THE COMPARISION OF SEGREGATION-FLOTATION, LEACHING AND BIOLEACHING TECHNIQUES FOR RECOVERY NICKEL FROM LOW GRADE NICKEL BEARING LATERITE

Boris Krstev[1], Aleksandar Krstev[2]
[1]Goce Delcev Universiry, Faculty of Technical&Natural Sciences, STIP, The Republic of Macedonia
[2]Goce Delcev Universiry, Faculty of Informatics, STIP, The Republic of Macedonia

Abstract: The refractory or low grade nickel laterite domestic ores in Republic of Macedonia are investigated by conventional magnetic separation technology or segregation-flotation-magnetic separation, or production and smelting to ferronickel. In the mean time, investigations are directed to the new possibilities of leaching by microorganisms – bioleaching. The paper is result of these technologies and investigations carried out for recovery of in the mentioned ores. The average grade from segregation-flotation process as a nickel metal concentrate was cca 80-90% Ni, and recovery was up to 80-85%. The average recoveries from leaching were cca 87-90% for nickel and the average recoveries from bioleaching were cca 93-95% for nickel.

INTRODUCTION

A combination of current trends and developments may undermine the sulphides supremacy and might tip the balance in favour of oxide-silicated ores – garnierites and laterites for new investigations or studying. A list of previous laterite operations or laterite processing was following: Ferronickel smelting, Matte smelting, Reduction roast-ammonia leaching and High pressure sulphuric acid leaching. Apart from the above mentioned processes routes, there have been many attempts to develop processes known as alternative processes which have included: Nitric Acid Leaching, Chlorine Leaching, Acid Pugging and Sulphation Roasting, especially Sgregation Process with combination of Flotation, Magnetic Separation or Leaching etc.

Leaching and bacterial leaching

Future sustainable development requires measures to reduce the dependence on nonrenewable raw materials and the demand for primary resources. New resources for metals must be developed with the aid of novel technologies, in addition, improvement of already existing mining techniques can result in metal recovery from sources that have not been of economical interest until today. Metal-winning processes based on the activity of microorganisims offer a possibility to obtain metals from mineral resources not accessible by conventional mining. Microbes such as bacteria and fungi convert metal compounds into their water-soluble forms and are biocatalysts of these leaching processes. Additionally, applying microbiological solubilization processes, it is possible to recover metal values from industrial wastes which can serve as secondary raw material.

Generally speaking, bioleaching is a process described as being “the dissolution of metals from their mineral sorces by certain naturally occurring microorganisms” or “the use of microorganisms to transform elements so that the elements can be extracted from a material when water is filtered through it”. Worldwide reserves of high-grade ores are diminishing at an alarming rate due to the rapid increase in the demand for metals. However there exist large stockpiles of low and lean grade ores yet to be mined. The problem is that the recovery of metals from low and lean grade ores using conventional techniques is very expensive due to high energy and capital inputs required. Another major problem is environmental costs due to the high level of pollution from these techniques. Environmental standards continue to stiffen, particularly regarding toxic wastes, so costs for ensuring environmental protection will continue to rise.

Biotechnology is regarded as one of the most promising and certainly the most solution to these problems, compared to pyrometallurgy or chemical metallurgy. It holds the promise of dramatically reducing the capital costs. It also offers the opportunity to reduce environmental pollution. Biological processes are carried out under mild conditions, usually without addition of toxic chemicals. The products of biological processes end up in aqueous solution which is more amenable to containment and treatment then gaseous waste.

Bacterial leaching is a revolutionary technique used to extract various matals from their ores. Traditional methods of extraction such as roasting and smelting are very energy intensive and require high concentration of elements in ores. Bacterial leaching is possible with low concentrations and requires little energy inputs. The process is environment friendly even while giving extraction yields of over 85-90%.

Occurrence of nickel in oxide-silicated ores

For the metallurgical calculation nickel in the oxide-silicated minerals may be shown by means of the general formula:

$$NiSiO_3 . m\ MgSiO_3 . n\ H_2O$$

Or by possible transformation:

$$(Si_2O_5)^{2-} \rightarrow (SiO_4)^{2-} \rightarrow (SiO_3)^{2-}$$

$$NiO.2SiO_2 \rightarrow 2NiO.SiO_2 \rightarrow NiO.SiO_2$$

Olivine → *Piroxen*

The amorphous crystal structure is transformed to the stable crystal structure. The iron in the Ni- bearing minerals and ores is appeared as $Fe_2O_3.nH_2O$ and as a nontronite $(Fe, Al)_2(Si_4O_{10})(OH_2).nH_2O$. The oxide-laterite ores are with low Ni-content. The generally, nickel and iron are as Ni-Fe- limonite $(Fe, Ni)O(OH).nH_2O$, garnierite or in the talc form $(Mg, Ni, Fe)_3Si_4O_{10}(OH)_2.nH_2O$.

