATE ORE DETERMINED ON THE BASIS OF X-RAY DIFFRACTION ANALYSIS

Compound Name	Formula	S-Q
Talc	$Mg_3(OH)_2Si_4O_{10}$	61.6
Nontronite	$(Na,Ca)_{0.3}Fe_2(Si,Al,Mg)_4O_{10}(OH)_2 \cdot nH_2O$	21.4
Clinochlore	$(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$	9.5
Quartz	SiO_2	7.4

TABLE III: ELEMENTAL ANALYSIS OF THE TESTED ORE SAMPLE

Sample	Si	Mg	Al	Na	P	S	Cl	K	Ca	Y
Ore sample, %	18.991	7.448	2.16	0.314	0.029	0.07	0.159	0.474	0.474	0.004
Sample	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Sr
Ore sample, %	0.045	0.024	0.867	0.369	18.182	0.073	0.824	0.026	0.016	0.01

Quantitative and qualitative analysis of minerals conducted in the Chemical-Analytical Laboratory of

the Institute of Metallurgy and Ore Beneficiation showed that the iron-silicate ore contains 0.82 % Ni and 0.073 % Co and are associated in the iron-silicate ore as the main minerals: Nontronite – clay mineral, sheet silicate of the montmorillonite group (smectite group), by the formula $(\text{Fe, Al})_2 [\text{Si}_4\text{O}_{10}] [\text{OH}]_2 \times n\text{H}_2\text{O}$. It usually contains substantial amounts of Al_2O_3 (up to 14%) and Mg (up to 8%), also CaO (up to 2%), in small amounts of K_2O , Na_2O , sometimes NiO, Cr_2O_3 . And also cobalt and nickel in the same ore isomorphically associated with the mineral beidellite $\text{Al}_2[\text{Si}_4\text{O}_{10}][\text{OH}]_2 \times n\text{H}_2\text{O}$ (Fig. 1).

It should be noted that the above minerals in HCl are relatively difficult to decompose with the formation of jelly silica.

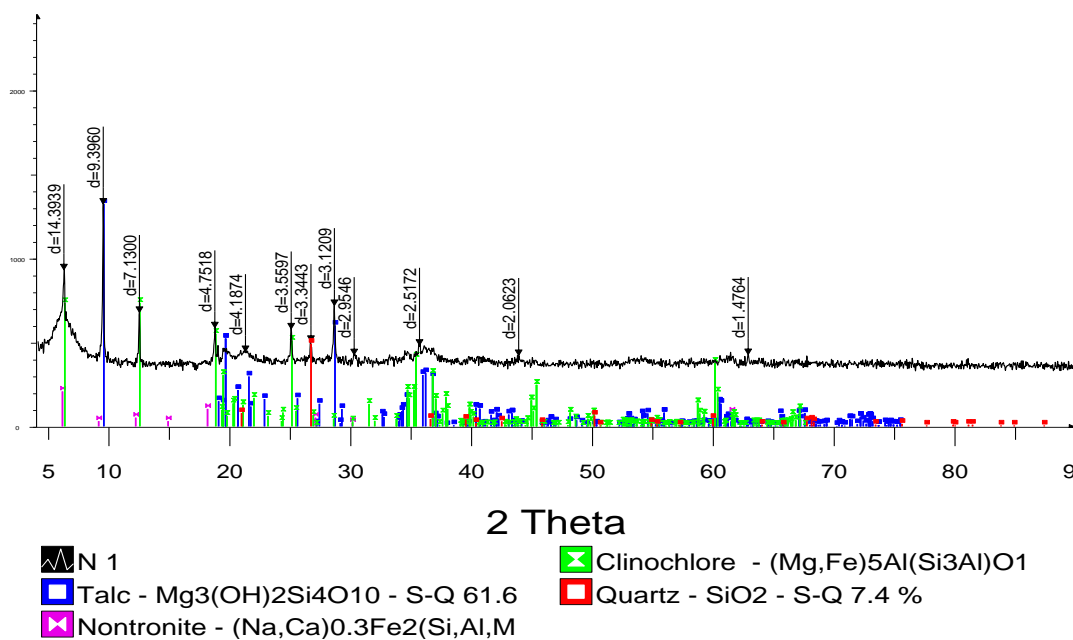


Fig. 1. Diffractogram of iron-silicate ore.

IV. RESULTS AND DISCUSSION

As can be seen from the X-ray phase analysis, nickel and cobalt are associated with hardly soluble silicates.

Therefore, at first, ammonium fluoride in hydrochloric acid medium was used to destroy the silicate groups in order to transfer nickel and cobalt minerals from the solid phase into the solution. The results of these studies are given below in Table IV and Table V.

Experiments on the extraction of nickel and cobalt from the iron-silicate ore of the Batamshy deposit depending on various factors (concentration of ammonium fluoride, calcium hypochlorite, hydrochloric acid, stirring speed, duration of the experiment and solid-liquid ratio (S:L)) were conducted. When selecting the optimal conditions for the complex extraction of nickel and cobalt, orthogonal planning of the experiment of the second order with a “star shoulder” ($\alpha = \pm 1.215$), where it is necessary to change only one particular factor while keeping the others strictly constant, was used [8]-[10].

