

Nickel laterite concentration through a non-conventional method with surface sulfidization

Moisés Oswaldo Bustamante-Rúa, Sindy Dayanis Gonzalez-Arias & Pablo Bustamante-Baena

Universidad Nacional de Colombia, Sede Medellín, Facultad de Minas, Medellín, Colombia. mobustam@unal.edu.co, sdgonzaleza@unal.edu.co, pabustamanteba@unal.edu.co

Received: March 31th, 2020. Received in revised form: June 5th, 2020. Accepted: July 7th, 2020.

Abstract

Nickel ores are found mainly as sulfides and laterites in oxidized ores, such as iron oxides, which are usually “Ni-bearing”. This investigation determined the physical-chemical conditions necessary to increase the tenor and recovery in lateritic deposits, with the implementation of a new technology that allows the increase of the tenor (a process called “up-grading”). The froth flotation is proposed as a concentrating process to increase the Nickel content in the lateritic deposits. By means of sulfidization and direct flotation, specific hydrophobicity of the mineral is achieved, substantially improving the nickel concentrations in the process, with recoveries close to 86%, which, compared with conventional direct and inverse floats without effecting this activation with Na_2S , results in recoveries of 70% and 16%, respectively. The reverse flotation also increases the Nickel content with an approximate recovery of 70%; however, the froth flotation, with activation Na_2S is still better.

Keywords: Ni-bearing; laterites; concentration; sulfidization; froth flotation.

Concentración de lateritas de níquel a través de un método no convencional de sulfidificación de la superficie

Resumen

Las menas de Níquel se encuentran principalmente como sulfuros y en lateritas en menas oxidadas las que son denominadas “Ni-bearing”. Esta investigación determinó las condiciones fisicoquímicas para incrementar el tenor y recuperación en los depósitos lateríticos, con la implementación de una nueva tecnología que permita aumentar el tenor (proceso denominado “up-grading”). Se propone la flotación espumante buscando aumentar el tenor de Níquel en los yacimientos lateríticos. Mediante la sulfidización y la flotación directa se alcanza hidrofobicidad específica del mineral mejorando sustancialmente las concentraciones de níquel en el proceso, con recuperaciones cercanas al 86%, lo cual comparado con las flotaciones convencionales directas e inversas sin efectuar esta activación con Na_2S dan como resultados recuperaciones de 70% y 16% respectivamente. La flotación inversa también alcanza aumento del tenor de Níquel con una recuperación aproximada del 70% sin embargo la flotación espumante con activación Na_2S sigue siendo mejor.

Palabras clave: Ni-bearing; lateritas; concentración; sulfidización; flotación espumante

1. Introduction

Research around the world showed 70 percent of worldwide nickel deposits are classified as laterites, while 30 percent are sulfides. According to Geology for Investors, nickel laterite deposits occur in the 23.5 parallels of the north and south of the equator. The deposits are present in these

areas for their warm, tropical environments, which in turn allow for chemical and mechanical weathering to take place. Meanwhile, some deposits are also found beyond the tropical belt, such as in Oregon, Russia and Canada and with the characteristic that replacing atoms in the other minerals such as iron oxides, which are called “Ni-bearing”. Almost three-quarters of the world nickel resources belong to laterite type

How to cite: Bustamante-Rúa, M.O., Gonzalez-Arias, S.D. and Bustamante-Baena, P., Nickel laterite concentration through a non-conventional method with surface sulfidization. DYNA, 87(215), pp. 18-27, October - December, 2020.

deposits, but less than half of the primary production nickel comes from this type of deposits. On the other hand, the total production of nickel has increased more than 10 times since 1950. Whereas sulfide-type ores contributed up to 90% of nickel in the world, in 2009 laterite-type ores marked a production higher than 42% and is expected to reach 72% in the coming years [1].

Globally, deposits with high nickel content become scarce. For this reason, the development of technologies that can process many nickel laterites of lesser degree in the concentration process is being proposed in order to eliminate a substantial amount of gangue that participates in the subsequent processes of metallurgical extraction [1,2]. The conventional practices for the increase of the tenor in lateritic deposits are based on a separation of sizes, which metallurgically is known as "up-grading" [3], presuming that in the range of fine sizes there is an increase in the percentage of Nickel due to the same genesis of the deposit. However, this practice presents serious problems in the recovery, which is unsustainable in the long term [4], and strongly favors the selective mining of the deposits and punishing the reserves. Other techniques such as magnetic separation and gravimetric separation have been tested but have not generated acceptable concentrates mainly for pyrometallurgical processes [5,6] and have been finely tested hydrometallurgical extraction processes as "heap leaching" as an alternative to the extraction in poor ores of nickel [7,8] unfortunately, though, the selectivity of the leaching reagents seriously compromises this technology.

The froth flotation as a nickel concentrating process from lateritic deposits has not been as successful as the recovery of Nickel from sulfide deposits. However, several investigations have been conducted trying to find alternatives to increase nickel concentration in laterites and oxidized ores [3,9]. The main regions where nickel deposits are found from lateritic soils in the world and where froth flotation research has been carried out to process these minerals are New Caledonia, Australia, Indonesia, South America (Colombia and Brazil), the Philippines, India and Russia [10] lateritic deposits have become a major attraction of economic geology due to the depletion of high-grade nickel ores in sulfide ores [9,11]. Table 1 summarizes the main results of the investigations using froth flotation and compares the conditions and flotation results of lateritic ores.

The maximum allowed deep of headings in the manuscript is three. Headings are numerated using Arabic numbers. Primary headings use bold face, and size 10. Secondary headings use bold face, italics and size 10. Tertiary headings use normal text and size 10, for example: Flotation has been widely used for the separation of valuable minerals from the gangue based on their surface characteristics and differences in the hydrophobicity of the mineral surfaces. Since the hydrophobicity of minerals differs widely from one another, their separation by flotation will be easier [19,20] and depends on the adhesion of some solids to the gas bubbles generated in the pulp by some external means, which is determined by the hydrophobicity of the particle surface through selective adsorption of surfactants called collectors [19,21].

