

TECHNOLOGICAL AND ENVIRONMENTAL ASPECTS OF NICKEL PRODUCTION IN SERBIA

Željko Kamberović^{1*}, Marija Korac¹, Zoran Anđić², Jelena Uljarević³,
Aleksandar Mihajlović³, Dušan Vučurović†¹

¹*Faculty of Technology and Metallurgy, University of Belgrade,
Belgrade, Serbia*

²*Innovation Center of the Faculty of Chemistry, University of Belgrade,
Belgrade, Serbia*

³*Innovation Center of the Faculty of Technology and Metallurgy, University of
Belgrade, Belgrade, Serbia*

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Abstract

Demand for nickel is constantly growing due to the versatility of its application, at the first place for stainless steel production. Ore reserves and possibility of nickel production of today's Serbia and in neighboring countries were thoroughly investigated, and presented work is part of a wider project of sublimation of scientific and professional experience in the field of nickel extractive metallurgy on domestic raw materials. Presented research explores the possibility of high pressure sulfuric acid leaching of Serbian lateritic ores from localities Rudjinci, Ba and Lipovac. All three investigated ore deposits behaved differently both during preparation and during hydrometallurgical treatment. As optimal method for ore preparation proved to be crushing-milling-sieving route, but without possibility of concentrate production. Only for Rudjinci ore deposit achieved leaching efficiency reached satisfactory level of 95%. Within presented paper flow-sheet is proposed for processing high-magnesium laterite ores, with iron and magnesium oxide Both could be recirculated and used again in technological process; MgO for iron precipitation and SO₂ for production of leaching agent, sulfuric acid. Final decision on the sustainability of the process will be made according to techno-economic and environmental evaluation. Estimated overall impact of the project implementation on the environment is negative.

Key words: nickel laterite, HPAL, sustainability, environmental impact

*Corresponding autor: Željko Kamberović, kamber@tmf.bg.ac.rs

Introduction

Nickel is a naturally occurring, lustrous, silvery-white metallic element. It is the fifth most common element on earth and occurs extensively in the earth's crust. Nickel has been found in metallic artifacts dating back more than 2,000 years. It was first identified and isolated as an element by the Swedish chemist, Axel Cronstedt, in 1751 [1].

Demand for nickel is constantly growing due to the versatility of its application, at the first place for stainless steel production. Today nickel is mostly used in transportation sector; more than one half of total nickel consumption is in airplane industry, and one third in ship making. Taking into account nickel withstanding different environmental influences, high heat, corrosion and acid resistivity, it presents ideal material for production of pumps, valves, pipes, turbines used in oil, airplane and military industry [2]. Nickel demand significantly increased in last 20 years and is linked to economic development. Economic growth leads to increased demand for stainless steel, which a key component is nickel. Nickel use is growing at about 4% each year while use of nickel-containing stainless steel is growing at about 6% [3].

Main production of nickel is situated in Russia, Canada, Japan, China, Australia, Brazil and Norway, in total 68% of world production [2].

The average annual growth rate of nickel demand is 4.2 %, but the trend constantly followed with ups and downs. The price of nickel has shown significant volatility in the last forty years [4]. In past 10 years maximum price of nickel was in May 2007 51 783 \$/t, and minimum in March 2009 of 9 711 \$/t.

Nickel occurs in nature in combination with oxygen, sulfur, silicon and other elements. From sulfide ores 58% of nickel worldwide is produced, and from oxide 42%. Nickel reserves are spread around the world. Ores of nickel are mined in over 23 countries and are smelted or refined in 25 countries. In European Union there are no plants for primary nickel production or concentration from laterite ores.

Possibilities of nickel production on territory of today's Serbia and neighboring countries were intensively investigated in second half of XX century. It was found that significant deposits are located in areas of Vardiste-Mokra Gora-Sumadija (Ba, Lipovac, Veluce, Rudjinci)-Kosovo-Kavadarci, and are continued in Greece and Albania. These deposits are low grade (1-1.3% Ni). In 1980' on territory of former Yugoslavia two ferronickel smelters were founded: FENI Industries, Kavadarci and Feronikel Plants, Glogovac [5].

The processes used for the nickel laterite ores processing can be classified into:

1. Pyrometallurgical processes and
2. Hydrometallurgical processes.

Pyrometallurgical processes make 75%, and hydrometallurgical 25% of total nickel production. Most of the pyrometallurgical process includes drying, calcination/reduction and electric furnace smelting.

