# Kinetic behaviour of the roasting/selective reduction process with the use of a mixture of bituminous coal and fuel oil as the additive

**Hugo Javier Angulo-Palma[1,2], Manuel Saldana[3,4], Ángel Legrá Legrá[1], Alisa Lamorú Urgellés[1], Carlos Hernández Pedrera[5], Sandra Gallegos[3], Felipe M. Galleguillos Madrid[6] and Norman Toro[3]**

[1]*Centro de Investigaciones del Níquel ``Alberto Fernández Montes de Oca´´ (CEDINIQ), Moa, Holguín, Cuba*
[2]*Departamento de Metalurgia Química, Universidad de Moa, Holguín, Cuba*
[3]*Faculty of Engineering and Architecture, Universidad Arturo Prat, Iquique, Chile*
[4]*Departamento de Ingeniería Química y Procesos de Minerales, Universidad de Antofagasta, Antofagasta, Chile*
[5]*Facultad de Ingeniería Química y Agronomía, Universidad de Oriente, Santiago de Cuba, Cuba*
[6]*Centro de Desarrollo Energético Antofagasta, Universidad de Antofagasta, Antofagasta, Chile*

TECHNICAL PAPER

**UDC: 622.782:622.348.1**

*Hem. Ind.* **79(2)** 69-77 (2025)

*Abstract*

Lateritic ore is currently the main raw material that allows extraction of Ni by the Caron process. To date, the kinetic behaviour of the roasting/selective reduction process of lateritic nickeliferous ores on a pilot scale is largely unknown. In the present study, the kinetic behaviour, the controlling stage and the mechanisms that describe this process with the use of a mixture of 2 wt.% bituminous coal and 1.25 wt.% fuel oil as a reducing additive were determined during the evaluation of the high and low thermal profiles, respectively. The phases of the reduced/leached minerals and the fed ore were analysed by X-ray powder diffraction. It was observed that the mixture used as a reducing additive guarantees an adequate transformation in both thermal profiles; the relationship between the residual Ni and residence time is described by a first-order reaction with the determination coefficients greater than 0.949. Although the influence of post-combustion air is not analysed, the controlling stage was diffusion through the ash layer with an activation energy of 14.4060 kJ mol$^{-1}$. Thus, the most precise combination to describe the process is diffusion through the ash layer and the growth of the nuclei.

*Keywords:* Reaction kinetics and mechanisms; furnace operation; pyrometallurgy; lateritic nickeliferous ore; Caron process.

*Available on-line at the Journal web address:* http://www.ache.org.rs/HI/

## 1. INTRODUCTION

Nickel is considered a strategic and critical chemical element used in the production of nickel-cadmium and nickel-metal hydride batteries, as well as in the production of special steels and aerospace alloys [1]. With the explosion in the production of electric vehicles, the global demand for this metal is forecast to increase around 10 times from 2018 to 2025 [2]. Main reserves of this metal are found in sulphide and lateritic ores. As the supply of Ni sulphide ores gradually depletes, its extraction from laterite ores generates significant attention [3]. Laterites contain 72.2 % of the world's Ni reserves, with an increase in annual production from 2004 to the present from 42 to 69 % [4]. These deposits are produced by prolonged and deep weathering of Ni-silica-bearing ultramafic rocks, generally in humid tropical or subtropical climates, where the minerals will be classified into hydrated silicates, clay silicates and oxide deposits. One of the main technologies that is capable of extracting Ni from lateritic ores is the Caron process [5]. This technology combines pyrometallurgical and hydrometallurgical processes [6], and is based on leaching of previously reduced lateritic minerals with solutions of ammonium-ammoniacal carbonate ($(NH_4)_2CO_3$), reduction being one of the stages that most influences the extractions [7-9] and final costs [10,11].

Reduction of lateritic ore is carried out in Herreschoff multiple hearth furnaces. The furnaces are oil-fired and are operated at air deficiency to produce the required ratio of carbon monoxide to carbon dioxide in each hearth. Temperatures in the reduction zone are maintained at 700 to 800 °C [12].

---

Corresponding author: Norman Toro, Faculty of Engineering and Architecture, Antofagasta, Chile
E-mail: notoro@unap.cl
Paper received: 18 September 2024; Paper accepted: 20 March 2025; Paper published: 7 May 2025.
https://doi.org/10.2298/HEMIND240918005A

In general, different investigations recognize that the characteristics of the lateritic ore [13-15], the furnace operation [16-20] and the use of reducing additives [7,21-24] constitute the most important variables to control during the roasting/selective reduction process.

In previous research studies [25,26], specifically the ones focusing on the use of reducing additives in multiple hearth furnaces, it has been shown that the use of the mixture of bituminous coal and fuel oil at the concentrations of 2.0 wt.% and 1.25 wt.%, respectively (denoted here as BC2.0-FO1.25) benefits the process technically and economically.

Since the introduction of the reducing additive BC2.0-FO1.25 on commercial scales currently constitutes one of the main technological modifications that can benefit the Caron process, it is necessary to determine the kinetics and the controlling mechanism during the selective roasting/reduction of NiO, which is also justification of the present study.

## 2. METHODOLOGY

In this research, the main kinetic parameters and the controlling mechanism of the selective roasting/reduction process of NiO are determined with the use of the reducing additive of bituminous coal at 2.0 % by weight and fuel oil at 1.25 wt.% (denoted here as BC2-FO1.25) on a pilot scale. For this purpose, the installation that simulates the Caron process was used in the Centro de Investigaciones del Niquel: Alberto Fernández Montes de Oca, Moa, Cuba (CEDINIQ) [16,26]. The reduction process was carried out in a multi-hearth furnace (Fig. 1) composed of 17 hearths, listed from top to the bottom from hearth 0 (H-0) to 16 (H-16), enclosed in a metal cylinder 11 m high and 2.51 m in diameter, coated internally by a refractory material; the post-combustion air being fed by the furnace hearths 4 (H-4) and 6 (H-6). The residence time in the furnace is 80 min, considering the initial and final time at the exit of hearths 0 and 16, respectively.

