LEACHING IN A TUBULAR REACTOR, EXPERIENCE AND POTENCIAL INDUSTRIAL APPLICATION

LIXIVIACION EN UN REACTOR TUBULAR, EXPERIENCIA Y APLICACIÓN POTENCIAL INDUSTRIAL

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La extracción y producción de metales es un tema muy importante para la hidrometalurgia. En general, el proceso de lixiviación de minerales y aleaciones de metales, que tienen un valor comercial, se lleva a cabo en reactores de agitación o tanques a presión atmosférica o baja presión. Este proceso requiere un tiempo de lixiviación típica de 1 - 2 horas o incluso más tiempo.
El uso de un reactor tubular puede constituir una opción interesante, si tenemos en cuenta que la reacción puede ser acelerada y durar sólo unos pocos minutos.
En el caso de que existan otras reacciones secundarias o físico - químicos, los procesos que aumentan la pérdida de los metales disueltos, el uso del reactor tubular vuelve a ser una alternativa hidrometalúrgico eficiente para este proceso porque se disuelve metales rápidamente, lo que permite separar los mismos antes de la pérdida de metal por los procesos no deseados, tales como precipitación y adsorción, entre otros. El presente trabajo presenta los resultados del estudio de laboratorio del sistema sólido - líquido-gas en un reactor tubular y la experiencia industrial de esta aplicación de proceso para lixiviar y recuperar níquel y cobalto en el proceso de carbonato de amoniaco.

Palabras clave: Níquel, cobalto lixiviación en reactor tubular

The metal extraction and production is a highly important subject for Hydrometallurgy. In general, the leaching process of minerals and other metal bearing materials, which have a commercial value, is carried out in reactors or stirring tanks at atmospheric pressure or under pressure. This process requires a typical leaching time of 1 – 2 hours or even longer.
The use of a tubular reactor can constitute an interesting option, if we take into account that the reaction can be accelerated and last only a few minutes.
In the case there are other secondary reactions or physic – chemical processes, that increase the loss of the metals dissolved, the use of the tubular reactor turns to be an efficient hydrometallurgical alternative for this process because it dissolves metals quickly, so it permits to separate them before the metal loss by the undesired processes, such as precipitation and adsorption, among others, occur. The present work presents the results of the laboratory study of the liquid-solid-gas system in a tubular reactor and the industrial experience of this process application to leach and recover nickel and cobalt in the ammoniac carbonate process.
Nickel, leaching in a tubular reactor

Keywords: Nickel, cobalt leaching in a tubular reactor

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INTRODUCTION

NiLeach process: Flash intensive leaching of nickel oxide ores (Laterite)

The ammonia/ammonium carbonate leaching process, known as the Caron Process, developed by Professor Caron at Delf University (1920), was first put in operation during the 1940s at Nicaro Plant in Cuba.

The reduction roast ammonia leaching process for laterites is more advantageous than the smelting process, since it allows to recover part of the cobalt contained in the ore.

The Caron Process has been improved and there are several plants in production, of which: Nicaro and Punta Gorda, in Cuba; Marinduque in Nonoc (out of operation) Phillipines; Yabulu Refinery, Australia; and Tocantins, Brazil.

The process applied in Cuba operates at moderate ammonia and carbon dioxide concentrations (60/75 g/L NH_3 and 30/40 g/L CO_2) and a leaching time of 3-4 hours, while the plants abroad operate at higher concentrations (95/100 g/L NH_3 and 45/65 g/L CO_2) with a leaching time at Yabulu plant of 1-1,5 hours.

Cuban plants are designed with three leaching stages and washing/stages: Marinduque plant has two leaching stages and Yabulu has a single leaching stage and 7-8 washing tanks. Yabulu uses solvent extraction (ASX) to extract nickel directly from product liquor and cobalt is precipitated with ammonium hydrosulphide.

Yabulu and Tocantins plants use giant turboaerators (mechanically aerated stirred tanks), more efficient than the conventional equipment operating in the Cuban plants (using 66 stirred tanks). The operation at Yabulu plant using a low percentage of solids and high concentration of the leaching reagents favored nickel and cobalt dissolution and compensated temperature increase.

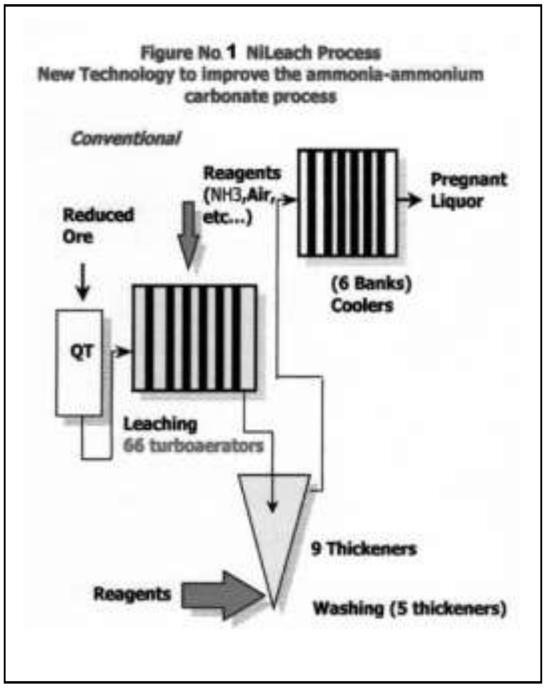
Higher simultaneous extractions of cobalt and nickel by SX, with the separation of cobalt from raffinate as mixed sulphide (Ni+Co) rendered a reduction in cost by cobalt credit.