Two main hydrometallurgical processes that are currently practiced are: reduction-ammonia leaching and autoclave process.

After evaluation of available processes for nickel production from lateritic ores and taking into account nickel content in domestic ores (0.8-1.3 %) it could be concluded that only hydrometallurgical processes, either ammonia leaching or autoclave

processes are suitable [5, 6]. These methods allow the extraction of nickel in the metallic form or as a salt, as well as valorization of other useful components [7].

High pressure acid leaching (HPAL) is a successful alternative for obtaining nickel from laterite ores that have traditionally been processed by pyrometallurgical methods. Laterite ore consisting of several minerals and usually have very complex mineralogy. They vary in composition from the site to the site, and thus leaching method depends on the ore composition. [8]

Autoclave process requires that the ore mainly contains limonite, some sprotite, low magnesium content (<4%) and low aluminium content. Increase in magnesium and aluminium content significantly influence increase in acid consumption [9].

There were some previous attempts for sulfuric acid leaching of the Serbian nickel lateritic ores under atmospheric pressure [10], but results show that even at 90°C nickel extraction efficiency is 78%, and that nickel extraction increase with increase of temperature. At the same time leaching efficiency for magnesium and iron are 20 % and 10%, respectively. For further processing of leaching solution, leached iron content is significantly higher than desirable [11].

In this paper presented are tests of high pressure sulfuric acid leaching process of Serbian lateritic ores using modification of high pressure sulfuric acid leaching used by AMAX Nickel, Inc. This process is capable of efficient extraction of nickel from high-iron, limonite, and high-magnesium, garnierite fractions in laterite ore body [12].

Experimental part

Chemical compositions of ores used in presented research are presented in Table 1.

Table 1. Chemical composition of used Serbian ores

Element/compound	Deposit			
	Rudjinci	Ba	Mokra Gora	Lipovac
Fe	15.45	30.66	18.55	38.70
Fe ₂ O ₃	19.28	34.79	19.40	30.70
FeO	0.99	5.68	6.05	21.38
SiO ₂	52.67	33.61	39.11	13.95
Al ₂ O ₃	5.17	8.59	6.30	7.22
MnO	1.13	0.25	0.32	0.54
Cr ₂ O ₃	0.54	2.41	2.40	4.16
Ni	1.20	1.12	0.602	1.02
Co	0.05	-	0.04	
MgO	4.40	1.58	11.50	0.052
CaO	1.30	0.9	0.80	6.16
CuO	0.32			
TiO ₂		traces	0.03	4.05
S	0.009		0.10	0.05
CO ₂	0.018		0.10	0.025
H ₂ O ⁻			4.00	1.60
H ₂ O ⁺			8.75	1.65
L.O.I.	12.29	14.95		3.40

Chemical analysis was performed by combination of Atomic Absorption Spectroscopy, Atomic Emission Spectroscopy, Inductively Coupled Plasma and volumetric methods.

Western Morava Region

Rudjinci is deposit of silicate nickel and cobalt ores and it is located near Vrnjacka Banja. Exploration of this deposit started in 1970 with long-hole-drilling. Nickel is bonded with silicates, oxides and sulfides. Majority of nickel is in silicate form, as mineral nontronite, which is predominant in ore.

Ba deposit is located 9 km south of Ljig. Nickel is bonded in silicate mineral garnierite. Identified are also milarite and bravoite.

Ore reserves in Western Morava region are estimated at ~30 000 000 t of ore with average 1.2 %Ni and 0.05% Co. Calculated to nickel metal reserves are ~360 000 t of Ni.

Šumadija Region

Lipovac and Kolarevic is deposit of silicate and sulfate nickel mostly as milerite, pentlandite and garnierite minerals.

Ore reserves of Šumadija Region are estimated at ~20 430 000 t of ore with average 0.80 % Ni and 33.58 % Fe. Calculated to nickel metal reserves are ~164 000 t of Ni.

Mokra Gora deposit was not experimentally investigated within presented research.

Investigation of hydrometallurgical process, HPAL, for nickel extraction from domestic ores included:

- 1) Commutation and preparation of ore slurry;
- 2) Leaching with sulfuric acid at elevated temperature and pressure;
- 3) Solid-liquid phase separation;
- 4) Leaching solution purification;
- 5) Selective extraction of Ni from solution;
- 6) Production of metallic nickel;
- 7) Regeneration of leaching solution.

All presented process phases are mutually dependent, so the main goal of presented research was to establish optimal process parameters for each of the listed operations, at which satisfactory nickel efficiency is achieved and quality of finished products.

