Use of a mixture of coal and oil as an additive for selective reduction of lateritic ore by the Caron process

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Abstract

Lateritic ores constitute the main source of raw material for extraction of Ni and Co by the Caron process. Consumption of oil in the reduction furnace is one of the key indicators if the metallurgical process is economical. To date it has not been possible to replace the additive fuel oil that is used at commercial scales, therefore, the aim of this study was to partially replace the oil with bituminous coal on a pilot scale by using a mixture of 2 % coal and 1.25 % oil as the reducer additive. Phases of the reduced/leached ores were analyzed by powder X-ray diffraction, while the metallic state of the ore was determined by leaching the reacted samples with a bromine-ethanol solution followed by the atomic absorption spectrometry analysis. Extractions of Ni and Co were confirmed by leaching the reduced ore with ammoniacal-ammonium carbonate solutions. It was observed that the mixture used as a reducer additive can replace the fuel oil since it allows the adequate transformation of the main mineralogical phases of the laterite ore during the reduction process and the average extraction yields of Ni and Co for ~3 and ~8 %, respectively. Although the effect of bituminous coal particle size in the process was not analyzed, the reducing mixture ensured that the Caron process was more efficient.

Keywords: nickel and cobalt recovery, furnaces operation, pyrometallurgy.

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1. INTRODUCTION

Nickel and cobalt are critical elements that are currently in high demand in the production of special steels, aerospace alloys, and lithium-ion batteries for electric vehicles because they improve material properties such as durability, resistance to corrosion, ductility, and thermal and electrical conductivities. Predominant ore types in nature are sulfides and laterites, with a world reserve of the latter close to 60 % [1,2]. Currently, lateritic ores are considered as the main sources of these metals, concentrating Ni in more than 0.7 % by weight [3]. These deposits are produced by prolonged and deep weathering of Ni silica containing ultramafic rocks, usually in humid tropical or subtropical climates. The mineral ores shall be classified as hydrated silicates, clay silicates, and oxide deposits; those are processed by using a variety of processes, including the Caron process. [4-7]

The Caron process is a technology that combines the pyrometallurgical and hydrometallurgical processes, and is based on leaching of previously reduced lateritic ores with ammoniacal-ammonium carbonate solutions ($(NH_4)_2CO_3$) with the reduction being one of the stages that mostly influence the final extractions [8-10]. Also, the use of the Caron process is recommended when the contents of Ni, Fe, and MgO in the lateritic ore exceed 0.9, 25 and 2 %, respectively

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[8,11]. Rodríguez *et al.* [12] recognize that the Caron process, generates high consumption of fuel oil during its operation, and the reduction stage in the production process induces one of the most important costs.

Reduction of lateritic ore is carried out in Herreschoff multiple hearth furnaces. The furnaces are oil-fired and are operated at air deficiency in order to produce the required ratio of carbon monoxide to carbon dioxide in each hearth. Temperatures in the reduction zone are maintained at 750-800 °C [13].

Main reactions involved in roasting/reduction in the Caron process are [11,14]:

$$2FeOOH \rightarrow Fe_2O_3 + H_2O \quad (1)$$

$$3Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2 \quad (2)$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \quad (3)$$

$$FeO + CO \rightarrow Fe + CO_2 \quad (4)$$

$$NiO + CO \rightarrow Ni + CO_2 \quad (5)$$

$$CoO + CO \rightarrow Co + CO_2 \quad (6)$$

$$C + CO_2 \rightarrow 2CO \quad (7)$$

Different studies focused on the reduction of lateritic minerals indicating that the particle size [15], temperature profile, and the composition of the reducing atmosphere are the most important variables in the process [16-19], which is why the use of reducing additives has been one of the most analyzed variables in recent years [20,21]. Some additives used during the reduction in the Caron process are FeS_2 [8], NaCl [8,20], $CaCl_2$ [8], S [21,22], Na_2SO_4 [22] and coal [23-25]. Still, it has not been possible to replace the 2.5% of fuel oil (denoted here as FO-2.5 [11,13,25] implemented at the industrial scale.

Specifically, the use of coal as a substitute for fuel oil in the roasting/reduction in the Caron process has been considered a technological alternative in recent years to reduce operating costs [22-27].