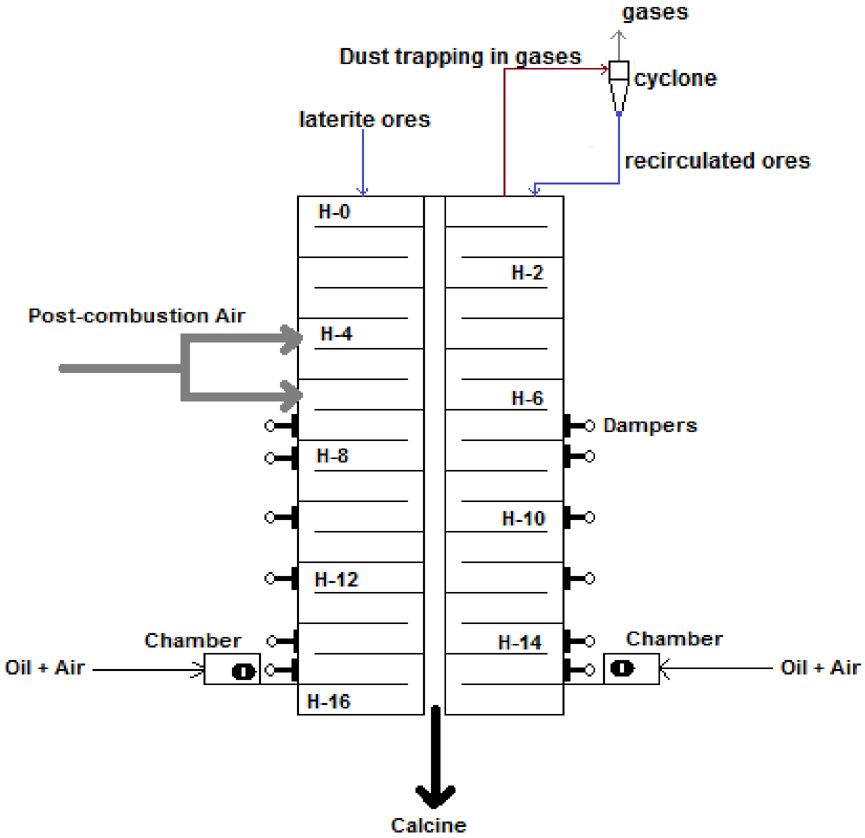

***Figure 1.*** *Pilot plant scale reduction furnace; letter H designate hearth [26]*

The study was based on evaluating the conversion of NiO by analysing the kinetic data by the integral method, through the selection of kinetic equations with the objective of identifying the best fit of the experimental data, considering that the effect of reoxidation is insignificant. To confirm the controlling mechanism in the roasting/reduction processes, the value of the activation energy was used as a criterion, based on the development of the Arrhenius equation:

$$E_A = \frac{\log\left(\frac{k_{T_2}}{k_{T_1}}\right)\frac{R}{0.434152}\left(\frac{T_2T_1}{T_2\text{-}T_1}\right)}{1000} \tag{1}$$

where:

$T_1$ is the final temperature of the mineral reduced by the low thermal profile (LTP), K

$T_2$ is the final temperature of the mineral reduced by the high thermal profile (HTP), K

$k_{T_1}$ is the reaction rate constant corresponding to the low thermal profile, $\text{min}^{-1}$

$k_{T_2}$ is the reaction rate constant corresponding to the high thermal profile, $\text{min}^{-1}$

$R$ is the universal gas constant, 8.314 J $\text{mol}^{-1}$ $\text{K}^{-1}$

$E_A$ $E_A$ is the activation energy of the reduction process, kJ $\text{mol}^{-1}$

Thermal profiles shown in Figure 2 were used in the investigation. The high and low thermal profiles were used to facilitate the weakening of the crystalline structure by gradual heating in the temperature ranges that are used in commercial scales [10,12,16,26]. Temperature measurements within different hearths were carried out by using type K thermocouples (Taizhou Best Electric Equipment Co., Ltd., China). Experiments were repeated 3 times for each thermal profile.