The hydrophilic and hydrophobic minerals of an aqueous pulp can be separated from each other, after being finely ground and conditioned with the chemical reagents, passing through air bubbles through the cell. The wetted hydrophilic particles are depressurized and exited by the discharge of the reactor, and the hydrophobic particles adhere to the air bubbles and exit through the foam; in this way, a mineral can be separated that contains the simplest two components [17]. Unlike other methods of concentration, in flotation, it is possible to vary the difference between the material of interest and the gangue, modifying the chemical and electrochemical environment of the system by means of the appropriate selection of the added chemical reagents: collectors, foamers, activators, depressors or pH modifiers (Fig 1.) [3,22–24]. The pulp is a mixture of solid particles containing mineralogical species, water, and dissolved chemical reagents, however, it must meet certain conditions, that is, that the material is properly ground no greater than 295 μm , nor less than 53 μm [9,22,23] for this specific case. Flotation reagents are the most important variable since they are responsible for changing the properties of wettability [29]. Oxide minerals have a greater affinity for oxygen-containing reactive chains, and their surface chemistry is largely determined by ion exchange reactions. Physical adsorption plays an important role together with chemical adsorption; the adsorption of the collector in non-sulfurous minerals is much less specific than in the case of sulfide minerals [3,15,17,22,24,25]

This investigation studied the flotation of oxide minerals, which contain significant amounts of primary slats, such as clays and iron oxides. In addition, the same valuable minerals are generally very soft forming silts. This can be a problem when carrying out the flotation since it can present high viscosity in the pulp, which is covered with slimes of a mineral "slime coating" on the particles more thicker than another mineral, thereby generating greater collector consumption caused by the indiscriminate adsorption and large areas of mineral surfaces, reducing efficiency by the incorporation of ultrafine particles into the air bubbles and the dilution of the concentrate by means of gangue slats entrained in the foam. In addition, the physical adsorption of sparingly soluble collectors, such as fatty acids [4, 26] is much slower and less efficient in the case of fine particles than in coarser ones.

Likewise, in the froth flotation process for oxides, theories are evaluated to explain the adsorption mechanisms of collectors (cationic and anionic) in non-sulfur mineral surfaces (oxides, silicates, carbonates, phosphates, nitrates, sulfates, and others). In addition to the theory of ionic adsorption, or the formation of hemimicelles, the theory of solubility, and the theory of the formation of ion-molecular complexes [27], the theory of ionic adsorption, or the formation of hemimicelles [26] states that the adsorption of collectors occurs by the electrostatic interaction of the collector ions with the surface of the mineral according to the theory of the electric double layer, and by the association of the hydrocarbon chains of the collector ions by Van der Waals lateral forces, forming hemimicelles.

Table 1.
Works carried out on Nickel flotation from lateritic ores in the world.

Country	Conditions and aspects	Ni grade initial (%)	Ni grade final (%)	Recovery (%)
Brazil	Flotation with octanedione dioxin as a collector for three laterite samples [12]	1,2	1,4	63
New Caledonia	Micro flotation of the fraction 53-74 μm, with cetyl trimethyl ammonium bromide (CTAB) or sodium oleate [13]	NA	NA	NA
India	Anionic collectors, in addition to sodium silicate [14]	0,6	1,6	60
India	Cationic collectors and starch to recover Ni from a cyclone overflow of 20 μm [15]	0,8	1,3	86
India	Pre-concentration of the discharge of a hydrocyclone (coarse fraction) with low amount of Ni. The flotation of this cyclone stream using sulfonate, sodium silicate and pine oil [16]	0,5	1	82
India	Use of sodium lauryl acetic acid methylamino and sodium salt modified by carboxylic acid [13]	0,5	1	70-80
India	They used as reagents quinoline hydroxy, dimethylglyoxime, nitroso pyrazolone, 2,2 bipyridal, triethanolamine and sodium oleate [15]	0,5	-	40-60
Côte d'Ivoire	The segregation of nickel minerals in laterites followed by flotation using sodium silicate as a dispersant [17]	1,2	6-8	35-40
Australia	Several techniques of preparation of feeding before flotation [18]	1	1,4	43

Source: Adopted from [12-18].

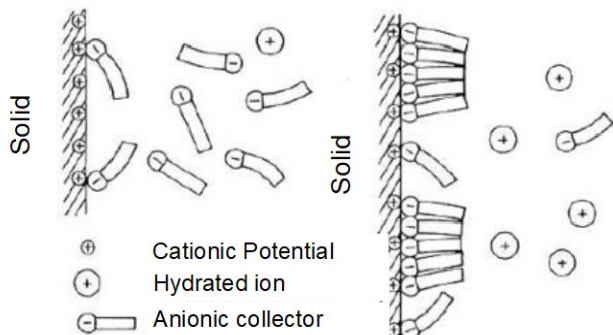


Figure 1. Schematic representation of the electric double layer in the presence of an anionic collector.
Source:[26].

An example is seen in Fig. 1 [15,28,29]. The theory of solubility assumes that the adsorption of collectors in minerals is due to chemical bonds that follow the laws that govern the precipitation of substances of low solubility [30,31]. The theory of the formation of ionomolecular complexes indicates that diverse molecular associations between the two unitary species, ion and neutral molecule, would be formed in solution before adsorption. These associations would be quite simple and would be abundant in different ranges of pH in concentrations lower than the respective critical micellar concentrations (CMC), since at such a point no floats would occur due to collector characteristics. Particularly active at the interface, both solid/liquid and liquid/air, would be the ion-neutral molecule dimers, the so-called ionomolecular complexes [3,23,26].

Due to the oxide compounds present in the study mineral and the little reaction with traditional methods require special treatment, sulfidization activation is carried out with sodium sulfide (Na_2S), followed by flotation using xanthate and others tiocolectores. Sulfidizing agents such as sodium sulfide (Na_2S), sodium sulfhydrate or ammonium sulfide ($(NH_4)_2S$) are usually added in stages for greater efficiency and control. A common example in this technique is for

copper oxide ores, since they do not respond well to traditional concentration methods [17].