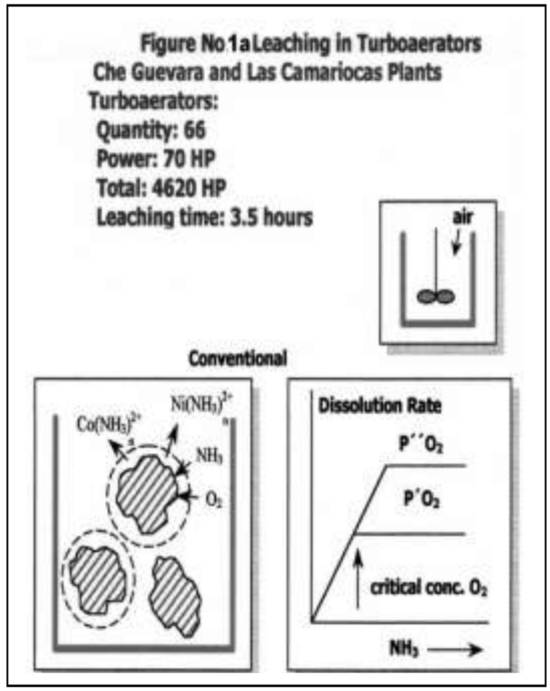
At all, it has been noticed that through leaching stage I (and sometimes in stage II) a passivation phenomenon (neither extraction nor a drop in metal extraction) is evident resulting in the thickener nickel extraction reported falling by 1-3% of nickel potential extraction, and cobalt’s between 10-20% of cobalt potential extraction, likely attributable to precipitation, readsorption by the massive iron hydroxide precipitate, of metals cementation by metallic iron (Castellanos Suárez, J. and others, 1999, Alvarez Villanueva and others, 2000).

Recently, new concepts about the leaching process have been incorporated (Flash Intensive Leaching in Cuban plants, 1997), which allows an extraordinary acceleration of the leaching process and the changes arising in the leaching time, that reported an increase in the nickel and cobalt recovery by the low precipitation and loss of both metals, in particular cobalt.

Theoretical aspects of Ammonia Leaching Caron Process

The Caron process is based in the selective reduction (Ni and Co in relation to iron) in a multi hearth, Herreshoff – type roast. Reducing gas moves in a countercurrent flow to the ore mixed with fuel oil additive. Ore is reduced with gas (H_2+Co) and/or petroleum additive (1,5-2,5% w/w) the reduced ore is leached in the countercurrent process (Fig. No 1).





The reduction process is characterized by its selectivity wherein most of the nickel and cobalt and a very little amount of iron are reduced to metallic.

The Caron process is based on the property of metals to form stable ammonia complexes:

$$Ni(NH_3)_6^{2+}(logKn = 9{,}08), Co(NH_3)_5^{2+}(logKn = 5{,}75), Co(NH_3)_6^{3+}(logkn = 35{,}2)$$

In the case of iron, these complexes are metastable and decomposed, precipitating as Fe $(OH)_3$.

Dissolution of the active forms of nickel and cobalt present in reduced ore, takes place during its leaching in the presence of air, for example:

$$\text{Ni} + {}^{1}\!/_{2}\, O_2 + 6NH_3 + H_2O = Ni(NH_3)_6^{2+} + 2OH^- \quad (1)$$

As it is well-known, the controlling kinetic stage is oxygen diffusion, therefore, an increase in the amount of dissolved oxygen with a simultaneous change in NH_3 and CO_2 concentration at the reaction interphase increases metal dissolution rate. For every NH_3 and CO_2 concentration there is a critical oxygen partial pressure; for which the metal dissolution rate reaches a maximum value (Figure No.1a) (Zelikman, A. H., 1976).

If oxygen concentration is much lower than the ammonia in the solution, O_2 concentration would be close to solution concentration (2). In this case, oxygen diffusion toward the interphase controls the dissolution rate of metals and is given by the expression:

$$J(Ni) = 2J(O_2) = 2\frac{DO_2}{YO_2}Co((O_2) \qquad (2)$$

Where:

DO_2 – Diffusiveness coefficient

Y – Effective thickness of liquid film (or double layer, as it is known) where diffusion takes place.

Ammonia concentration at the interphase can be calculated by:

$$J(Ni) = {}^1/_6\left(\frac{DNH_3}{YNH_3}.(Co(NH_3)\right) - Co(NH_3)interphase = 2\frac{DO_2}{YO_2}.Co(O_2) \qquad (3)$$

$$Co(NH_3)interphase = \frac{YNH_3}{DNH_3}.\left[\frac{DNH_3}{YNH_3}.(Co(NH_3) - 12\frac{DO_2Co(O_2)}{YO_2}\right] \qquad (4)$$

As oxygen concentration increases in solutions, nickel dissolution, also increases.