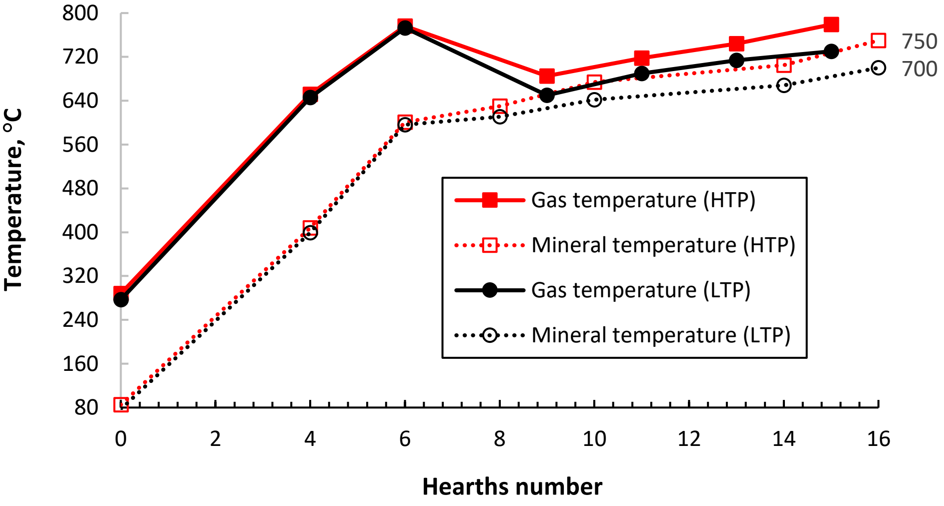

***Figure 2.*** *Temperature profiles in the reduction furnace*

### 2. 1. Physical chemistry characteristics of the fed lateritic ore

Lateritic ore with a degree of homogenization greater than 90 % was fed to the furnace at a rate of 750 kg $\text{h}^{-1}$, after being dried and ground until the moisture content was less than 4 mass. % and the size distribution of particle less than 75 μm was from 84 to 88 %. Table 1 shows the main average (avg) characteristics of the mineral showing insignificant differences between the processed samples during the evaluation of the two thermal profiles in terms of the contents of Ni, Co, Fe, MgO, $SiO_2$, $Al_2O_3$, $H_2O$, C and S. The average component content (avg) of lateritic mineral in both LTP and HTP was similar with standard deviation ($\sigma$) values less than 1.56 and particle size distribution of the ore suitable for processing by the Caron process.

***Table 1.*** *Characteristics of the lateritic mineral with the two thermal profiles evaluated in the reduction process.*

| Thermal profile | | Content, wt.% | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Component | | | | | | | | | Particle size, μm | | | |
| | | Ni | Co | Fe | MgO | $SiO_2$ | $Al_2O_3$ | $H_2O$ | S | C | 150 | 75 | 45 | <45 |
| LTP | avg | 1.165 | 0.098 | 38.921 | 3.153 | 7.696 | 7.916 | 3.225 | 0.255 | 2.081 | 3.844 | 10.078 | 6.598 | 79.481 |
| | $\sigma$ | 0.014 | 0.005 | 0.873 | 0.168 | 0.367 | 0.357 | 0.420 | 0.016 | 0.010 | 0.694 | 1.552 | 1.365 | 0.918 |
| HTP | avg | 1.167 | 0.099 | 39.323 | 2.828 | 7.788 | 8.080 | 3.660 | 0.251 | 2.088 | 3.425 | 9.783 | 7.392 | 79.400 |
| | $\sigma$ | 0.013 | 0.001 | 0.416 | 0.513 | 0.249 | 0.228 | 0.190 | 0.018 | 0.032 | 0.698 | 0.585 | 1.133 | 1.500 |

### 2. 2. Chemical analysis and mineralogical characteristics of the reduced/leached samples

The reduced ore samples were taken from the even hearths of the furnace using the procedure proposed previously [16,18]. Each sample was then leached with the ammonium carbonate solution at a concentration of $NH_3$ from 80 to 85 g $dm^{-3}$ and $CO_2$ from 40 to 42 g $dm^{-3}$ for 2 h at a liquid/solid mass ratio (L/S) of 10/1.

The individual elements of interest in the leached mineral were determined by atomic absorption spectrometry (AAS, model SOLAR 929, Solar System ATI, Unicam Analytical Technology Inc., Cambridge, UK).

The crystalline structure and composition of the reduced/leached minerals were analysed by powder X-ray diffraction (XRD) by a PANalytical X'PERT3 diffractometer (Malvern Panalytical, UK) with Gonio type sweep in $2\theta$ angular registration from 4.0042° to 79.9962°, with step distance of 0.0080° with Cu radiation and nickel filter, potential difference of 40 kV, current of 30 mA and a calibration checked by an external silicon standard scanning. Fractions of nickel, iron, and cobalt reduced to the metallic state of the ore in H16 were determined by leaching the reacted samples with a bromine-ethanol solution [27] followed by AAS analysis with flame and generator hydride (model SOLAR 929, Solar System ATI, Unicam Analytical Technology Inc., Cambridge, UK).

### 2. 3. Determination of the controlling mechanism in the roasting/reduction process

The controlling mechanism of the roasting/reduction process was determined by evaluating the equations of the unreacted core model reported by Levenvspiel [28] and the nucleation models reported by Bo *et al.* [29], typical of heterogeneous solid-fluid reactions. Table 2 shows the equations used.

*Table 2. Controlling mechanisms analysed*

| Model type | Controlling mechanism | Equation |
|---|---|---|
| Unreacted core | Diffusion through the gas film (DGF) | $x_{Ni}=k_{DGF}t$ |
| | Diffusion through the ash layer (DAL) | $1\text{-}3(1\text{-}x_{Ni})^{2/3}+2(1\text{-}x_{Ni})=k_{DAL}t$ |
| | Chemical reaction (ChR) | $1\text{-}(1\text{-}x_{Ni})^{1/3}=k_{ChR}t$ |
| Nucleation | 2-D growth of nuclei (GN-2) | $\left[-\ln(1\text{-}x_{Ni})\right]^{1/2}=k_{GN\text{-}2}t$ |
| | 3-D growth of nuclei (GN-3) | $\left[-\ln(1\text{-}x_{Ni})\right]^{1/3}=k_{GN\text{-}3}t$ |
| | 5-D growth of nuclei (GN-5) | $\left[-\ln(1\text{-}x_{Ni})\right]^{1/5}=k_{GN\text{-}5}t$ |

In Table 2 $x_{Ni}$ is the conversion ratio of Ni (degree of reduction) and $t$ is the time, while $k_{DGF}$, $k_{DAL}$, $k_{ChR}$, $k_{GN\text{-}2}$, $k_{GN\text{-}3}$ and $k_{GN\text{-}5}$ are the rate constants for each proposed mechanism.