However, it was demonstrated [26] that the use of anthracite coal to replace 20 % of the additive fuel oil is not economically feasible.

Ilias *et al.* [22,27] evaluated coal (fixed carbon and sulfur contents of 58.6 and 7.5 % respectively) from Pakistan in the roasting/reduction of lateritic ores using the Caron process. The optimal reduction condition was found for the mixture of laterite ore with 10 wt.% coal and 9 wt.% of Na_2SO_4, roasted at 800 °C for 120 min. Leaching of the reduced roast product carried out in $NH_{3(ac)}$-$(NH_4)_2CO_3$ solutions (150 g dm^{-3} total NH_3) was influenced by the concentration of carbonate ions and produced >90 % Ni and 67 % Co. The research presented as a difficulty the use of a residence time and the concentration of NH_3 in the first stage of leaching higher than those that have been used on a pilot and industrial scale (residence time in the furnace: 70-80 min [25] and NH_3 concentration in the first leaching stage: 60-100 g dm^{-3} [28].

Angulo *et al.* [23,24,29] analyzed the use of bituminous coal (fixed carbon and sulfur contents of 55.40 and 0.55 %, respectively) to replace the fuel oil. The studies showed that the substitution is technically and economically feasible by using the coal content of less than 4 % in the grinding and roasting/reduction processes. The highest extractions of Ni (> 90 %) and Co (> 68 %) were achieved when using the mixture of coal and fuel oil at 2.0 and 1.25 %, respectively. The residence time in the furnace was of 80 min and the NH_3 concentration used in the leaching was in the range of 80 to 85 g dm^{-3} on a laboratory scale.

Consequently, in the present work, we investigate the reduction-roasting behaviour of the laterite sample of mixtures from different Moa-Cuba deposits when using the same mixture of coal and fuel oil at 2.0 and 1.25 %, denoted here as BC2-FO1.25 as a reducing additive in the Caron process on a pilot scale. The ultimate goal was to investigate the possibility to replace the fuel oil at 2.5 % currently used on commercial scales so to assess whether the Caron process could be carried out more economically and efficiently. Still, it should be noted that the effect of bituminous coal particle size on extractions was not studied.

2. MATERIALS AND METHODS

2. .1 Methodology

In this research, two lateritic ore processing schemes were evaluated in a pilot-scale reduction furnace. The first was the use of the reducing additive conventional fuel oil at 2.5 wt.% (denoted here as FO-2.5), while the second was based on analyzing the effect of the reducing additive mixture of bituminous coal at 2.0 wt.% and fuel oil at 1.25 wt.% (denoted here as BC2-FO1.25) under similar operating conditions. 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) [11]. The reduction process was carried out in a Herreshoff furnace (Fig. 1) composed of 17 hearths, listed from top to 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 study was based on comparing the results when using both reducing additives in the reduction-leaching processes. The evaluation of each reducing additive was carried out during five days of continuous operation. To analyze the effect of the modification 12 daily samples were taken in each experiment, which were averaged to obtain the daily behavior of the variables under study.