The process of sulfidization activation is quite attractive, but in practice, care should be taken not engender two important disadvantages. The first is the dosage of the sulphiding agent: excess produces a depression in both the sulfide minerals and in the oxides, and an insufficient quantity produces a poor recovery. The second disadvantage pertains to the oxide minerals, since they respond differently to sulfidization [17]. Fig. 2(a) shows an outline of the activation process using in aqueous solution, as shown in the eq. (1):



The sulfur ion is adsorbed on metal oxides that include the Ni-bearing and do not compromise the surface alteration of the silicates. The result is a surface sulfide of *Fe* and *Ni* mainly, which can be hydrophobicized selectively by a thio-collector. In order to have efficiency in sulfidization activation, the pulp must be conditioned at a neutral to alkaline pH no higher than 10.5 [32], and preferably with caustic soda instead of lime. The variation of the collectors

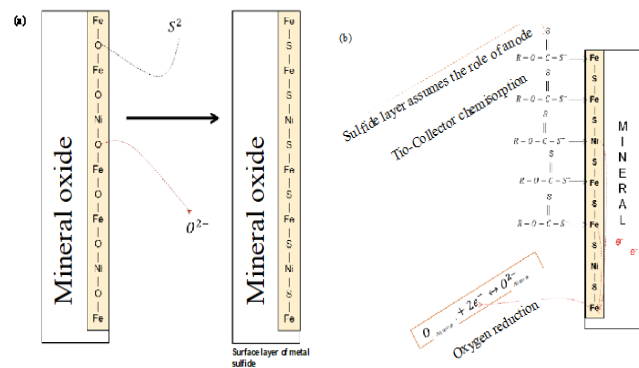


Figure 2. (a) Activation process by means of Na_2S in aqueous solution. (b) TiO-collector Adsorption.
Source: The Authors.

can range from ethyl and amyl xanthates to the promoters AERO 8474, 8475 and 8649 among others, which are dithiocarbamates, especially the thio-collector reagents that favor chemisorption on metallic bonds, as shown in Fig. 2(b) for the flotation of metal sulphides frequently used in the flotation of metal sulfides with a concentration of 250 g/ton and using Aerofroth 65 as a foaming agent, which is a polyglycol that exhibits strength in the flotation circuits [29].

2. Methodology

2.1. Samples

The mineral with which the froth flotation tests were carried out belongs to a lateritic soil extracted from a deposit located in the northwest of Colombia, in the Córdoba department (Fig. 3). The soil was dried and then ground, taking it to an optimum granulometry for froth flotation tests. All tables and figures occupy the entire width of the column. Use figures and tables of two columns of width only when necessary. The SG of the mineral was 2,475. With the atomic absorption spectrometry (AAS) ICETM 3000, the concentration of each of the analytical elements in the sample was determined. Table 2 shows the results of the chemical analysis by atomic absorption performed on the mineral in percentage by weight. This was in order to observe what amount of material of interest was retained in each of the meshes, which were made with a series of Taylor (USA STANDARD TEST SIEVE) screens in the Rotap RX-29® sieve. Approximately 20 tests were performed in SEM (scanning electron microscopy) type JEOL JSM-5910LV, with a quantitative and qualitative analyzer for the three-dimensional observation of high-resolution images, surface analysis at high magnifications, grain shape, and chemical composition. Fig. 4 shows the microanalysis for the mineral that accompanies the nickel in the lateritic deposit.



Figure 3. A mineral of interest from the lateritic deposit of Ni. Source: The Authors.

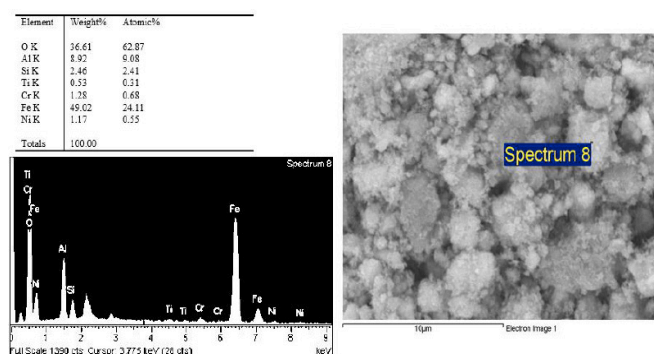


Figure 4. Scanning electron microscope (SEM) for the float mineral. Source: The Authors.

The mineral has an approximate content of 1.5% in the mineral, with a range from 1.2% to 1.7%, with 39% insoluble and SiO_2/MgO ratio of 1.8. For XRD tests, X'pert-pro analytical equipment was carried out with X'pert-pro data collector software. For the measurement of the ore, it was crushed and then 10 grams of mesh 200 were taken to finally be analyzed, resulting in what is shown in Fig. 5 and Table 3.

Table 2. Chemical analysis by atomic absorption.

Mesh	% Fe_2O_3	% Ni	% MnO	% CaO	% Al_2O_3	% MgO	Insoluble
-70/+100	12,099	1,697	0,201	0,180	0,689	13,491	43,050
-100/+170	11,970	1,749	0,186	0,183	0,667	12,304	43,420
-170/+200	11,928	1,711	0,179	0,183	0,667	13,152	43,650
-200/+230	12,684	1,779	0,174	0,144	0,647	13,308	41,160
-230/+270	12,787	1,802	0,175	0,143	0,634	12,393	42,630
-270/+325	12,588	0,169	0,140	0,140	0,737	13,151	42,220
-325	13,896	0,163	0,163	0,132	0,766	13,263	39,520

Source: The Authors.

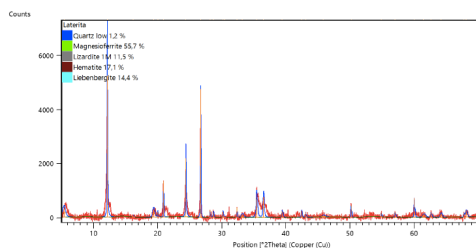


Figure 5. DRX for the mineral. Source: The Authors

Table 3. XRD (X-ray Diffraction) results.

Name of the compound	Quantity (%)
Quartz	1,2
Magnesioferrite	55,7
Lizardite	11,5
Hematite	17,1
Liebenbergite	14,4

Source: The Authors

Table 4.
Flotation reagents.

Reagent	Description
Aero 825 Promotor	Traditional oil sulfonates, which must be dispersed in water at 82 °C to reduce viscosity and improve handling characteristics [32].
Aeromine 3030c	It is a cationic promoter, it can be used in acidic or alkaline media. It is associated with micas [32].
Aerofroth 65	Soluble polyglycol that exhibits strength and persistence in flotation circuits. It is used for floating with difficult foaming obtaining a froth with low reagent consumption [32].
Aerofroth 70	Low molecular weight alcohol foam when the selectivity is important for the feed that contains a percentage of fines higher than normal [32].
Starch or Dextrins	They possess strong flocculating properties, but when they are negatively charged by substitution of an anion, we obtain negatively charged macromolecules which are used as selective depressants of talc and siliceous minerals [36].