## 3. RESULTS AND DISCUSSIONS

### 3. 1. Effect of the thermal profile with the use of the BC2-FO1.25 additive

Figure 3 shows the XRD patterns of the fed and reduced/leached lateritic ore samples corresponding to each thermal profile analysed.

It is observed that iron oxides and oxihydroxides (goethite, maghemite and hematite) as well as aluminium hydroxide (gibbsite) predominated in the lateritic ore fed. The secondary phases grouped the contents of silicon and magnesium, identifying the phases of hydrated magnesium silicate (lizardite), aluminium and magnesium oxide (spinel) and some silicon oxide (quartz).

The main mineralogical phases identified in the reduced/leached mineral, regardless of the thermal profile evaluated, were iron oxides (magnetite and maghemite, syn), magnesium iron aluminium chromium oxide (magnesiochromite, ferroan) and magnesium iron silicate (fayalite). These identified phases coincide with those reported by different studies [26,30] and indicate that during the evaluation of both thermal profiles an adequate roasting reduction process is achieved.

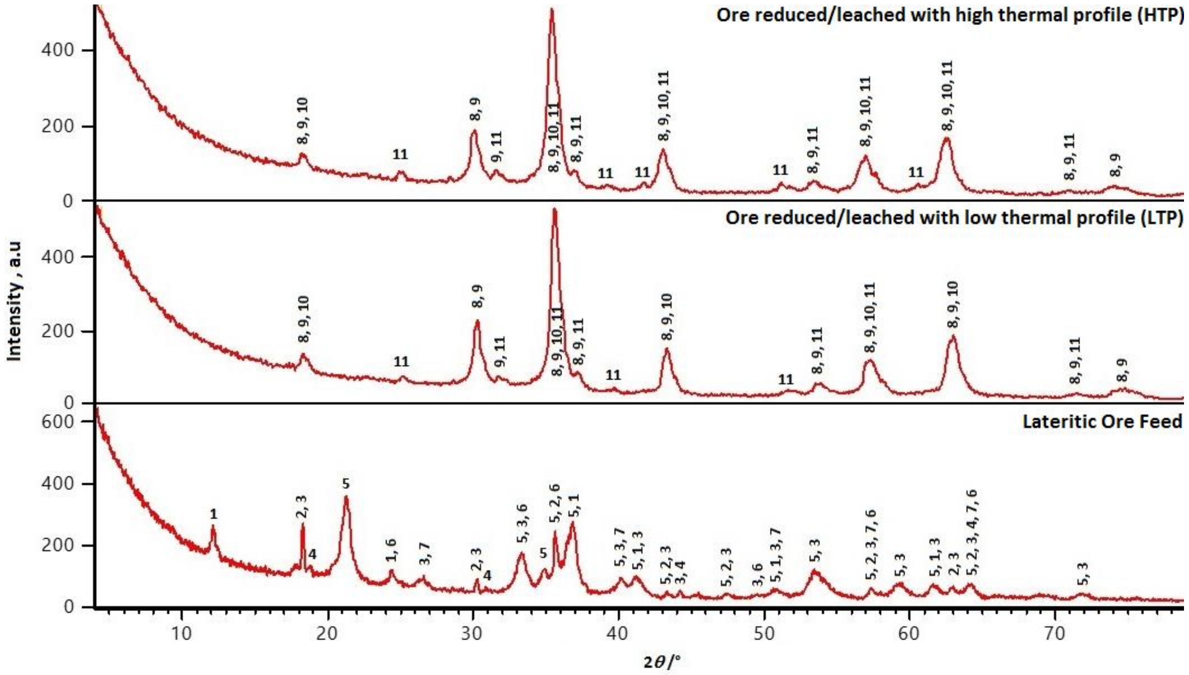

*__Figure 3.__ XRD patterns of reduced/leached lateritic mineral samples with the use of BC2-FO1.25 additive and two thermal profiles. 1 - lizardite: $Mg_3Si_2O_5(OH)_4$; 2 - maghemite: $Fe_{21.16}O_{31.92}$; 3 - gibbsite: $Al(OH)_3$; 4 - spinel: $MgAl_2O_4$; 5 - goethite: FeOOH; 6 - hematite: $Fe_2O_3$; 7 - quartz: $SiO_2$; 8 - magnetite, syn: $Fe_3O_4$; 9 - maghemite, syn: $Fe_2O_3$; 10 - magnesiochromite, ferroan: $[(Mg, Fe)(Cr, Al)_2O_4]$ and 11 - fayalite: $Mg_{26}Fe_{1,74}(SiO_4)$.*

Formation of fayalite and magnesiumchromite, ferroane in the reduced and leached mineral (Fig. 3), justify the presence of non-leachable Ni contents in the process. These results agree with those obtained by Rhamdhani *et al.* [31-33], when identifying that the mineralogical phases of olivine and ferro-chromite spinels are not leached by the carbonate-ammonia technology. The presence of fayalite in both thermal profiles confirms that the reduced mineral reaches temperatures greater than and equal to 700 °C and that the use of the additive BC2-FO1.25 allows an adequate transformation of the serpentinitic phases. This finding coincides with the results of Valix & Cheung [34,35] during the evaluation of S as a reducing additive in the Caron process in the temperature range of 600 to 800 °C.

Although both thermal profiles present similarity, the shape of the peaks in the high thermal profile (HTP) became sharper, indicating an increase in the crystalline nature of the roasted product.