This involves a decrease in NH_3 concentration at the reaction interphase. At the same time, ammonia entrainment by air stream causes a drop in the concentration at the reaction interphase (see expression 4).

In order to remove the adverse effect or conditions during leaching process, there was proposed and studied the operation with a tubular reactor which provided the formation of a ring-shaped liquid film, moving around the gaseous stream in a concurrent flow.

Under these conditions mass transfer can occur by three phenomena: transfer by diffusion between the nucleus and the liquid annulus, transfer between the gas nucleus, the droplets entrained and the liquid interchange between the gaseous nucleus and the annulus.

Under the conditions of this flow pattern, kinetic resistance by diffusion decreases to a minimum, which accelerates the oxidation process of the active forms of non ferrous metals and also their passage into the solution as complexes.

Leaching in the NiLeach reactor solved the critical drawbacks of the conventional process and was characterized by high oxygen absorption and high concentration of reagents at the interphase, the great turbulence in the slurry annulus moving around the air nucleus, or breaking as a turbulent wave into the same and a high mass transfer between the slurry droplets entrained and suspended in the gaseous stream moving arbitrarily in a turbulent regime.

This flow pattern decreases the thickness, according to the expression: $J = Di\,\frac{Co-Ci}{Y}$; Co and Ni concentration of metals in the active form.

As the gaseous phase moves faster, dynamic interchange of reagents (NH_3, CO_2 and O_2) between both phases is favored, which provides their high concentrations at the interphase.

New leaching conditions (NiLeach process) offer:

- ✓ Higher concentrations of reagents at the reaction interphase.
- ✓ High dissolution rates of metals.
- ✓ The maximum utilization of reagents that is for a given ammonia concentration, metal extraction bottle

solution is higher than by the conventional process.

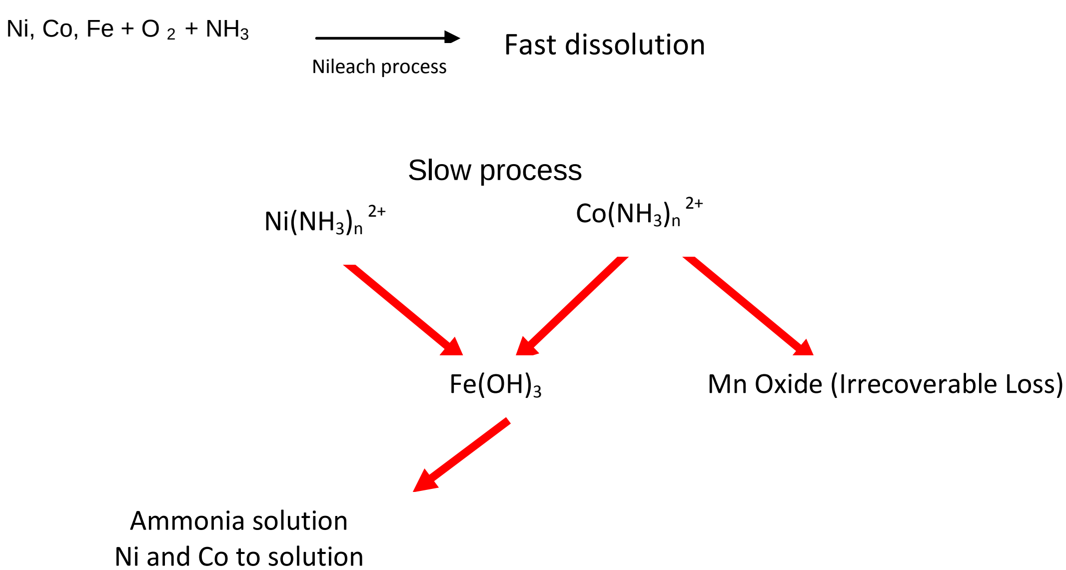
- ✓ To attain the maximum efficiency from reagents used, oxygen in excess is required.
- ✓ Leaching time required will be shorter than for the conventional process.
- ✓ It's highly important to operate under hydrodynamic conditions, which provide the mass transfer pattern outlined above.
- ✓ It was compulsory to consider these factors on equipment design.

Flash Intensive Leaching process

The NiLeach process provides an increment in oxygen and ammonia concentrations at the liquid double layer surrounding ore particles which accelerates formation of nickel *and* cobalt ammonia complexes (Castellanos Suárez, J.; Conference No 1, 1996, and Conference No 2, 1997).

The new process allows leaching of most of the nickel and cobalt present in the relatively short time.

Under these conditions, nickel and cobalt losses due to readsorption on Fe $(OH)_3$ surface are reduced, as a consequence of the sluggishness of this process:



RESULTS AND DISCUSSION

Experience of the implementation of the NiLeach Process

Results of the laboratory studies.