Serpentine: **$Mg_6(Si_4O_{10})(OH)_8$**

↑ ↖ **=→ $(Mg,Fe^{2+},Ni)_{6-x}[Si_{4-x}(Fe^{3+},Al, Cr)_x o_{10}](OH)_8$**

Fe^{2+}, Fe^{3+}, Al, Cr	Fe^{3+}, Al, Cr

Talc: **$(Mg, Ni)_3 (Si_4O_{10})(OH)_2 . H_2O$**

↑ ↖ **= → $(Mg, Ni)_3 [Si_{3,75},Al_{0,25} , O_{10}](OH)_2.H_2O$**

Fe^{2+}, Fe^{3+}	Fe^{3+}, Al, Cr

Garnierite : $(Ni, \mathbf{Mg)_6 (Si_4O_{10})(OH)_8.4H_2O}$

Nontronite : **$(Ni, Fe, Al)_2(Si_4O_{10})(OH_2).nH_2O$**

The experimental investighations from the nickel bearing natural ores by segregation process

The experimental investigations are carried out to determine impact by the addition of the activators (2%, 3,5% BaS, FeS, S or $BaSO_4$) to the metallurgical indicators from combined processes as segregation roasting – flotation – magnetic separation – ammonial leaching. The applied samples are from various deposits but their mineral contents are close to the limonite, nontronite, saprolite or garnierite types (Studena Voda, Rzanovo, Rudjinci or mixures from above mentioned ores).

The segregation roasting process was carried out in the presence of the chlorination addition of $CaCl_2.2H_2O$, reduction coke with addition of the sulphur or sulphur bearing compounds (2% BaS, FeS, S or $BaSO_4$) as process activators, on the operational temperatures of 1023-1223^{o}K and retainin times from 20 to 120 minutes in the atmosphere of argon.

There are some steps in this process as formation of the HCl or Cl_2, chlorination of the existing Ni-ferrites and Ni-silicates to $NiCl_2$, to elemental Ni on the coke parts or the SiO_2 grains. The next steps of these processes are the mineral processing technologies (flotation, magnetic separation) or ammonial leaching of the calcine with formed Ni metal.

Table 1. Comparision of segregation, flotation, MS and AL

Ore	T^{o}C	t(min)	Flotation	Mag. Sep.	A. Leaching
			R_{Ni}%	R_{Ni}%	R_{Ni}%
1	750	20	1,60	1,50	1,75
		40	3,55	3,20	3,65
		60	3,95	3,60	4,50
		120	4,65	4,55	6,00
	850	20	8,50	8,00	10,00
		40	16,80	16,50	20,30
		60	25,50	23,90	27,90
		120	45,50	43,80	46,80
	950	20	30,00	28,90	32,00
		40	40,10	39,10	43,50
		60	45,90	43,50	51,75
		120	65,00	62,50	67,60
2	750	20	3,00	2,65	3,50
		40	3,90	3,70	4,90
		60	5,50	5,20	6,20
		120	12,40	11,00	12,90
	850	20	15,00	14,30	16,80
		40	25,50	23,80	28,50
		60	39,80	35,70	42,30
		120	56,70	54,50	60,00
	950	20	35,60	33,90	39,60
		40	48,00	45,70	50,00
		60	60,50	56,70	64,50
		120	78,00	76,50	80,10

		20	2,50	2,00	2,80
		40	4,10	3,80	4,70
	750	60	7,50	6,75	7,90
		120	15,50	14,70	17,50
		20	17,80	17,00	18,25
3	850	40	30,40	28,90	33,50
		60	46,70	45,30	48,20
		120	60,00	57,90	63,50
		20	35,50	34,00	37,60
	950	40	50,55	50,00	53,45
		60	65,00	64,50	68,90
		120	80,90	79,60	84,50

The experimenting between leaching and bacterial leaching

According to the hydrometallurgy theory it's fact that the hydrometallurgy processes are more applicable to the limonitic laterites. Although the saprolitic laterites are often richer in nickel than the limonitic ores, the high Mg content results in higher acid consumption. The theory confirmed that primary hydrometallurgy processes are the Caron process, HPAL (high-pressure acid leaching) or atmospheric-pressure acid leaching process.