### 3. 2. Activation energy corresponding to the roasting/reduction process with the use of the additive BC2-FO1.25

Figure 4 relates the average $Ni_{residual}$ (residual Ni mass percentage after the reduction/leaching process) in the pilot Herreshoff furnace as a function of time, for the two thermal profiles evaluated. All data are presented in Supplementary Material S1 and S2. The decrease in the percentage of residual Ni as the residence time increases for both thermal profiles is observed as a trend, a regularity typical of an adequate reduction process in which the effects of reoxidation of the reduced mineral are minimized.

The behaviour presented by the high and low thermal profile curves indicates that the kinetic process of the general transformation of NiO into $Ni^o$ adjusts to a first-order reaction with a coefficient of determination greater than 0.9490; this behaviour coincides with that reported by Shoubao [36] and Castellanos [37] during the evaluation of the roasting/reduction process of nickel-bearing lateritic ores. The average feed Ni percentage ranged from 1.1550 to 1.1780 wt.%, which corresponds to the chemical characteristics of the lateritic ore used in the study, see Table 1.

The average reaction rate constant at the low thermal profile ($k_{T1}$) was 0.0176 $min^{-1}$, which is for about 8.3 % lower than that achieved when using the high temperature profile (Figure 4); aspect that confirms compliance with the Arrhenius equation. Substitution of the values of the reaction rate constant and the final temperature of the reduced mineral in Equation (1) allows obtaining an activation energy of 14.4060 kJ $mol^{-1}$ when using the additive BC2-FO1.25 in the process of roasting/reduction (Table 3).

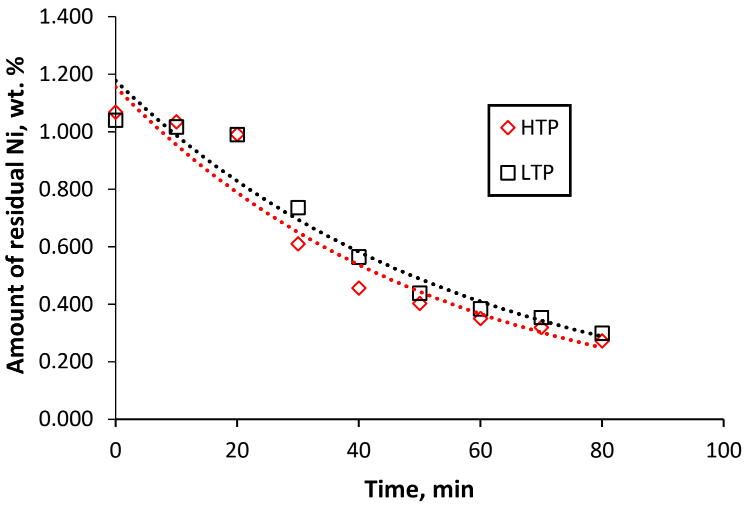

***Figure 4.*** *NiO reduction kinetics on a pilot scale at two temperature profiles and with the use of the BC2-FO1.25 additive*

***Table 3.*** *Activation energy and reaction rate constants with the reducing additive BC2-FO1.25*

| Thermal profile | | | | |
|---|---|---|---|---|
| Low | | High | | $E_A$ / kJ mol$^{-1}$ |
| $k_{T_1}$ / min$^{-1}$ | $T_1$/ °C | $k_{T_2}$ / min$^{-1}$ | $T_2$ / °C | |
| 0.0176 | 700 | 0.0192 | 750 | 14.4060 |

The value of the activation energy with the BC2-FO1.25 additive corresponds to those reported, at laboratory scale during the evaluation of the reduction process in the temperature range of 675 to 800 °C, by Castellanos [37] (17.1544 kJ mol$^{-1}$ for laterites from the Nicaro region with the fuel oil additive at 2.5 wt.%) and Ilyas [21] (13.80 kJ mol$^{-1}$ for laterites from Bajaur, Pakistan with a mixture of 10 wt.% of coal and 9 wt.% of $Na_2SO_4$).

### 3. 3. Determination of the controlling stage of the roasting/reduction process with the use of the additive BC2-FO1.25

Table 4 shows the results of determination of the controlling stage in the roasting/reduction process for the high and low thermal profiles, when considering the unreacted nucleus models for particles of constant size and growth of nuclei.

***Table 4.*** *Predicted times for reaction completion according to different controlling mechanisms shown in Table 2*

| Thermal profile | Complete reaction time, min | | | | | |
|---|---|---|---|---|---|---|
| | Chemical reaction | Diffusion | | Growth of nuclei | | |
| | | Through the gas film | Through the ash layer | GN-2 | GN-3 | GN-5 |
| High | 203 | 98 | 277 | 59 | 59 | 59 |
| Low | 230 | 103 | 336 | 64 | 62 | 61 |

The analysis of the complete reaction times allows us to identify that the controlling stage of the process is diffusion through the ash layer (DAL), with times necessary to complete the reaction of 277 and 336 min for the high and low thermal profiles, respectively. The controlling stage in the process was directly related to the activation energy value obtained in this study (value less than 17 kJ mol$^{-1}$, Table 3) and to the mechanism reported during the roasting/reduction of lateritic ores in different investigations [14,21,36-38].

To identify the mechanism that best describes the lateritic ore roasting/reduction process with the use of the additive BC2-FO1.25 and the high and low thermal profiles, possible combinations between the ChR, DGF, DAL and GN models were evaluated. To identify the mechanism that best describes the lateritic ore roasting/reduction process with the use of the additive BC2-FO1.25 and the high and low thermal profiles, possible combinations between the ChR, DGF, DAL and GN models were evaluated, according to the procedure described by Levenspiel [28]. The mechanism that best describes the roasting/reduction process in the low thermal profile (LTP) is the combination of the diffusion model through the ash layer (DAL) and growth of the nuclei (GN-5) with a coefficient of determination of 0.9838. In the case of the high thermal profile (HTP), it is observed that the most accurate combination to describe the process is diffusion through the ash layer (DAL) and the growth of nuclei (GN-3) with a correlation of 0.9623. (See Figure 5). These results are logical and justified because the increase in temperature causes an increase in the work per gram-molecule necessary to form a growth nucleus.