The first studies of a tubular reactor were reported by the researcher Alves (Alves, G.E., 1970) In this publication the flow patterns that occur when varying the flow in a reactor with a water-air system are established. Of the obtained patterns, the annular flow pattern gives the highest mass transfer coefficient, when keeping a dynamic movement of the double layer and a high reagent concentration in it.

Taking into account the potential use of the tubular reactor, the Research Center for Mining and Metallurgy (CIPIMM) decided to evaluate the application of this equipment for the ammoniac carbonate leaching of nickel and cobalt of the lateritic ores (Alvarez Villanueva, G.A.. and others, 1986, Castellanos Suarez, J., 1985).

The experimental studies of the air-mineral-ammoniac water system (air-laterite pulp) in a lab tubular reactor (of 3 m. Long) and in another bench tubular reactor (of 33 m. Long), permitted to establish the pattern map (Figure No 2) (Castellanos Suárez, J. and others, 1985).

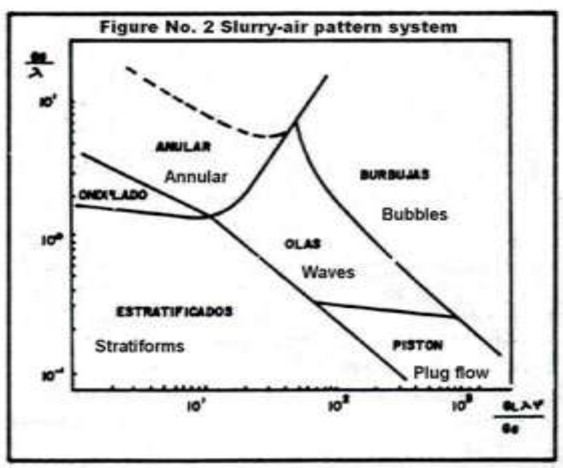


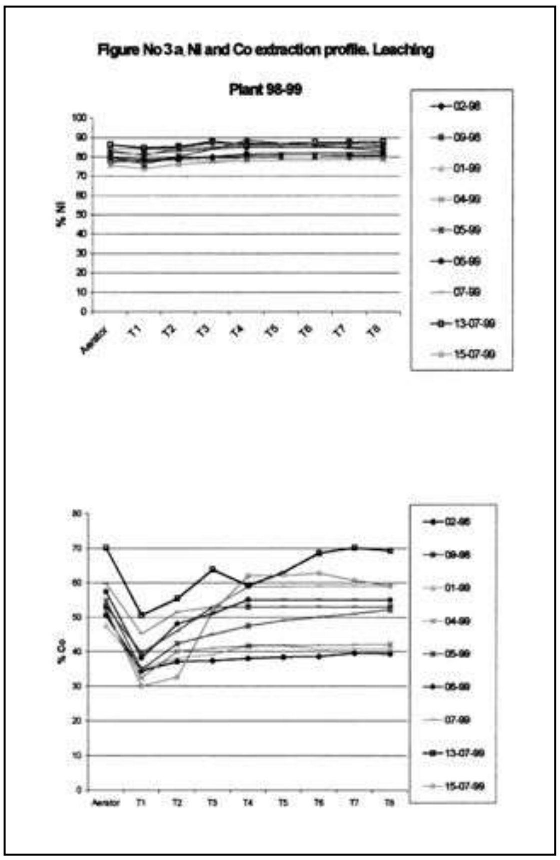
Figure No. 2 Slurry-air pattern system

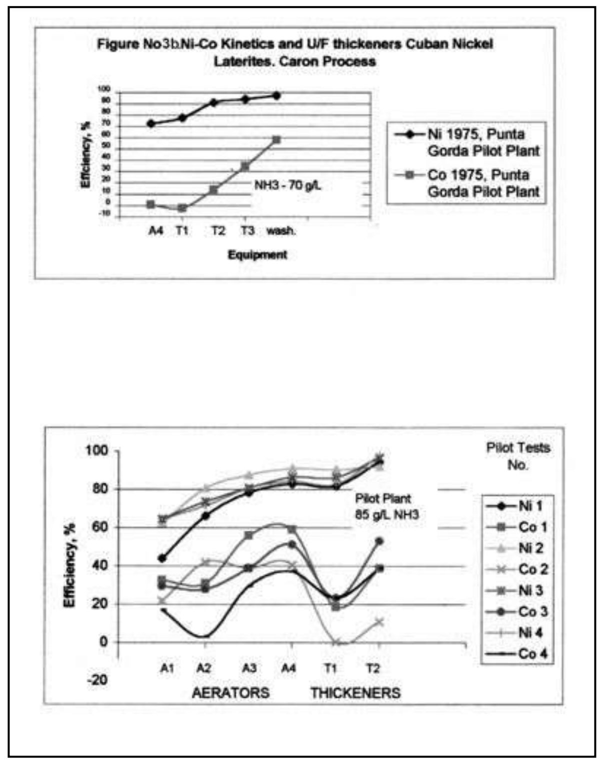
The researches about ammoniac carbonate leaching were carried out in the tubular reactor under experimental flow conditions that permitted to operate with an annular-wave flow pattern (Castellanos Suárez, J., Investigation Report, 1985.).