Source: The Authors.

2.2. Flotation reagents

Three different mechanisms of froth flotation were performed in which each of these was used as a type of reagent [22,23,32–34]. Oxide-type mineral collectors must emphasize better efficiency for the recovery of fine particles and aid in the improvement of the differential flotation of complex oxide ores, having greater selectivity in anionic flotation in relation to silica. The reagents that appear in Table 4 were used [35] in the investigation.

Froth flotation tests were performed under forward and reverse mechanisms. For direct flotation was used as collector oleic acid at a concentration of 20% solution at 250 g/t, similarly, they flotations with activation were performed by sulfidization with isopropyl xanthate sodium at a concentration of 20% in solution 250g/ton and for the reverse flotation the Aero 825 promoter was used with a concentration of 20% in solution at 250g/ton. Likewise, for the three tests, Aerofroth 65 at 200 g/ton was used. Finally analyzing each of the results and given that recoveries for the two cells are similar it was decided to perform laboratory tests with Denver cells.

2.3. Hydrophobicity mineral mechanisms

The first mechanism has been formed by the collector adsorption on the surface of the particle to be floated, as loads are increased. The second mechanism raises generate a laterite ore interface modifying the particle surface, achieving hydrophobizing mineral by thio-collectors. It is also necessary that measurements of contact angle and z are carried potential, which helps determine the mechanisms of the mineral hydrophobicity.

Testing contact angle measurement was performed with the goniometer type OCA 15 PLUS computer with software SCA 20 and measurements of zeta potential on the computer model Zeta Sazer nano zs90 zen3690 Malvern. The mineral was used in aqueous solution by varying the pH with sodium hydroxide to the basic area.

2.4. Laboratory process

A methodology is proposed as shown in Fig. 6 based on the processing and analysis of the samples, modifying variables during the different stages of the process. Initially, a quartering of the feed sample is performed along with the chemical and mineralogical characterization for the identification of the useful and gangue species, their associations, and release size. Once the characterization stage is completed, the granulometry of the mineral species useful for their concentration is determined. Subsequently, the appropriate cell was chosen for the flotation process and its volume was determined, the ore is subjected to grinding to take advantage of the optimum nickel mineral release size, without forgetting also the variables involved in the flotation process such as of flotation reagents, reagent dosing, pulp density, aeration and conditioning, pH, water type, temperature, and flotation time, in addition, contact angle measurements were made with different reagents to determine the hydrophobicity of the particles.

Flotation tests are carried out in conventional semi-batch (Denver) and column cells for direct and inverse. First, direct flotation tests were carried out in which the material of interest comes out through the foam and the gangue is depressed and exits through the reactor, followed by inverse foaming flotation tests in which the material that comes out through the foam is the gangue and by the tailings the material of interest, in this case, this process was done to float the greater amount of material that is not of interest. In each of the aforementioned tests, there was a previous analysis of reagents, dosage, pH, conditioning time, pulp density and collection time. The two currents of each of the tests both the concentrate and the tails were duly dried, weighed, and finally analyzed by atomic adsorption in order to determine the recovery that was obtained and, in this way, to determine the representative variable for the process (Fig. 6).

In addition, direct flotation tests were carried out on semi-batch flotation cells (Denver) and column with sulfidization activation using as sulfidizing agent the Na_2S making the material behaves as a sulfide material. This was achieved with modifications in dosing variables, pH, and time of

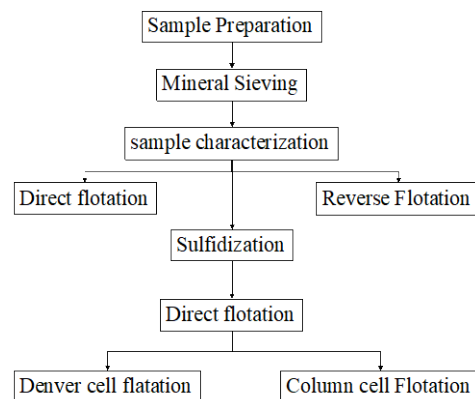


Figure 6. Flow chart of the methodology implemented for the development of the research work.

Source: The Authors.

collection. These were also collected properly by each of the streams, dried, and analyzed, thus making determining their recovery possible.

3. Results and discussion

3.1. Contact angle and z potential values

Fig. 7(a) shows the measurement of the contact angle of the surface of a quartz particle of the mineral of interest, which gave a very low angle, guarantees that the surface is hydrophilic and can be taken as a value of the reference. The collectors used for the modification of the quartz surface that provided the greatest hydrophobicity were the Aero 825 and the Aeromine 3030C both reactive with a concentration of 20% in solution and pH of 7.

Figs. 7(b) and Fig. 7(c) show the contact angle measurements obtained on the modified quartz surface with the Aero 825 and Aeromine 3030c manifolds, respectively. In Fig. 8, the summary of contact angle measurements on surface modified quartz occurs by immersion for 5, 10, 15, 20, 25, 30 minutes Aero 285, Aeromine 3030c collectors, and others like Aero 845.

According to Fig. 8, it is observed that the efficient conditioning time for the collector to act on the surface of the ore is 20 minutes, reaching a higher value of 82° the Aero 825 promoter. Likewise, the Aeromine 3030c promoter the 30 minutes reaches an angle with a value of 63° and the Genamin TAP 100 at 20 minutes reaches a maximum value

of 42 °, which indicates that greater hydrophobicity of the surface is obtained with the Aero 825 collector, which help as a reference for doing the reverse flotation.

With the results obtained from the contact angle measurement, the wettability of the surface was considered with the type of conditioner and the conditioning time. An important reason to determine the type of collector used for this type of flotation.

The result of the mineral z potential is shown in Fig. 9, it is observed that the surface charge of the mineral is negative at any pH used for this measurement, so it would be convenient to use a cationic collector to induce hydrophobicity to the mineral. However, it should be noted that the test established to determine the z potential was not carried out with the pure phase of the mineral; therefore, the oxide in which this metal is found is not individually discriminated.