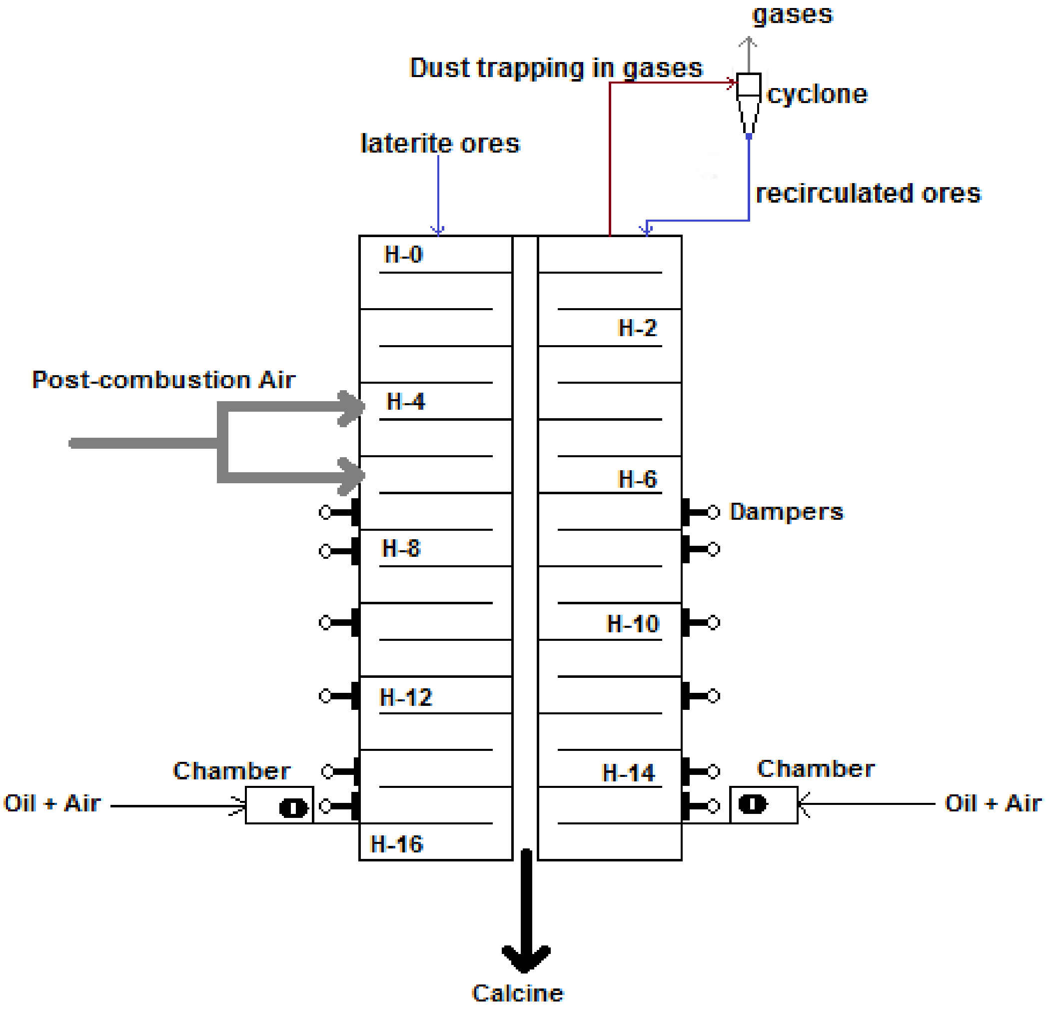

Figure 1. Pilot plant scale reduction furnace; letter H designate hearth [11]

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

Lateritic ore with a degree of homogenization greater than 91 % was fed to the furnace at a rate of 750 kg h^{-1}, after being dried and ground until the moisture content was less than 4 % by weight and the size distribution of particle less than 75 μm it was from 84 to 88 %. Table 1 shows the main average (a) characteristics of the mineral where it is observed that there were insignificant differences between the processed samples used in the two experimental series in terms of the contents of Ni, Co, Fe, MgO, SiO_2, Al_2O_3, H_2O and S. Even so, there was a significant difference in the C content due to the type of additive used. In general, the results presented a low dispersion with standard deviation values lower than 1.8.

Table 1. Characteristics of lateritic ore with the two types of additive fed to the reduction process

Additive		Content, wt%									Particle size, μm			
											150	75	45	< 45
		Ni	Co	Fe	MgO	SiO_2	Al_2O_3	H_2O	S	C	Contribution, %			
FO-2.5	a	1.170	0.099	39.635	2.733	7.769	8.002	3.378	0.231	0.091	3.954	10.428	7.241	78.380
	σ	0.008	0.002	0.555	0.495	0.254	0.460	0.374	0.009	0.009	0.678	1.340	1.234	1.754
BC2-FO1.25	a	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
	σ	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. 3. 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 by previously [11,25] Each sample was then leached with the ammonium carbonate solution with 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 scanning at 2θ angular log from 4.0042 to 79.9962° and a distance step in $2\theta = 0.0080°$, potential difference of 40 kV, current of 30 mA and a calibration checked with an external silicon standard. 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 [30] followed by AAS analysis with flame and generator hydride, (model SOLAR 929, Solar System ATI, Unicam Analytical Technology Inc., Cambridge, UK).