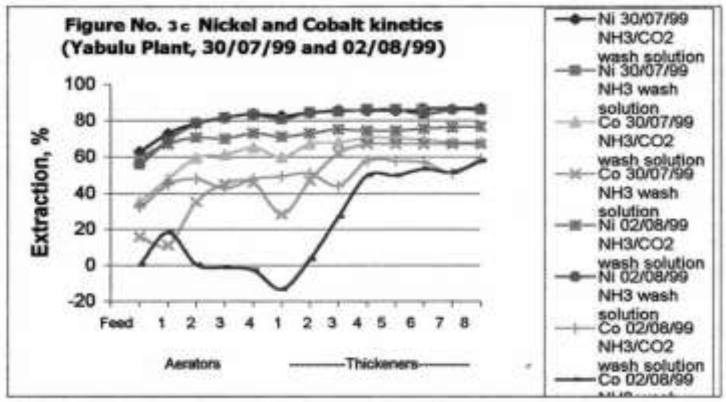
The leaching kinetics of nickel and cobalt, as was expected, achieved very high values, occurring the selective dissolution process of nickel and cobalt in a few seconds (Figure No 3) a short time in comparison with the leaching in the aerators that takes 3 – 3.5 hours.

The detailed investigation of the parameters of the ammoniac leaching process demonstrated the feasibility to apply the intensive leaching in the ammoniac carbonate process (CARON process). Among the advantages of using a tubular reactor for the intensive leaching (known as the NiLeach process) was the increase in nickel and cobalt extraction, as a consequence of the rapid dissolution of metals, avoiding or minimizing the nickel and cobalt loss in the process.

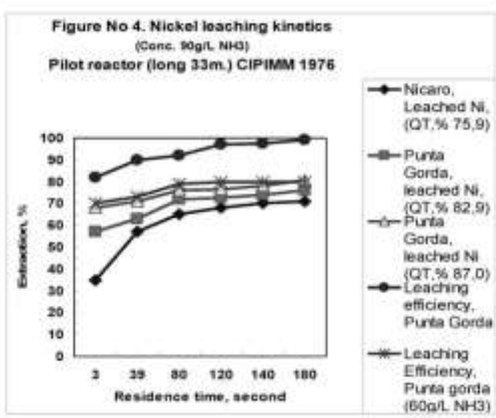
It is known that during the iron oxidation in the ammoniac solution, occurs the formation of a volume of Fe $(OH)_3$ precipitate that sweeps from 1- 3 % Ni and 10- 20 % Co. (Figures No 3a, b, c) (Castellanos Suárez, J. and others, 1999).

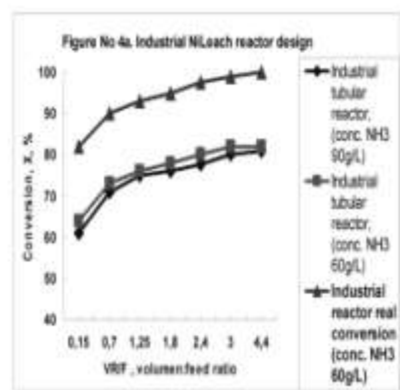






The results of the kinetics were reprocessed to obtain the models for the design of the industrial reactor (Figures No 4 and 4a) (Castellanos Suárez, J. and others, 1997).





Dissolution velocity: $r_{Ni} = (dx/d(V/F)) = dx/d(V_R/F)$ = value of V_R/F vs conversion (x).

The solution of this equation permitted to obtain the kinetic model of nickel leaching:

$V_R/F = 1/[0.475 *((1/(1-x)) - (1/(1-x_0)))]$ Industrial tubular reactor.

In the NiLeach process, nickel extraction will be:

Ni Leached = $[1 - (1/(0.475\, V_R/F + 2.89))]^* \, Ni_{QT}$

Where:

X – Efficiency of nickel leaching.

X_o –Maximum efficiency achieved in the first 15 m. Long of the reactor.

QT – Maximun Potential Nickel extraction in the ammonia/ammonium carbonate standard leaching.

Ni Leached – Ni extraction in the industrial tubular reactor.

Based on these models, 8 industrial tubular reactors were constructed (6 reactors of 600 m. long and 2 reactors of 1000 m.) and put into operation at the begining of the turboaerators series in the Punta Gorda plant.