3.2. Froth flotation tests

Conventional test cell (Denver) and cell column are performed; however, the results were similar in the two cell types as shown in Table 5. The flotation tests for each of the cells were performed under the same conditions.

Table 6 shows the results of the reagents used for the different flotation tests and in Fig. 10 the recovery percentage of each of these reagents.

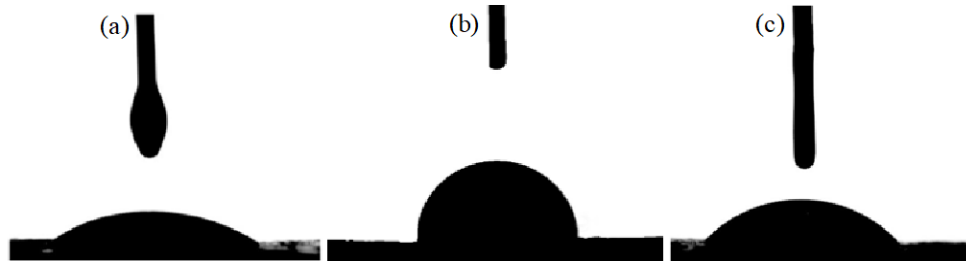


Figure 7. (a) Contact angle measurement of the quartz surface. (b) Contact angle measurement with Aero 825 promoter. (c) Contact angle measurement with Aeromine3030C promoter.

Source: The Authors

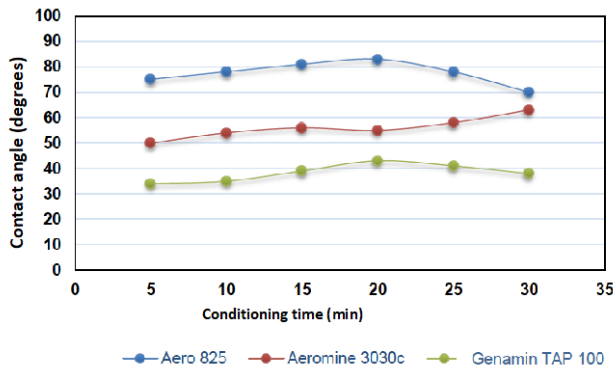


Figure 8. Contact angle on modified quartz surface with different collectors.

Source: The Authors.

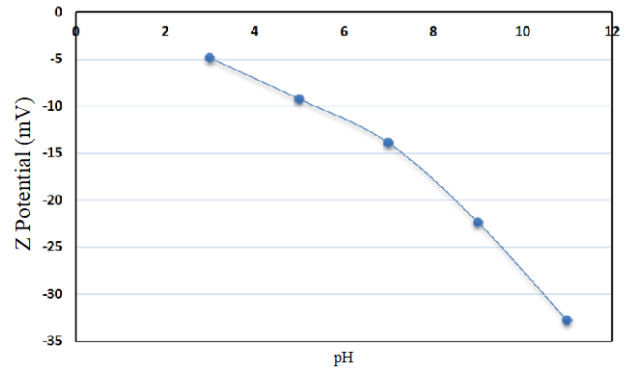


Figure 9. Measurement of z potential of the mineral.

Source: The Authors.

Table 5.
Flotation tests.

	pH=3 Recovery (%)	pH=7 Recovery (%)	pH=10 Recovery (%)
Denver Cell			
Direct Flotation	15	24	18
Reverse Flotation	72	70	59
Sulfidization Activation	69	86	84
Column Cell			
Direct Flotation	17	30	24
Reverse Flotation	71	70	60
Sulfidization Activation	68	86	85

Source: The Authors.

Table 6.
Reagents and type of flotation.

	Reagent	Direct flotation	Reverse flotation
1	Oleic acid	x	
2	Genamin TAP 100		x
3	Aero 845 Promoter		x
4	Sulfanate 869		x
5	Dodecilamina		x
6	Aero 825 Promoter		x
7	Xantato sulfidization	x	
8	Aeromine 3030c		x

Source: The Authors.

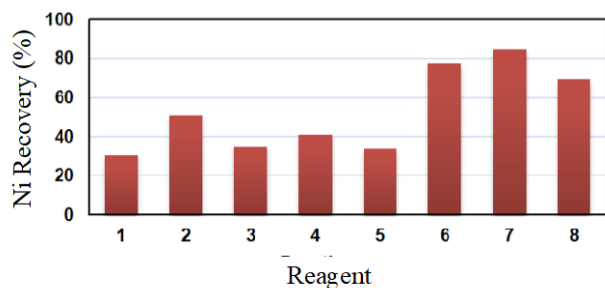


Figure 10. Recovery percent of each of the reagents used in different tests of froth flotation
Source: The Authors.

3.2.1. Direct flotation

The direct flotation process consists of a separation of hydrophobic minerals (material of interest) from hydrophilic minerals (Gangue or tailings) by air injection, in order to obtain a concentration of mineral of interest in the foam, in Fig. 11 observe the results of a direct flotation process. Tests direct flotation were used as collector oleic acid at 250 g/t, foaming the Aero froth 65 to 200 g/ton changing acidic pH with sulfuric acid and basic pH with sodium hydroxide, with a variety of pH between 3 and 9. in this test the results reported in the literature [13] it is confirmed that the direct flotation is not efficient for oxides in laterite deposits.

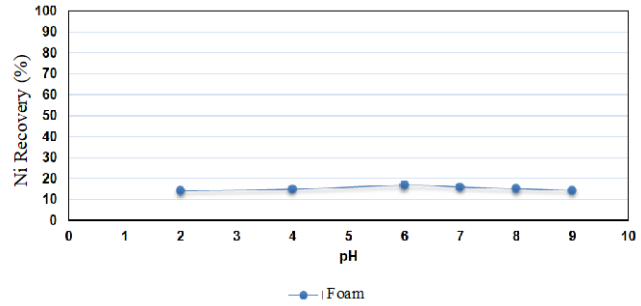


Figure 11. Direct flotation test.
Source: The Authors.