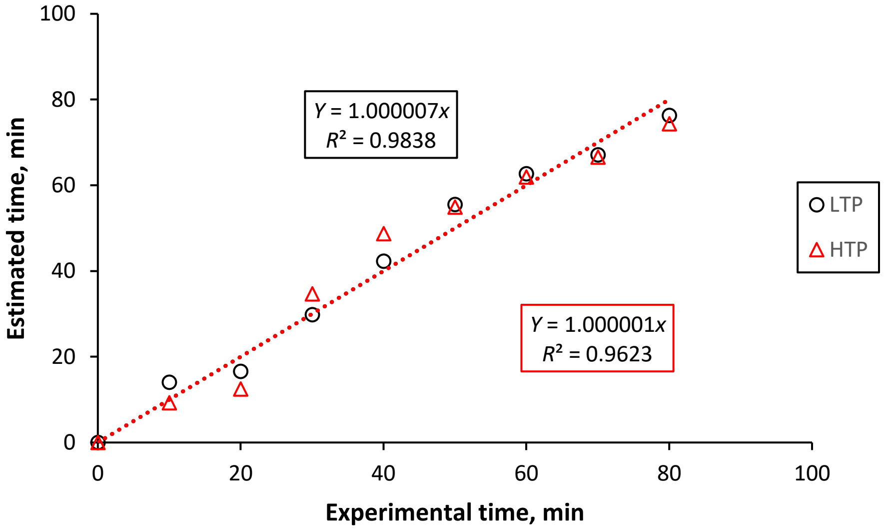

***Figure 5.*** *Combinations of mechanisms (DAL and GN) to describe the roasting/reduction process of lateritic ore with the use of the additive BC2-FO1.25*

## 4. CONCLUSIONS

The BC2-FO1.25 additive can guarantee adequate mineralogical transformations in the roasting/reduction process of lateritic ores with a predominance of iron oxides-oxihydroxides at the use of high and low thermal profiles. The results of this study suggest that the relationship between the average $\mathrm{Ni}_{\mathrm{residual}}$ percentage after the reduction/leaching process and residence time is described by a first-order reaction with determination coefficients greater than 0.9490. The pilot-scale kinetic behaviours for both thermal profiles evaluated indicate that the controlling mechanism is diffusion through the ash layer, with complete reaction times that ranged from 276 to 336 min and an activation energy of 14.4060 kJ mol$^{-1}$.

## Supplementary material

Additional data are available electronically at https://www.ache-pub.org.rs/index.php/HemInd/article/view/1385 or from the corresponding author on request.

***Declaration of interest statement:*** The authors declare they have no conflict of interest.

***Acknowledgement:*** Manuel Saldana acknowledges the infrastructure and support from Doctorado en Ingeniería de Procesos de Minerales at the Universidad de Antofagasta.

## REFERENCES

[1] Bartzas G, Tsakiridis PE, Komnitsas K. Nickel industry: Heavy metal(loid)s contamination - sources, environmental impacts and recent advances on waste valorization. *Curr Opin Environ Sci Heal.* 2021; 21: 100253. https://doi.org/10.1016/j.coesh.2021.100253

[2] Mitterecker J, Košević M, Stopic S, Friedrich B, Panić V, Stevanović J, Mihailović M. Electrochemical Investigation of Lateritic Ore Leaching Solutions for Ni and Co Ions Extraction. *Metals (Basel).* 2022; 12(2): 325 https://doi.org/10.3390/met12020325

[3] Hu X, Ma B, He F, Chen Y, Wang C. Mineralogical characterization of low-grade nickel laterites from the North Oman Mountains: Using mineral liberation analyses - scanning electron microscopy-based automated quantitative mineralogy. *Ore Geol Rev.* 2020; 120: 103429. https://doi.org/10.1016/j.oregeorev.2020.103429

[4] Zevgolis EN, Daskalakis KA. The Nickel Production Methods from Laterites and the Greek Ferronickel Production among Them.

*Mater Proc.* 2021; *5*(1): 104. https://doi.org/10.3390/materproc2021005104.

[5] Pintowantoro S, Widyartha AB, Setiyorini Y, Abdul F. Sodium Thiosulfate and Natural Sulfur: Novel Potential Additives for Selective Reduction of Limonitic Laterite Ore. *J Sustain Metall* .2021; 7(2): 481-494. doi: 10.1007/s40831-021-00352-4.

[6] Moats MS, Davenport WG: Chapter 2.3 Nickel and Cobalt, In *Treatise on Process Metallurgy*. 2nd ed. Elsevier; 2024: 575-604. https://doi.org/10.1016/B978-0-323-85373-6.00030-2.

[7] Caron MH. Fundamental and practical factors in ammonia leaching of nickel and cobalt ores. *JOM.* 1950; *2*(1): 67-90. https://doi.org/10.1007/BF03398981.

[8] Caron MH. “Separation of Nickel and Cobalt” *JOM.* 1950; 2(1): 91-103. https://doi.org/10.1007/BF03398982.

[9] Kießling F, Stopic S, Gürmen S, Friedrich B. Recovery of Diamond and Cobalt Powders from Polycrystalline Drawing Die Blanks via Ultrasound Assisted Leaching Process—Part 2: Kinetics and Mechanisms. *Metals (Basel)* 2020; 10(6): 741. https://doi.org/10.3390/met10060741.