Ore preparation

Processing of low-grade nickel ores starts with preparation phase, grinding and obtaining of ore pulp. Due to the different compositions of investigated ores, the preparation phase differs as presented in Table 2.

Concentrate preparation by segregation-flotation-magnetic separation show significantly better efficiency than results presented in Table 2.

Table 2. Preparation phase and concentrate quality for different Serbian ores

Element/compound	Deposit		
	Rudjinci	Ba	Lipovac
Slurrying, sieving	+	-	-
Magnetic separation	+	+	+
Flotation	-	-	+
Ni in concentrate, %	1.28	1.03	1.22
Ni efficiency, %	80	80	72.89

Segregation process was performed with ore and reagents. Ore, composition as presented in Table 1, was comminuted, and dried at 105°C. Used reagents were calcium-chloride (7.5 wt. % of charge) and coal (0.9 wt. % of charge). Segregation-flotation process parameters were:

Segregation roasting

Ore size	100 mesh
Temperature	950°C
Time on set temp	120 min
Heating rate	27°C/min
Cooling time	~90 min
Reactor rotation	2.5°/min

Froth flotation

Atmosphere	Air
Solid/liquid ratio	25%
Temperature	50°C
pH	5-6
Time	10 min

Concentrate quality after segregation-flotation-magnetic separation process is presented in Table 3.

Table 3. Efficiency of segregation-flotation-magnetic separation process for different Serbian ores

Element/compound	Deposit		
	Rudjinci	Ba	Lipovac
Ni in concentrate, %	18.5	6.0	6.5
Ni efficiency, %	64.0	50.0	80.0

Due to the higher nickel efficiency, as process of concentration for domestic ores, process of slurring and sieving was chosen.

High pressure acid leaching

Leaching conditions used for assessment of nickel leaching in autoclave from domestic ores were:

Ore size	100 % <20 mesh
Acid concentration	210 g H ₂ SO ₄ /L

Leaching time	120 min
Leaching temperature	220-240°C
Pressure	37 atm
Solid/Liquid ratio	40%

First experiment showed significant difference in behavior of three investigated ores.

For ores from deposits Lipovac and Ba high pressure sulfuric acid leaching proved not to be adequate procedure.

For Lipovac ore nickel leaching efficiency was 10%. With addition of oxidizing agents H_2O_2 and HNO_3 , leaching efficiency increased to 16 % and 37 % respectively, but still remained at very low level. Low process efficiency could be consequence of unfavorable mineralogical composition and large particle size (~20 mesh), i.e. 50% of nickel is bonded in stable mineralogical-chemical forms, so without pyrometallurgical pretreatment higher leaching efficiencies could not be expected

For Ba ore similar behavior was noticed. Even though higher leaching efficiencies were achieved, 45-85%, more severe leaching conditions must be applied in order to reach 90% leaching efficiency.

HPAL investigations for ore Rudjinci showed that high leaching efficiencies are achieved under high temperature and pressure conditions, with, at the same time, lower iron leaching efficiency. Achieved nickel leaching efficiency was 95%, at sulfuric acid concentration of 210-220 g/L. With increase of sulfuric acid concentration increased is iron leaching rate, with no significant effect on nickel leaching, which is not economically feasible for further processing and also on acid consumption.

Leaching solution under aforementioned conditions had following composition in g/L: 8-10 Ni, 2-6 Fe, 35 MgO, 25-30 H_2SO_4 .

Critical phase in this process is selective leaching of nickel and cobalt from iron at elevated temperatures and pressures by sulfuric acid. Above certain critical point, with increasing of temperature sulfate salts of metal ions are less soluble. These critical points for iron, aluminium and magnesium on one side, and nickel and cobalt on the other are favorable for selectivity based on their sulfates solubility. Solubility of nickel and cobalt sulfates increase with increase of temperature, while of all others solubility decreases. Magnesium sulfate solubility decreases with increase of temperature, whereas it remains in same form. Iron sulfate in presence of sulfuric acid form $Fe_2(SO_4)_3$ (Equation 1), which on temperatures above 200°C hydrolysis and form Fe_2O_3 and sulfuric acid (Equation 2):



Process presented by equations (1)-(2) enables regeneration of sulfuric acid. Formed solid Fe_2O_3 is removed with gangue.

Treatment of leaching solution

Treatment includes following steps:

- 1) Purification of solution from iron;

- 2) Extraction of nickel-hydroxide concentrate;
- 3) Extraction of MgSO_4 from leaching solution.