2. 4. Temperature profile and reducing atmosphere in the reduction process

The thermal profile shown in Figure 2 was used in the investigation, regardless of the type of additive under study. Temperature measurements within different hearths were made by using K-type thermocouples (producer, country). To determine the effect of the additives FO-2.5 and BC2-FO1.25 in the reducing atmosphere of the furnace, the CO/CO_2 volumetric ratio was determined in each even hearth by the method used previously [25].

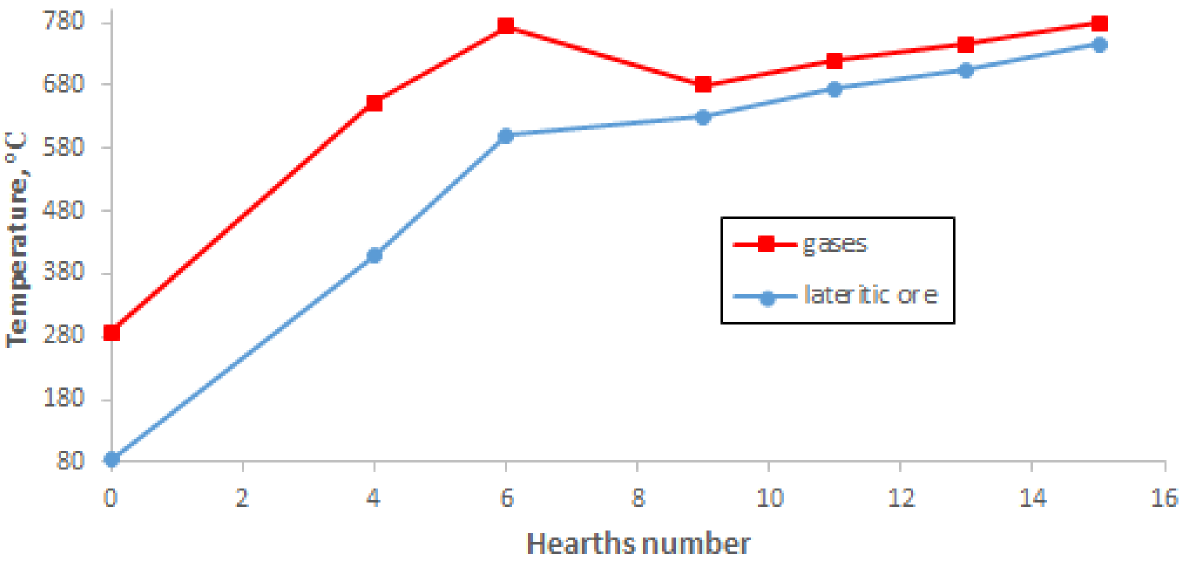

Figure 2. Temperature profile in the reduction furnace

2. 5. Nickel and cobalt extractions

Ni and Co extraction content were determined by the following equation, with an estimate of the error for Ni and Co of ±1.5 and ±2.5 %, respectively:

$$c_{\text{Ext-Met}} = \left(1 - \frac{c_{\text{Met-leached ore}}\ c_{\text{Fe-fed}}}{c_{\text{Met-fed}}\ c_{\text{Fr-leached ore}}}\right)100 \qquad (8)$$

where:

$c_{\text{Ext-Met}}$ is the extracted content of the metal under analysis, Ni or Co;

$c_{\text{Met-leached ore}}$ is the content of the Ni or Co in the ore after leaching

$c_{\text{Met-fed}}$ is the content of Ni or Co in the ore fed to the reduction furnace

$c_{\text{Fe-fed}}$ is the content of iron in the ore fed to the reduction furnace

$c_{\text{Fe-leached ore}}$ is the content of iron in the ore after leaching

3. RESULTS AND DISCUSSIONS

3. 1. Effect of BC2-FO1.25 additive on the mineralogical composition and structure of reduced/leached ore

Figures 3 and 4 show the XRD patterns of the reduced/leached lateritic ore samples corresponding to each even hearth of the reduction furnace.