[10] Rodriguez R. Reduction in energy cost in Cuban Caron Process Plants. In: *International Laterite Nickel Symposium 2004 (as held during the 2004 TMS Annual Meeting)*. The Minerals, Metals & Materials Society 2004, pp. 657-664. ISBN: 0-87339-550-6.

[11] Caetano GC, Ostroski IC, de Barros MASD. Lateritic Nickel and Cobalt Recovery Routes: Strategic Technologies. *Miner Process Extr Metall Rev.* 2024; 400-414. https://doi.org/10.1080/08827508.2024.2328696.

[12] Canterford Jh. Oxide Ores of Nickel — The Australian Situation. *Miner Process Extr Metall Rev.* 1983; 1(1-2): 85-109. https://doi.org/10.1080/08827508308952590.

[13] Coello-Velázquez AL, Quijano Arteaga V, Menéndez-Aguado JM, Pole FM, Llorente L. Use of the Swebrec Function to Model Particle Size Distribution in an Industrial-Scale Ni-Co Ore Grinding Circuit. *Metals (Basel).* 2019; 9(8): 882. https://doi.org/10.3390/met9080882.

[14] De Graaf JE. The treatment of lateritic nickel ores — a further study of the caron process and other possible improvements. Part I. Effect of reduction conditions. *Hydrometallurgy* 1979; 5(1): 47-65. https://doi.org/10.1016/0304-386X(79)90027-6.

[15] Mano ES., Caner L., Petit S., Chaves AP., Mexias, A. S. Ni-smectitic ore behaviour during the Caron process. *Hydrometallurgy.* 2019; 186: 200-209. https://doi.org/10.1016/j.hydromet.2019.04.010.

[16] Angulo Palma HJ, Legrá AL, Urgellés AL, Gálvez E, Castillo J. Post-combustion Effect on Nickel and Cobalt Extractions from the Caron Process. *In: Bindhu V, Tavares JM, Ţălu Ş, eds.* Proceedings of Fourth International Conference on Inventive Material Science Applications. *Springer, Singapore* 2022; 515-527. https://doi.org/10.1007/978-981-16-4321-7_43.

[17] Ramírez Pérez IM, Ramírez Serrano B. Efecto de la postcombustión sobre los principales índices técnico-económicos en un horno Herreshoff para la producción de níquel. Post-combustion effect on the main technical-economic indices in the Herreshoff furnace for nickel production. *Min Geol.* 2021; 37(4): 426-444. (Spanish).

[18] Angulo Palma HJ, Terencio Guevara PL, Legrá AL, Videaux Arcia L. Análisis especiales en un horno de reducción de níquel a escala de Planta Piloto. Special Analysis in a Nickel Reduction Furnace at Pilot Plant scale. *RTQ.* 2017; 37(3): 484-499. (Spanish).

[19] Pickles CA, Anthony W. A Thermodynamic Study of the Reduction of a Limonitic Laterite Ore by Methane. *High Temp Mater Proc.* 2018; 37(9-10): 909-919. https://doi.org/10.1515/htmp-2017-0106.

[20] Pickles CA, Anthony W. Thermodynamic modelling of the reduction of a saprolitic laterite ore by methane. *Miner Eng.* 2018; 120: 47-59. https://doi.org/10.1016/j.mineng.2018.02.006.

[21] Ilyas S, Kim H, Srivastava RR. Carbothermic Reduction Roasting of a Low-Grade Nickel Laterite Ore in the Modified Caron Process. *In: C. Anderson et al., eds*. The 5th International Symposium on Nickel and Cobalt. Switzerland: Springer Nature; 2021: 317-328. https://doi.org/10.1007/978-3-030-65647-8_27.

[22] Ilyas S, Srivastava RR, Kim H, Ilyas N, Sattar R. Extraction of nickel and cobalt from a laterite ore using the carbothermic reduction roasting-ammoniacal leaching process. *Sep Purif Technol.* 2020; 232: 115971. https://doi.org/10.1016/j.seppur.2019.115971.

[23] Angulo Palma HJ, Legrá AL, Hernández Pedrera C, Lamorú Urgellés A, Vega Cala RJ. Efecto de la sustitución del petróleo aditivo por carbón bituminoso en el proceso de reducción de lateritas. Effect Substit Addit Oil with Bitum Coal Process Reducing Laterites. *RTQ.* 2018; 38: 750-764. (Spanish).

[24] De Alvarenga Oliveira V, dos Santos CG, de Albuquerque Brocchi E. Assessing the Influence of NaCl on the Reduction of a Siliceous Laterite Nickel Ore Under Caron Process Conditions. *Metall Mater Trans B.* 2019; 50(3): 1309-1321. https://doi.org/https://doi.org/10.1007/s11663-019-01552-w.

[25] Angulo Palma HJ, Legrá AL, Hernández Pdrera C, Lamorú Urgellés A, Toro Villarroel N. Reducción de menas lateríticas utilizando como aditivo mezclas de carbón bituminoso y petróleo. Reduction of lateritic minerals using additive mixtures of bituminous coal and oil. *RTQ.* 2020; 40: 93-105. (Spanish).

[26] Angulo Palma HJ., Legrá AL., Lamorú Urgellés A., Hernández Pedrera C., Gallegos S., Galleguillos Madrid FM., Toro Villarroel, N. Use of a mixture of coal and oil as an additive for selective reduction of lateritic ore by the Caron process: *Hem Ind.* 2024; 78: 17-27. https://doi.org/10.2298/HEMIND230118017A.

[27] Sant B. Chemical reaction engineering. *Talanta.* 1968; 15(12): 1483-1486. https://doi.org/10.1016/0039-9140(68)80211-5.