Purification of solution from iron was performed using precipitation with MgO and liquid-liquid extraction. Process parameters for this process were 100°C/1h at solution pH 4.5. Quantity of added MgO was 8% higher than stoichiometric value. Under these conditions achieved level of iron removal was 98.70%, while the co-precipitation of nickel was 1.03%. Obtained iron deposit had following composition:

0.62% Ni, 32.4% Fe and 4.10% MgO

Extraction of iron from these solutions could be successfully performed using primary amine, for example JMT dissolved in kerosene. Because of the fact that capacity of extracting agent is limited, number of extraction steps is determined by iron content in the solution. For case of investigated solution with 5-7 g/L of Fe, four step extractions is necessary for achieving 98.5% of iron extraction.

Extraction of nickel hydroxide concentrate, from solutions purified from iron, was performed at 100°C using MgO water suspension. Investigations proved that by addition of MgO in quantities 15-20% higher than stoichiometric value enables reaching pH value of 8-8.2. At these conditions in 3h, all present nickel from the solution is precipitated.

Quality of produced nickel-hydroxide concentrate was in wt. %: 48.50 NiO, 2.20 Fe_2O_3 , 4.60 MgO, 0.60 CaO, 0.30 Al_2O_3 , 2.10 SiO_2 , 1.30 CoO, 0.40 MnO, 0.40 CuO, 4.20 S (SO_4^{2-}) and L.O.I. 33.

Final step in treatment of leaching solution is valorization of MgSO_4 . Content of MgSO_4 in remaining solution is 220 g/L, with minimal quantity of impurities.

There are several competitive ways for valorization of magnesium-sulfate. One is based on the fact that solubility of MgSO_4 decreases with increase of the temperature, so it could be valorized from the solution by heating the solution up to temperatures above 200°C and continuous filtration. Magnesium sulfate would crystalize as a monohydrate.

The second is based on water vaporization in 3-6 steps. Saturated MgSO_4 solution is than rapidly cooled and MgSO_4 crystalize as heptahydrate.

The third method is desalinization of magnesium sulfate by addition of organic solvent. This method is based on the fact that large number of inorganic salts has low solubility in organic solvents. Desalinization procedure consists of addition of organic solvent (methyl alcohol), filtration of magnesium-sulfate crystals, and distillation of organic solvent. By this method valorization of magnesium-sulfate is achieved in short time, 0.5-1 h, under following conditions: temperature 30°C, and solution/solvent ratio 1:1.5.

Crystallization product had anticipated purity: 29.9% MgO, 72.40% SO_4 , 0.35% Ni, 0.020 % CoO, 0.11 % Al_2O_3 and 0.003% SiO_2 . Crystallization product is than thermally decomposed at 900°C in presence of reducing agent. As products high-grade MgO and SO_2 gas were obtained. SO_2 gas is used for production of sulfuric acid, necessary for ore leaching.

According to presented research result flow-sheet for processing of nickel ore from locality Rudijinci was derived (Figure 1).