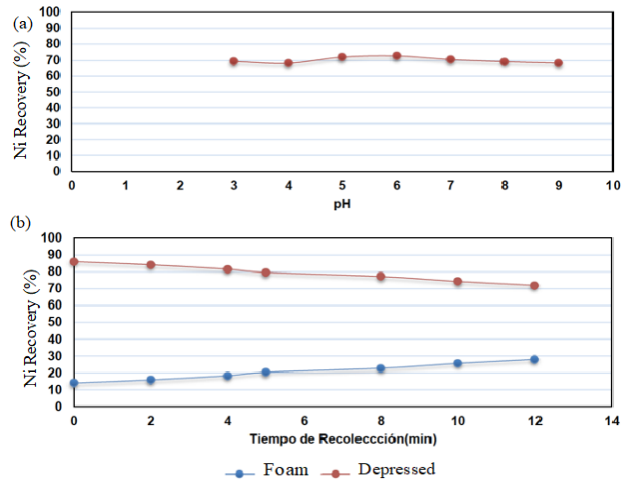


Figure 12. (a) Reverse floating test. (b) Ni Recovery Vs time.
Source: The Authors.

3.2.2. Inverse flotation

The inverse flotation process selectively hydrophobes the gangue, which is collected in the foam, therefore, the mineral of interest is depressed, in this case, it is desired to float the largest amount of sterile ore with the minimum percentage of nickel [37]. Fig. 12 show the results obtained with the Aero 825 promoter, with variation in pH and collection time. Reverse flotation tests 825 Aero promoter was used at a concentration of 20% solution at 250 g/t, the foaming Aero froth 65 to 200 g/t and the mineral depress with corn starch.

3.2.3. Sulfidization activation

The results of the sulfide flotation are shown in Fig. 13 with variation in two variables such as pH and collection time. Sulfide flotation was accomplished by direct mechanism, in which direct flotation test was performed with pH neutral to alkaline, using isopropyl xanthate collector sodium with an amount of 250 g/ton and foaming the Aero froth 65.

Fig. 14 shows the recovery results adjusted to the García-Zuñiga model for the flotation process by sulfidization

activation. For this case in the investigation García-Zuñiga model was performed for a batch operation in a conventional Denver cell, represented by the eq. (2):

$$R = R_{\infty} [1 - e^{-kt}] \tag{2}$$

where K represents the kinetic constant of flotation and R_{∞} is the maximum recovery achievable in a real process. Since the flotation constant is 0.12 min^{-1} and is relatively small, it implies that for short flotation times the recovery in the cell is low.

Noting the results and those obtained by previous authors, can admit that this work progresses to a proposal oriented towards recovery and enrichment (Ni-bearing) in laterites, because today the plants of lateritic nickel have no formal processes concentration of minerals, which is considered as an exception to mining-metallurgical plants, it is necessary then to introduce this concept, because several of the concentration processes have failed and it only remains to work techniques related to surface chemistry including froth flotation and selective agglomerations (flocculation with polymers or coagulation with salts).

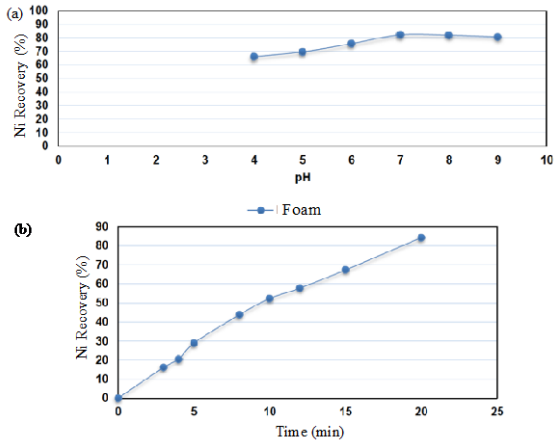


Figure 13. (a) Direct flotation test by activation by sulfidization. (b) Ni recovery Vs time in the activation process by sulfidization. Source: The Authors.

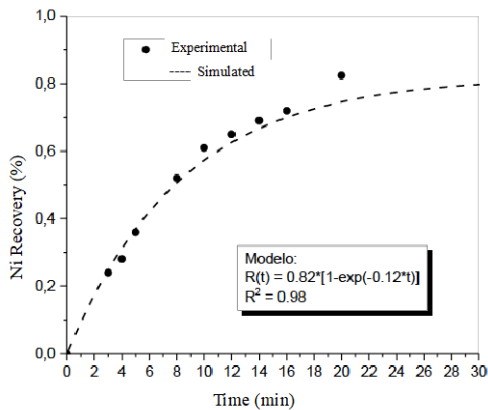


Figure 14. Ni recovery according to the García-Zuñiga model. Source: The Authors.

According to the objectives, an innovative methodology is presented, which has not been used previously in the flotation of laterites, which consists of generating a laterite mineral interface formed by an iron sulfide (FeS), which can be hydrophobicized by means of the use of thio collectors in intervals of neutral and alkaline pH, which is not reported in the literature, which usually operates at acid pH intervals mainly. Together with the above, the literature [3,18] does not reach to present appreciable enrichment and recovery, and the actions that lead to pre-treatments that motivate the selectivity of the hydrophobicization of the Nickel ores are not clear; The direct flotation by them effected to selectively separate from the complex of lateritic oxides is not entirely clear.

This research had to deal with a change in the conception of mineralogy commonly held in lateritic nickel ores in Colombia. A very determining role for the composition of the minerals of Nickel to the oxides is usually assigned; however, the characterization led to conclude that nickel ores are presented as are silicates, which induces a difficulty in selectivity hydrophobing related to two families of minerals containing nickel (oxides and silicates).

In addition to the above, no minerals are presently nickel, if not iron oxide-type minerals mainly, so it can be deduced that Nickel is mainly in Iron replacements, and possibly Magnesium, which confirms the hypothesis of Ni-bearing. Therefore, not all the nickel of the ore is in the form of simple oxides accompanying the iron oxides as it appears in the literature [11]. Table 3 shows the results of the characterization of nickel associated with silicates, which will prevent a high recovery of nickel under a hydrophobicity strategy of simple oxides associated with iron.

On the other hand, in the reverse flotation where it is intended to hydrophobized silicates (mainly quartz), the hydrophobicization also has the opportunity to act on nickel silicates (Liebenbergite). Sulfidization of simple oxides allows adsorption of thiocolecule-type surfactants, such as those used in the research (Table 6), and in which, in the natural pH flotation scenario, they do not interact with silicates. In this sense, sulfidizing generates a sulfide-metallic surface that masks nickel's oxidized ores, which accounts for the losses of this metal in the tails.