Ammonia/ammonium carbonate process

Experimental results

The researches carried out (laboratory, pilot plants and industrial) demonstrated that the NiLeach process, at the begining of the turboaerators, reported an increase in the Ni and Co extraction, even when operating with low reagents concentration (NH_3 y CO_2) (Figures No 5 and 5a)

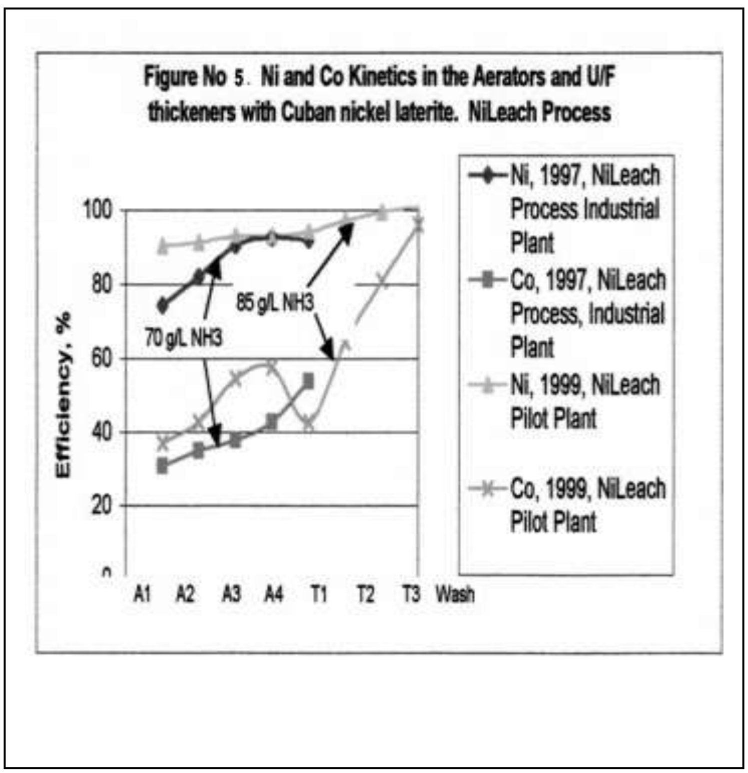


Figure No 5. Ni and Co Kinetics in the Aerators and U/F thickeners with Cuban nickel laterite. NiLeach Process

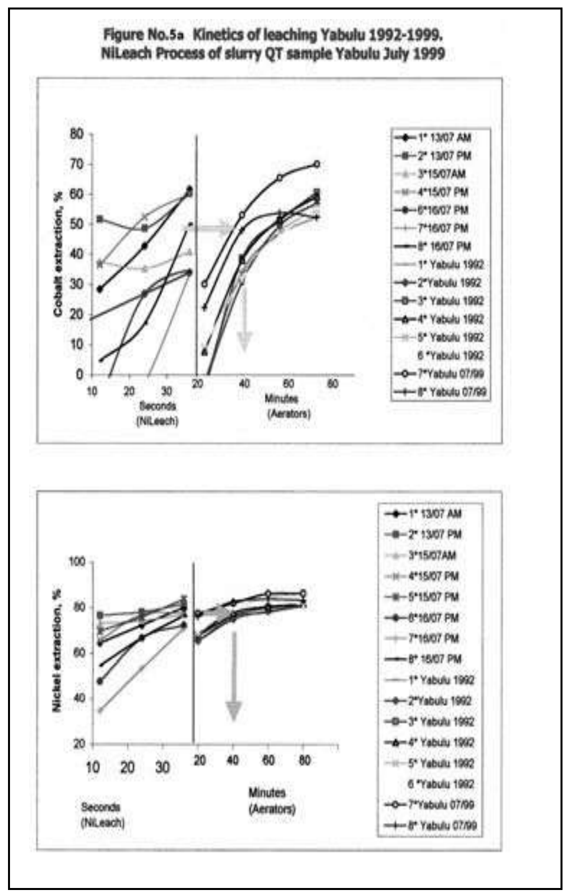
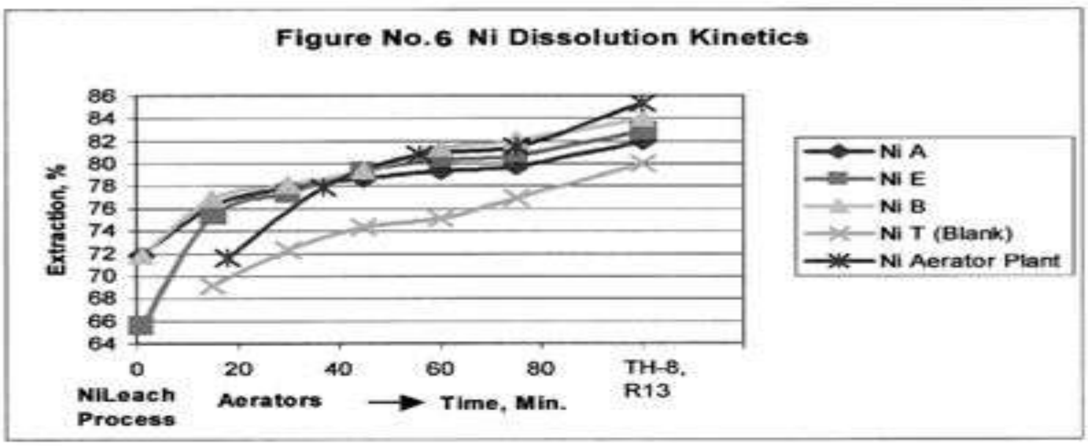