It is observed that the processed lateritic ore is characterized by the predominance of iron oxides and oxy-hydroxides (goethite, maghemite, and hematite), as well as aluminium hydroxide (gibbsite). Silicon and magnesium contents are mainly expressed in the phase of magnesium silicate hydrate (lizardite), magnesium aluminium oxide (spinel,) and some silicon oxide (quartz).

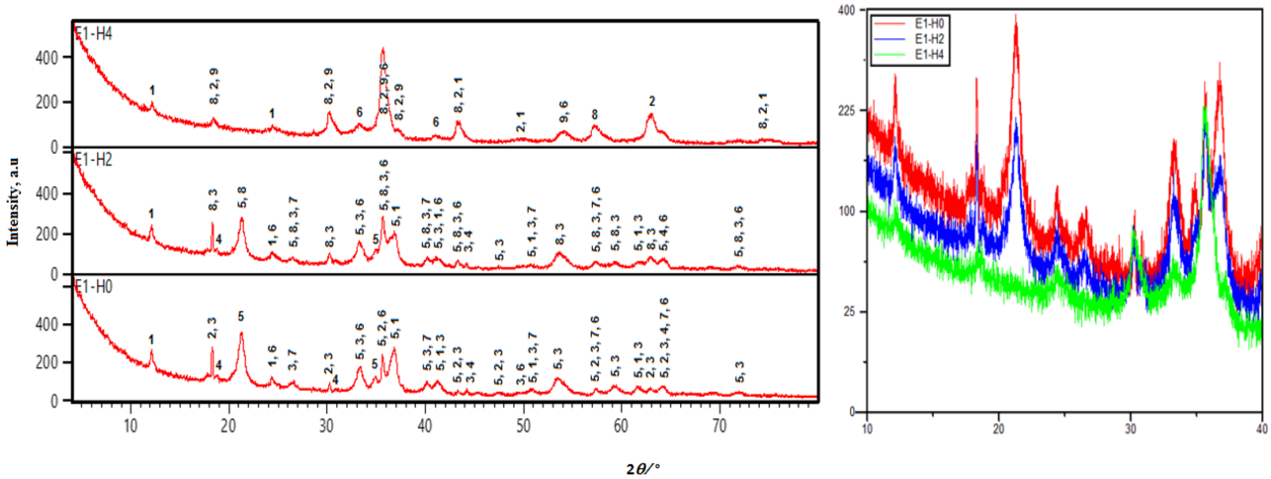

Figure 3. XRD patterns of reduced/leached lateritic ore samples from hearths H-0 through H-4 with the use of additive BC2-FO1.25. 1-Lizardite: $Mg_3Si_2O_5(OH)_4$; 2-Maghemite: $Fe_{21.16}O_{31.92}$; 3-Gibbsite: $Al(OH)_3$; 4-Spinel: $MgAl_2O_4$; 5-Goethite: FeOOH; 6-Hematite: Fe_2O_3; 7-Quartz: SiO_2; 8-Magnetite, syn: Fe_3O_4; 9-Chromite, aluminian: $Fe(Cr, Al)_2O_4$.

The furnace heating zone (from H-0 to H-4) is characterized by the loss of crystalline mineral water linked to the dehydroxylation process, with a predominance of transformations of goethite into hematite-magnetite, gibbsite in spinels containing aluminum and the decomposition of lizardite in H-4. The identification of hematite in the feed ore justifies the low presence of magnetite in H-2.

Different investigations agree that the goethite dehydroxylation process occurs in the temperature range of 250 to 400 °C to release iron oxide in the form of Fe_2O_3 as well as NiO [14,20,21,31-34].

In the literature [21] it was recognized that saprolite dehydroxylation has to be achieved between approximately 400 and 800 °C to obtain the complete recovery of Ni and Co.

The main mineralogical phases identified in the furnace reduction zone (from H-6 to H-16) were iron oxides (magnetite and maghemite, syn) and magnesium iron aluminum chromium oxide (magnesiochromite, ferroan). Magnesium iron silicate (fayalite) was only observed in hearths H-14 and H-16 (Fig. 4). The mineralogical phases detected in this study coincide with the investigations carried out previously [35,36], which identified maghemite, magnetite, magnesiochromite and fayalite as the main phases in the residues of the Caron process.