The measured Z potential cannot be used as a tool for the selection of physical-chemical flotation conditions as shown in Fig. 9 since this value does not discriminate individually the oxide in which this metal is found. The use of the Z potential would involve the isolation in the laboratory of nickel ore only, and this process is one of the main difficulties in laterite deposits.

On the other hand, for pyrometallurgical nickel extraction processes, the ratio SiO/MgO should not be higher than 2, since they are conditions for the melting and efficiency of the process [52], this investigation reports a ratio SiO/MgO of 1.8 so it is located in the desired range 1.5~2.0. The direct and inverse flotation without activation with a recovery of 16% coincide with the results of the literature previously had Table 1 [3,13]. It is for this reason that pretreatments are

suggested to the ores before the concentration processes. From the above, this research, as well as the literature conclude that the absence of activation decreases recovery and enrichment reasons.

4. Conclusions

Through the sulfidization and direct mechanisms of the Ni-bearing ores, specific hydrophobicity of this type of minerals is achieved by substantially improving the Nickel concentrations in the process, with recoveries close to 86% as shown in Fig. 13(b), which compared with conventional direct and reverse flotation without performing this activation with Fig. 11 and Fig. 12(a) give recoveries of 70% and 16% respectively. The reverse flotation also reaches an increase in the nickel content (Fig. 12(a)) with an approximate recovery of 70%; however, the froth flotation with activation is still better.

The interfacial adsorption mechanisms were evaluated with different types of collectors without pretreatment and no selectivity is presented. Therefore, the flotation theory of oxides for this type of ores is not validated by direct flotation, while by sulfidization activation and the use of thiocollector the mechanism approached the theory of metal sulfide flotations where the role of oxygen has been shown to be very important. Nickel concentrates are obtained using froth flotation, with innovative technologies with pretreatment of nickel ores with sulfide, which does not report results in the literature at present.

The froth flotation for concentration Nickel laterite soils showed better selectivity in processes reverse flotation for processes usually used directly froth flotation reaching approximately 72% recovery (Fig. 12(a)) using as Aeromine 825 promoter, a natural pH of 7.0, using starch as a depressant and AeroFroth 65 as a foaming agent.

References

- [1] Oxley, A. and Barcza, N., Hydro-pyro integration in the processing of nickel laterites. *Miner. Eng.* 54, pp. 2-13, 2013. DOI: 10.1016/j.mineng.2013.02.012.
- [2] UPME. El Niquel en Colombia 2009, 46 P.
- [3] Quast, K., Connor, J.N., Skinner, W., Robinson, D.J., Li, J. and Addai-Mensah, J., Preconcentration strategies in the processing of nickel laterite ores part 2: laboratory experiments. *Miner. Eng.*, 79, pp. 269-278, 2015. DOI: 10.1016/j.mineng.2015.03.016.
- [4] Gupta, A. and Yan, D.S., Introduction to mineral processing and operation. In: Gupta, A. and Yan, D.S., Eds., *Mineral processing design and operation*, Elsevier Science, 2006, pp. v-vi, ISBN: 9780444516367.
- [5] Li, G., Zhi, Q., Rao, M., Zhang, Y., Cai, W. and Jiang, T., Effect of basicity on sintering behavior of saprolitic nickel laterite in air. *Powder Technology*, 249, pp. 212-219, 2013. DOI: 10.1016/j.powtec.2013.08.018.
- [6] Rao, S.R., *Resources recovery and recycling from metallurgical wastes*. Volume 7, 1st Ed. Elsevier, 2006, ISSN 1478-7482, ISBN 9780080451312,.
- [7] Li, S., *Study of nickeliferous laterite reduction*. Thesis, McMaster University, Hamilton, Canadá 1999, pp. 1-10.
- [8] Velásquez, C.A., Durango, J., Gleeson, S.A., Koll, G. and Herrington, R.J., The mineralogy and geochemistry of the Cerro Matoso S.A., Ni Laterite Deposit, Montelibano, Colombia. *Econ. Geol.*, 99, pp. 1197-1213, 2011. DOI: 10.2113/gsecongeo.99.6.1197.
- [9] Farrokhpay, S. and Filippov, L., Challenges in processing nickel laterite ores by flotation. *Int. J. Miner. Process.*, 151, pp. 59-67, 2016. DOI: 10.1016/j.minpro.2016.04.007.
- [10] Mohammadreza, F., Mohammad, N. and Ziaeddin, S.S., Nickel extraction from low grade laterite by agitation leaching at atmospheric pressure. *Int. J. Min. Sci. Technol.*, 24, pp. 543-548, 2014, DOI: 10.1016/j.ijmst.2014.05.019.
- [11] Hunter, H.M.A., Herrington, R.J. and Oxley, E.A., Examining Ni-laterite leach mineralogy & chemistry - A holistic multi-scale approach. *Miner. Eng.*, 54, pp. 100-109, 2013. DOI: 10.1016/j.mineng.2013.05.002.
- [12] Witney, J.Y. and Yan, D., Reduction of Magnesia in Nickel concentrates by modification of the froth zone in column flotation. *Miner. Eng.*, 10, pp. 139-154, 1997.
- [13] Onodera, J., Inoue, T. and Imaizumi, T., Attempts at the beneficiation of Lateritic Nickel Ore. *Int. J. Miner. Process.*, 19, pp. 25-42, 1987.
- [14] Bohidar, S., Mohapatra, S. and Sukla, L.B., Nickel recovery from chromite overburden of Sukinda using fungal strains Bioleaching of the ore Calcination of ore. *Control*, 5, pp. 103-107, 2009.
- [15] Rao, G.V., Nickel and Cobalt ores: flotation. *Encycl. Sep. Sci.*, pp. 3491-3500, 2004. DOI: 10.1016/b0-12-226770-2/05861-0.
- [16] Beukes, J.P., Giesekke, E.W. and Elliott, W., Nickel retention by goethite and hematite. *Miner. Eng.*, 13, pp. 1573-1579, 2000. DOI: 10.1016/S0892-6875(00)00140-0.
- [17] Harris, C.T., Peacey, J.G. and Pickles, C.A., Selective sulphidation and flotation of nickel from a nickeliferous laterite ore. *Miner. Eng.*, 54, pp. 21-31, 2013. DOI: 10.1016/j.mineng.2013.02.016.
- [18] Fornasiero, D., Quast, K., Addai-Mensah, J., Otsuki, A. and Robinson, D.J., Preconcentration strategies in the processing of nickel laterite ores part 3: flotation testing. *Miner. Eng.*, 79, pp. 279-286, 2015. DOI: 10.1016/j.mineng.2015.03.018.
- [19] Gerson, A. and Napier-Munn, T., Integrated approaches for the study of real mineral flotation systems. *Minerals*, 3, pp. 1-15, 2013. DOI: 10.3390/min3010001.
- [20] Aghazadeh, S., Mousavinezhad, S.K. and Gharabaghi, M., Chemical and colloidal aspects of collectorless flotation behavior of sulfide and non-sulfide minerals. *Adv. Colloid. Interface. Sci.*, 225, pp. 203-217, 2015. DOI: 10.1016/j.cis.2015.09.007.
- [21] Gui, X., Liu, J., Cao, Y., Cheng, G., Li, S. and Wu, L., Flotation process design based on energy input and distribution. *Fuel Process Technol.*, 120, pp. 61-70, 2014. DOI: 10.1016/j.fuproc.2013.12.011.
- [22] Bustamante-Rúa, M.O., Daza-Aragón, A.J., Bustamante-Baena, P. and Osorio- Botero, J.D., Recovery evaluation of P₂O₅ through three models of froth flotation of phosphoric rock. *Bol. Ciencias de la Tierra*, 45, pp. 41-46, 2019. DOI: 10.15446/rbct.n45.72354.
- [23] Haseman, J.F., Flotation of phosphate ores. USA, 1968, 3 P. DOI: 10.1016/B978-0-444-53083-7.00001-4.
- [24] Bustamante-Rúa, O.M., Naranjo-Gómez, D.M., Daza-Aragón, A.J., Bustamante-Baena, P. and Osorio-Botero, D.J., Flash flotation of free coarse gold using dithiophosphate and dithiocarbamate as a replacement for traditional amalgamation. *DYNA* 85, pp. 163-170, 2018, DOI: 10.15446/dyna.v85n205.69882.