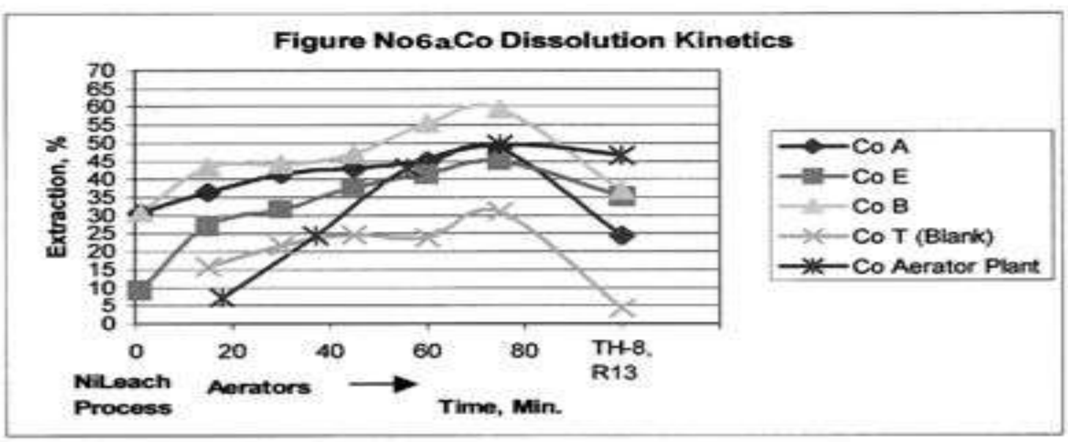
Figure No.5a Kinetics of leaching Yabulu 1992-1999. NiLeach Process of slurry QT sample Yabulu July 1999

The studies carried out in the Yabulu Refinery laboratories trials demonstrated in the process modeling, that under the work conditions of the plant, the Ni extraction was increased between 0,5 – 3 % and Co extraction between 7 – 10 % (Table No 1 and Figures No 6 and 6a) (Alvarez Villanueva, 2000).

Table 1. Results in Yabulu Refinery (Year 2000)

Test	Last Aerator (%)		Total air Kg/t calcine
	Ni	Co	
B (NiLeach + lab. Aerators)	82.04	59.2	95
Plant (aerator A12)	81.5	49.3	170
Difference	0.5	9.9	-





The pilot plant researches at the Laterites Research Center reported and increase in extraction of 2,3% Ni and 20,6 % Co, operating the leaching with concentrations of 82 – 85 % NH_3 and 59 – 63 % CO_2. (Tables No 2 and 3).

The results achieved in the NiLeach industrial process in the nickel plant of Punta Gorda confirmed the pilot plant studies and permitted to increase productivity in the leaching section in 130 % (Table No 4), obtaining a faster dissolution kinetics of metals. The leached nickel was increased in 5 -7 % and the leached cobalt in 7 – 16 %, even when operating with low ammoniac concentrations (41 – 57 g/L NH_3 vs. 70 – 75 g/L required by design) (Castellanos Suárez, J., 1999).

Table 2. Pilot plant average (20 t/d)
Ore fed: 1,20% Ni, 0,10% Co and 41,2% Fe
Iron metallization: 5,8% Nota: Pilot Test 2 use Nileach process+ aerators

Pilot Test	Leaching Process	Leaching Eficiency (%)		Washing Eficiency (%)		Washing and Leach efficiency (%)		Relative Leaching (g/L)			Relative Leaching time	Extraction increase	
		Ni	Co	Ni	Co	Ni	Co	NH_3	CO_2	CO_2/NH_3		Ni	Co
1	Caron	98,5	66,6	0,9	8,9	99,4	75,5	82,3	59,0	0,72	1,0		
2	NiLeach Process	99,4	81,0	2,3	15,1	101,7	96,1	85,4	62,8	0,73	0,56	2,3	20,6

Table 3. Test run with NiLeach Industrial Reactor.

Test No.	NH_3 Conc. I Stage g/L	Efficiency I Stage, %		Leaching Time (min)	Comments
		Ni	Co		
1	60-63	97,8	104,0	60	Leaching plant productivity 80% of productivity in 1997-99
2	56-58	96,1	70,4	60	
3	53	90,4	72,9	60	

Table 4. Average Results from Nileach Process exploitation.

Date	Process	Leaching Efficiency		Ammonia concentration g/L Stage I	Plant capacity
		Ni	Co		
Oct/96	Caron	89,0	27,0	45-56	80% of aerators capacity in 1997-99
Oct/96	NiLeach +aerators	92,5	49,8	54-56	130% of design
En/97	NiLeach +aerators	94,3	42,9	56-58	130% of design capacity
Average May/98	NiLeach +aerators improved	97,0	54,7´	60-64	

An important result observed in the industrial exploitation of the NiLeach process was the diminish of the leaching process temperature in 6 – 7 ºC (Figure No 7). As a consequence of operating at a lower temperature, the ammoniac loss and the scales in the final liquor coolers diminish. Another indirect effect is that the leaching velocity of cobalt increases while it diminishes in the CARON process and the cobalt loss by co-precipitation is reduced.