Studies of nickel and cobalt extraction degree from iron-silicate ore were carried out in the beginning using only ammonium fluoride solution in hydrochloric acid medium, in particular from the composition of the solvent: in 10 % hydrochloric acid (by volume) and ammonium fluoride concentration from 3.0 % to 6.0 % (by mass) at room temperature. Stirring duration 120 minutes, stirring speed 100 rpm, S:L ratio 1:10, particle size -200 mesh (-0.074 mm).

As can be seen from Table 4, the extraction degree of nickel and cobalt from the iron-silicate ore using ammonium fluoride is relatively low and does not exceed 94.5 % for nickel and 87.2 % for cobalt.

It follows that in addition to ammonium fluoride a second component is needed as an oxidizer to increase the extraction of nickel and cobalt. We chose calcium hypochlorite in hydrochloric acid medium to create an oxidizing environment as the second component.

In this regard, we investigated the choice of optimal conditions for the complex extraction of nickel and cobalt and associated metals from iron-silicate ore using a mixture of ammonium fluoride and calcium hypochlorite in hydrochloric acid medium.

Studies of the nickel and cobalt extraction degree from iron-silicate ore were carried out using a solution of ammonium fluoride in the presence of calcium hypochlorite in hydrochloric acid medium depending on various factors: 100 ml of solution in 10 % hydrochloric acid medium, ammonium fluoride concentration

from 3.0 % to 6.0 % and 1.0-7.5 % calcium hypochlorite at room temperature. The time duration of the experiment was 120 minutes, the stirring speed was 100 rpm, the ratio S:L 1:10, particle size -0.074 mm.

As shown in Table V, the degree of nickel and cobalt extraction depending on the concentration of ammonium fluoride from 3 % to 6 % and calcium hypochlorite 1.0-7.5 % varies from 83.4 % to 97.0 %, respectively.

According to Table IV and Table V, the following factors are **the most optimal conditions for nickel and cobalt extraction:**

- concentration of dissolving reagents for NH_4F , $\text{Ca}(\text{OCl})_2$ and HCl – 6 %, 7.5 % (by mass) and 10 % (by volume) respectively;
- experiment duration – 120 minutes;
- solid to liquid (S:L) ratio – “1:10”;
- stirring speed – 100 rpm.

Under these conditions the extraction of Ni is 97.0 %, Co 92.8 %, and associated metals such as Cr, Fe, Mn is almost 99.9 %. It should be particularly noted that the reduction of the above values leads to a decrease in the degree of extraction of the target metals.

Use of calcium hypochlorite 7.5 % and ammonium fluoride 6 % (by mass) in 10 % hydrochloric acid (by volume) for treatment of nickel-cobalt-containing ore is the peculiarity of the suggested technology which allows to decrease toxicity, reach high extraction rate and make the technological process cheaper. Dissolution is carried out at room temperature (23-25°C) for 120 minutes at a S:L ratio of 1:10 and stirring speed of 100 rpm. The obtained solutions are precipitated by various known methods. As a result of leaching cobalt, nickel and associated metals are extracted in a complex manner.

TABLE IV: DEGREE OF EXTRACTION OF NI AND CO-DEPENDING ON VARIOUS FACTORS

NH_4F concentration, % (by mass)	Ni extraction rate, %	Co extraction rate, %
3.0	74.8	67.4
4.0	87.6	83.3
5.0	91.3	85.4
6.0	94.5	87.2
HCl concentration, % (by volume)	Ni extraction rate, %	Co extraction rate, %
2.5	37.0	19.5
5.0	52.0	26.3
7.5	75.8	33.7
10.0	94.5	87.2
15.0	94.6	88.9
Duration of experiment, min	Ni extraction rate, %	Co extraction rate, %
60	82.0	78.5
120	94.5	87.2
180	94.8	87.4
240	94.9	87.7
Ratio of solid to liquid (S:L)	Ni extraction rate, %	Co extraction rate, %
1:5	86.3	69.7
1:10	94.5	87.2
1:15	95.1	86.5
Stirring speed, rpm	Ni extraction rate, %	Co extraction rate, %
85	83.7	61.6
100	94.5	87.2
125	94.9	88.1

TABLE V: DISSOLUTION DEGREE OF NICKEL AND COBALT DEPENDING ON THE CONCENTRATION OF AMMONIUM FLUORIDE AND CALCIUM HYPOCHLORITE IN HYDROCHLORIC ACID MEDIUM

Ammonium fluoride concentration, in g.	Calcium hypochlorite concentration, in g.	Ni extraction rate, %	Co extraction rate, %
3.0	1.0	83.4	73.5
4.0	2.5	90.5	84.4
5.0	5.0	96.2	90.7
6.0	7.5	97.0	92.8

V. CONCLUSION

Thus, the authors obtained the following research results:

- i. The most optimal conditions for the dissolution of nickel and cobalt minerals were found.
- ii. An innovative technology for the complex extraction of nickel and cobalt from iron-silicate ores at room temperature has been proposed.

The advantage of the innovative technology of complex extraction of nickel and cobalt from nickel-

cobalt-containing raw materials developed by the authors is the elimination of the high-temperature process accompanied by the emission of toxic harmful gases and requiring large amounts of energy.

At the same time, in the hydrometallurgical method of nickel and cobalt extraction, the new method of nickel and cobalt extraction proposed by the authors using effectively operating reagents at room temperature is beneficial both economically and environmentally.

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CONFLICT OF INTEREST

Authors declare that they do not have any conflict of interest.

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