- [25] Cruz, N., Peng, Y., Wightman, E. and Xu, N., The interaction of pH modifiers with kaolinite in copper-gold flotation. *Miner. Eng.*, 84, pp. 27-33, 2015. DOI: 10.1016/j.mineng.2015.09.019.
- [26] Yianatos, J., Flotación de minerales. *Estud. Filológicos*, 2005, pp. 1-126. DOI: 10.4067/S0071-17132000003500023.
- [27] Bustamante-Rúa, M.O., Notas de clase flotacion avanzada de minerales, Facultad de Minas, Universidad Nacional de Colombia, 2016, 20 P.
- [28] Agatzini-Leonardou, S., Tsakiridis, P.E., Oustadakis, P., Karidakis, T. and Katsiapi, A., Hydrometallurgical process for the separation and recovery of nickel from sulphate heap leach liquor of nickeliferous laterite ores. *Miner. Eng.*, 22, pp. 1181-1192, 2009. DOI: 10.1016/j.mineng.2009.06.006.
- [29] Castello, P., Niu, Y. and Gesmundo, F., The sulphidation of copper-rich Cu-Ag alloys in H₂-H₂S at 550-750°C. *Corros Sci.* 41, pp. 919-939, 2002. DOI: 10.1016/s0010-938x(98)00163-2.
- [30] Nacional Institute of Advance Industrial Science and Technology. Atlas of Eh-pH diagrams, 2005.
- [31] Joseph-Soly, S., Quast, K. and Connor, J.N., Effects of Eh and pH on the oleate flotation of iron oxides. *Miner. Eng.*, 83, pp. 97-104, 2015. DOI: 10.1016/j.mineng.2015.08.014.
- [32] Cytec. Manual de productos químicos para minería. Cytec Industries Inc., Nueva Jersey, Estados Unidos, 2002.
- [33] Castro, S. and Garcia, J.A., Flotacion, fundamentos y aplicaciones. DIMET. Concepción, Chile, 2003.
- [34] Barros-Daza, M.J., Bustamante-Baena, P. y Bustamante-Rúa, M.O., Blanqueo de caolín por medio de lixiviación en pilas con ácido oxálico. *Respuestas* 21, pp. 65-76, 2016. DOI: 10.22463/0122820X.638.
- [35] Shean, B.J. and Cilliers, J.J., A review of froth flotation control. *Int. J. Miner. Process.*, 100, pp. 57-71, 2011. DOI: 10.1016/j.minpro.2011.05.002.
- [36] Kar, B., Sahoo, H., Rath, S.S. and Das, B., Investigations on different starches as depressants for iron ore flotation. *Miner. Eng.*, 49, pp. 1-6, 2013. DOI: 10.1016/j.mineng.2013.05.004.
- [37] Larsen, E. and Kleiv, R.A., Towards a new process for the flotation of quartz. *Miner. Eng.*, 83, pp. 13-18, 2015. DOI: 10.1016/j.mineng.2015.08.004.
- M.O. Bustamante-Rúa**, is BSc. in Mining and Metallurgy Eng. from the Universidad Nacional de Colombia, MSc. in Sciences of Engineering with a Mention in Extractive Metallurgy - Mention - Mineralurgy from the University of Concepción -Chile, DSc. in Engineering Sciences with a Mention Extractive Metallurgy - Mining from the Universidad de Concepción - Chile. Is full professor of the Universidad Nacional de Colombia, Medellín, director and researcher of the Mineral Institute CIMEX.
ORCID: 0000-0002-1692-991X
- S.D. Gonzalez-Arias**, is BSc. in Mining and Metallurgy Eng. from the Universidad Nacional de Colombia, with a MSc. in Mineral Resources from the same university. She has worked on research projects at the Universidad Nacional de Colombia and currently works with the Argentine Ministry of Mines.
ORCID: 0000-0001-6470-4080
- P. Bustamante-Baena**, is BSc. in Mining and Metallurgy Eng. from the Universidad Nacional de Colombia. MSc. in Mineral Resources of the same university. Has winner for best undergraduate work and Otto de Greiff National Contest. Belongs to the research group CIMEX Institute of minerals. He is currently the winner of the "Joven Investigador" for Colciencias. Has worked in the industry in the underground coal sector, open pit coal, mineral processing and transformation.
ORCID: 0000-0002-8409-5531