In the investigated HPAL, limonitic mixure ores are leached at high pressure (33-35 atm) and temperature (240-270^{o}C) I autoclave apparatus with stirring s[peed from 450-1500 rpm, with slurry densities of about 20%, and acid consumption or acid to ore ratio of 200-500 kg/t ores.

The (temperature 250-270 ^{o}C interaction effect of one factor on the response of another, generally **A**(temperature 250 ^{o}C) by **B** (or acid to ore ratio of 200-500 kg/t ores) effect is the change in the effect of A as B goes from – to + values ([plan of experiments 2^2). There are four data points on each chart and the interpret the interaction plot is simply. In the case of the 2^3 or 2^4 plan of experiments the magnitude and direction of the effect can be determined from the relative location of the appropriate data points.

Table 2. Investigation by HPAL process

SAMPLE	**A**	**B**	**R_{Ni}%**
1	250	O,24	78,50
2	250	0,40	91,10
3	270	0,24	82,35
4	270	0,40	94,55

The biohydrometallurgy, especially bioleaching, bacterial leaching or microbial technology is a promising novel technology for recovering the nickel from nickel laterites (valuable minerals traditionally difficult-to-process ores) using **chemolithotrophic microorganisms.**

Niockel laterite contains metal values but is not capable of participating in the primary chemolithotrophic bacterial oxidation because it contains neither ferrous iron nor substantial amount of reduced sulphur. But the recovery is allowed with the primary oxidation of pyrite, or similar iron/sulphur minerals to provide sulphuric acid solutions which nor solubilize the present metal content. It's very important to know the role of the sulphuric acid. The results showed that this acid performed better, in terms of $\mathbf{R_{Ni}\%}$, then citric acid or ferric sulphate of the same initial concentration. Using appropriate optimization strategy or methodology, the theoretical optimum optimum conditions for maximum $\mathbf{R_{Ni}\%}$ (***more then 85-90%***) within the range of operational conditions in the presence of mentioned bacteria or fungi, pH from 2,0, particle size of the samples less then 63 µm, pulp density from 2,5%.

Conclusion

The combined process Segregation – Flotation (F) – Magnetic separation (MS) – Ammonial Leaching (AL) by the nickel bearing laterite (nontronite, garnierite, limonite, saprolite, serpemtine or talk) ores with various nickel content from 0,89-1,20% Ni have achieved satrisfactory results trelated on the metal recoveries. In the same time, the existing environmental problems lead to increased interest for combined processes: Sehregation roasting and conventional methods of mineral processing or hydrometallurgical processes with existing leaching methods or bioleaching methods with high metallurgical recobverioes and unexpensive processes linked with better environmental and appropriate conditions.

The experimenting between leaching and bacterial leaching have showed the following results: leaching with ***HPAL*** process and recoveries from $\mathbf{R_{Ni}\%}$ **(80-95%)** and bacterial leaching with **chemolithotrophic microorganisms** recoveries from $\mathbf{R_{Ni}\%}$ **(80-90%).**

Literature:

[1] A.D. Dalvi, W.G. Bacon and R.C.Osborne, "The past and future of nickel laterites", PDAC 2004 International Convention, March 7-10, 2004, pp 1-27

[2] D. Gerorgiou and V.G. Papangelakis, "Sulphuric acid pressure leaching of a limonitic laterite: chemistry and kinetics", Hidrometallurgy, 49, 1998, pp 23-46

[3] D. Gerorgiou and V.G. Papangelakis, "Sulphuric acid pressure leaching of laterites – speciation and prediction of metal solubilities at temperature", Hidrometallurgy, 58, 2000, pp 13-26

[4] J.C. Arroyo and D.A. Neudorf, "Atmospheric leach process for the recovery of nickel and cobalt from limonite and saprolite ores", US Patent 6, 680, 035, Jan 20, 2004

[5] W.P.C. Duyvesteyn, D.A. Neudorf and E.M. Weeniink, "Resin-in-pulp method for recovery of nickel and cobalt", US Patent 6, 350, 420, Feb 26, 2002

[6] S. Stopic, B. Friedrich and R. Fuchs, "Kineteics of sulphuric acid leacvhing of the Serbian nickel lateritic ore under atmospheric pressure", MJoM, Erzmetall, pp 235-244

[7] S. Stopic, B. Friedrich, N. Anastasijevic and A. Onjia, "Experimental design approach regarding kinetics of high pressure atmospheric leaching", MJoM, Erzmetall, pp 273-282