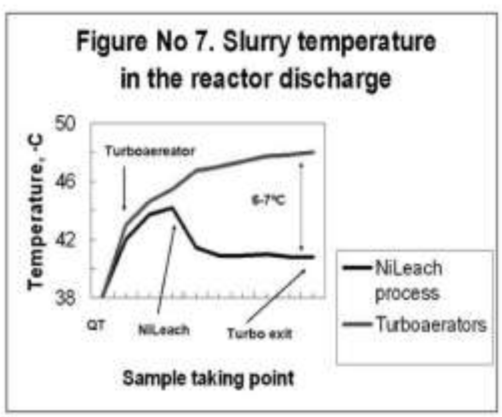
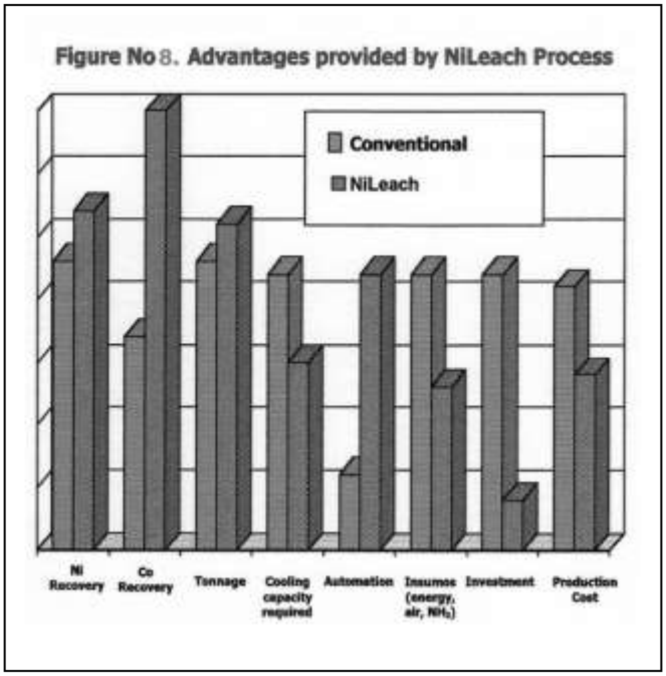
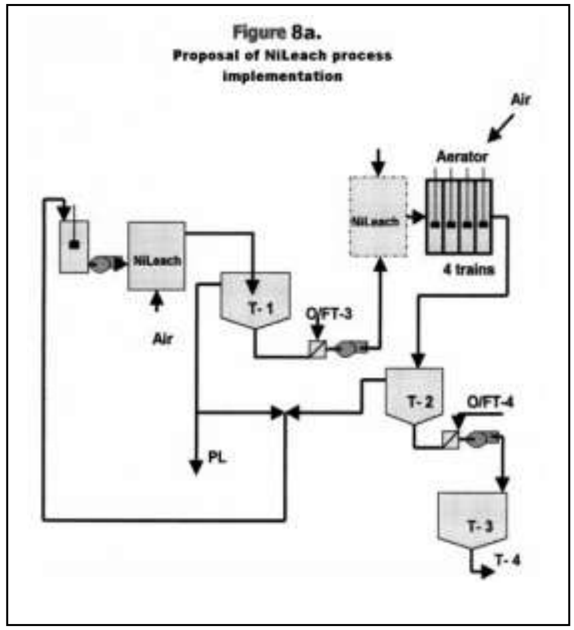


Figure No 7. Slurry temperature in the reactor discharge

The advantages of the use of the NiLeach process and proposal of Nileach process are summarized in Figures No 8 and 8a.





The NiLeach process was scaled up from lab to pilot plant results to industrial scale, after having constructed an industrial NiLeach reactor, which once technically adjusted, was put into operation. NiLeach industrial reactors are 8 at Punta Gorda, in combination with 47 aerators, from a total of 66 in conventional CARON process.

Over the period 1997 – 99, process studies proceeded at both, laboratory and pilot plant scales (Table 2). Results of the laboratory scale investigations were carefully confirmed at industrial plant through a wide range of ammonia concentrations (from 47 – 68 g/L NH_3) and pilot scale with 85 g/L NH_3.

The results agreed with the results reported by NiLeach process at Punta Gorda Plant (Tables 3 and 4).

NiLeach process was operated in combinations with aerators, keeping a leaching time of 60 minutes in the aerators. Cobalt extraction increased by more than 25% when ammonia concentration was increased, while nickel leaching efficiency also registered an increment, but to a lesser extent (7,4 % Ni).

Kinetics studies per equipment have demonstrated that nickel and cobalt precipitation phenomenon is less evident in thickening tank I, more likely by the extraction movement forward the process ahead, an also due to a more complete iron intensive oxidation (Patents 1-5).

CONCLUSIONS

1. Industrial results demonstrated the possibility of using the NiLeach process to increase the efficiency and the productivity of the Caron Process.
2. The industrial indexes confirmed the laboratory and pilot plant researches, because the tubular reactor designed from the bench scale nickel kinetics reported much closer indexes to the plant calculated performance.
3. The tubular reactor is an economical and practical alternative for some hydrometallurgical processes.

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