[28] Levenspiel O. Chemical Reaction Engineering. 3rd ed., New York, NY: John Wiley & Sons; 1999. ISBN 0-471-25424-X.

[29] Li B., Ding Z., Wei Y., Wang H., Yang Y., Barati M. Kinetics of reduction of low-grade nickel laterite ore using carbon monoxide. *Metall Mater Trans B.* 2018; 49: 3067-3073. https://doi.org/10.1007/s11663-018-1367-8.

[30] Cabrera G, Gómez JM, Hernández I, Coto O, Cantero D. Different strategies for recovering metals from CARON process residue. *J Hazard Mater.* 2011; 189(3): 836-42. https://doi.org/10.1016/j.jhazmat.2011.03.048.

[31] Rhamdhani MA, Chen J., Hidayat T, Jak E., Hayes P. Advances in research on nickel production through the Caron process. In: Harre J, ed. Proceedings of European Metallurgical Conference 2009. Germany: GDMB; 2009: 899-914. ISBN 978-3-940276-19-3.

[32] Rhamdhani MA, Hayes PC, Jak E. Nickel laterite Part 1-microstructure and phase characterisations during reduction roasting and leaching. *Miner Process Extr.* 2009; 118: 129-145. https://doi.org/10.1179/174328509X431391.

[33] Rhamdhani MA, Hayes PC, Jak E. Nickel laterite Part 2-thermodynamic analysis of phase transformations occurring during reduction roasting. *Miner Process Extr*. 2009; 118: 146-155. https://doi.org/10.1179/174328509X431409.

[34] Valix M, Cheung W. Effect of sulfur on the mineral phases of laterite ores at high temperature reduction. *Miner Eng.* 2002; 15(7): 523-530. https://doi.org/10.1016/S0892-6875(02)00069-9.

[35] Valix M, Cheung WH. Study of phase transformation of laterite ores at high temperature. *Miner Eng.* 2002; 15(8): 607-612. https://doi.org/10.1016/S0892-6875(02)00068-7.

[36] Shoubao L, Eng B, Eng M. Study of nickeliferrous laterite reduction. A Thesis Submitted to the School of Graduate Studies in Partial Fulfilment of the Requirements for the Degree of Master Engineering, University of Science and Technology, Beijing; 1999.https://translate.google.com/?sl=en&tl=es&text=Study%20of%20nickeliferrous%20laterite%20reduction&op=translate.

[37] Castellanos Suárez J. Cinética de la reducción de los minerales oxidados de níquel en Cuba. Kinetics of the reduction of oxidized nickel minerals in Cuba. *Min Geol.* 1984; *2*: 197-222. (Spanish).

[38] Shofi A, Supriyatna Y, Prasetyo AB. Selective Reduction of Southeast Sulawesi Nickel Laterite using Palm Kernel Shell Charcoal: Kinetic Studies with Addition of Na2SO4 and NaCl as Additives. *Bull Chem React Eng Catal.* 2020; *15*(2), 501-513. https://doi.org/10.9767/bcrec.15.2.7733.501-513.

# Kinetika procesa pečenja/selektivne redukcije uz upotrebu mešavine bitumenskog uglja i lož ulja kao aditiva

**Hugo Javier Angulo-Palma[1,2], Manuel Saldana[3,4], Ángel Legrá Legrá[1], Alisa Lamorú Urgellés[1], Carlos Hernández Pedrera[5], Sandra Gallegos[3], Felipe M. Galleguillos Madrid[6] and Norman Toro[3]**

[1]*Centro de Investigaciones del Níquel ``Alberto Fernández Montes de Oca´´ (CEDINIQ), Moa, Holguín, Cuba*
[2]*Departamento de Metalurgia Química, Universidad de Moa, Holguín, Cuba*
[3]*Faculty of Engineering and Architecture, Universidad Arturo Prat, Iquique, Chile*
[4]*Departamento de Ingeniería Química y Procesos de Minerales, Universidad de Antofagasta, Antofagasta, Chile*
[5]*Facultad de Ingeniería Química y Agronomía, Universidad de Oriente, Santiago de Cuba, Cuba*
[6]*Centro de Desarrollo Energético Antofagasta, Universidad de Antofagasta, Antofagasta, Chile*

(Stručni rad)

*Izvod*

Lateritna ruda je trenutno glavna sirovina koja omogućava ekstrakciju nikla Caron procesom. Do danas, kinetičko ponašanje procesa pečenja/selektivne redukcije lateritnih ruda nikla u pilot postrojenju je nedovoljno istraženo. U ovoj studiji, kinetičko ponašanje, faza koja kontroliše i mehanizmi koji opisuju ovaj proces primenom mešavine 2,00 mas.% bitumenskog uglja i 1,25 mas.% mazuta kao redukcionog aditiva određivani su tokom evaluacije visokog i niskog toplotnog profila. Faze redukovanih/izluženih minerala i polazne rude analizirane su rendgenskom difrakcijom praha. Pokazano je da smeša koja se koristi kao redukcioni aditiv garantuje adekvatnu transformaciju u oba termička profila; odnos između zaostalog nikla i vremena zadržavanja je opisan reakcijom prvog reda sa koeficijentima determinacije većim od 0,949. Iako nije analiziran uticaj vazduha posle sagorevanja, faza koja kontroliše proces je bila difuzija kroz sloj pepela sa energijom aktivacije od 14,4060 kJ $mol^{-1}$. Dakle, najpreciznija kombinacija za opisivanje procesa je difuzija kroz sloj pepela i rast jezgara.

*Ključne reči:* kinetika i mehanizmi reakcije; rad peći; pirometalurgija; lateritna ruda nikla; Caron proces