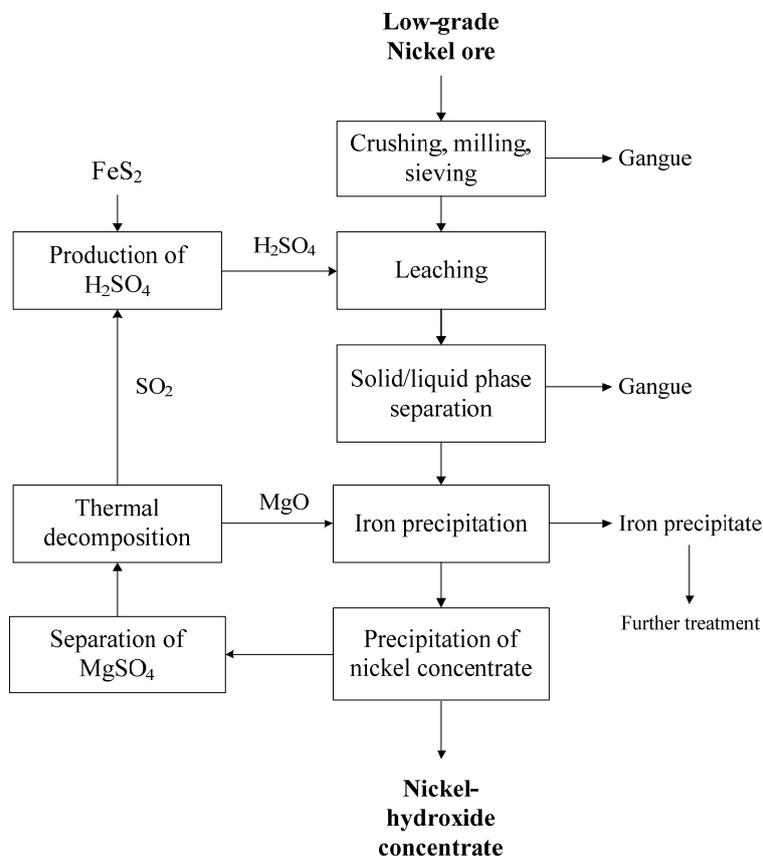


Fig. 1. Proposed flow-sheet for processing of Serbian laterite ores from Rudjinci ore

Environmental aspects of nickel exploitation

Proposed processing technology is such that the plant must be built relatively close to mine. Influences of processing plants for lateritic ore and nickel production on the environment occur during the construction, operation and accidents.

During construction, the main impacts on the environment may be danger of pollution of air, soil and water, as well as sounds. According to this dust, gas emissions and noise are the primary contaminants in the stage of construction works, during site preparation, building constructions and supporting infrastructure. The excavation of large quantities of low-grade ore creates huge costs for remediation and reclamation of land.

During normal operation of the plant for the processing of lateritic ore and nickel production, negative impacts that could occur are reflected in the impact on air pollution, water, and thus the land. In addition, the exploitation phase of the project will generate noise and vibration.

In the process of nickel autoclave process generated hazardous and toxic substances that can have a negative impact on the environment and human health if they would come into uncontrolled discharges [13].

Hazardous substances, which can have an adverse impact on the environment result from: emission of gaseous pollutants, the products of combustion of petroleum products in the internal combustion engine, emission of dust and fine particles, and impurities and harmful substances contained in the ore, such as iron, zinc, mercury, etc.

In the process of dressing and processing of ore and nickel production it is necessary to install appropriate systems for the treatment of waste gases, which will provide allowed levels of emission of hazardous and harmful substances in the ambient air.

One of the sources of pollution, in addition to emissions of dust and gases and inadequate treatment and disposal of solid waste, the discharge of waste water with high content of metals, without prior treatment. Heavy metals are leached from the tailings can have negative effects on the quality of the environment and human health.

Preliminary assessment of the potential impact of the project on the environment is negative, with the most significant action on: the degradation of large areas occupied by the project, flora and fauna, groundwater and surface water, air quality, noise and other (chemicals and hazardous waste, light, gases with greenhouse gases, cultural heritage).

Conclusions

The recent discussions of nickel exploitation in Serbia did not include technological and metallurgical aspect, only the environmental impact of the process. For these reasons this paper briefly presents work performed on this issue; processes and indicators for its study and solution.

Through extensive research performed in a period of about 50 years on this issue some of the possibilities of nickel processing of domestic lateritic ores are defined. In the first place choice of hydrometallurgical processing as promising technique was justified, due to the low-grade ore deposits.

All three investigated ore deposits behaved differently both during preparation and during hydrometallurgical treatment. As optimal method for ore preparation proved to be crushing-milling-sieving route, but without possibility of concentrate production. The first leaching experiment on Lipovac and Ba ore gave very low leaching efficiencies, 10 and 45-85%, respectively. In case of Lipovac ore, even addition of oxidizing agents did not significantly increase leaching efficiency. For Rudjinci achieved leaching efficiency reached satisfactory level of 95%.

Further treatment of leaching solution enabled valorization of 98.70% iron. After iron removal also valorization of MgO and SO₂ gas was achieved. Both could be recirculated and used again in technological process; MgO for iron precipitation and SO₂ for production of leaching agent, sulfuric acid. By proposed flow-sheet high-magnesium laterite ores could be processed. This will significantly improve economic effects of overall process, and, in the same time, decrease adverse impact on the environment.

Produced nickel-hydroxide concentrate will be used for nickel and cobalt production.

Presented research results show possibility of nickel exploitation of Rudjinci ore, but final decision on the sustainability of the process will be made according to techno-economic and environmental evaluation. But initially it could be concluded that quantity of ore deposit is insufficient for economic viability of the exploitation.

On the other side, potential impact of the project implementation on the environment is negative, with the most significant action on: the degradation of large areas occupied by the project, flora and fauna, groundwater and surface water, air quality, noise and other (chemicals and hazardous waste, light, gases with greenhouse gases, cultural heritage).

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