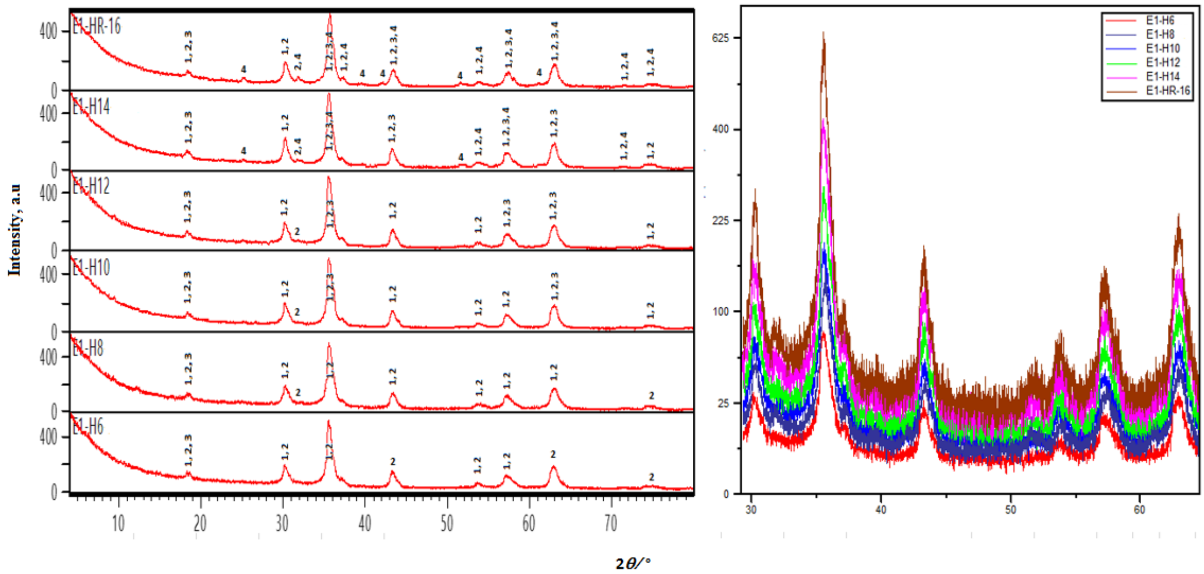

Figure 4. XRD patterns of reduced/leached lateritic ore samples from hearths H-6 through H-16 with the use of additive BC2-FO1.25. 1-Magnetite: Fe_3O_4; 2-Maghemite, syn: Fe_2O_3; 3-Magnesiochromite, ferroan: $[(Mg, Fe)(Cr, Al)_2O_4]$; 4-Fayalite: $Mg_{26}Fe_{1,74}(SiO_4)$

Magnetite increased in the content as each hearth corresponding to the reduction zone was passed. In the case of maghemite, loss of a part of oxygen from the $Fe_{21.16}O_{31.92}$ phase (heating zone) to Fe_2O_3 (H-6 to H-16) is observed, characteristic for the reduction process. Identification of magnesiochromite, ferroan, and fayalite indicates the formation of FeO and Fe^{2+}, and that the reduced ore reaches temperatures above 700 °C.

Similar magnetite content trend in the furnace reduction zone was described in a previous study on the Caron process with using 2.5 % fuel oil as the reducing additive [37]. Sanchez et al. [38] associated the identification of magnesiochromite and ferroane with processes in which partial substitution of Fe^{2+} by Mg, Cr, Al, and even by Fe^{3+} occurs in lower proportion. Also, it was recognized that fayalite is a product of transformation of the serpentine phase occurring at the highest reduction temperatures (600-800 °C) [21].

3. 2. Effect of substituting the reducing additive FO-2.5 with BC2-FO1.25 on chemical and physical characteristics of the reduced lateritic ore

Average chemical and physical characteristics of the reduced ore that were obtained when using each type of reducing additive are presented in Table 2 and Supplementary Material Tables S-1 and S-2.

Table 2. Chemical and physical characteristics of the reduced ore

Additive		Content, wt.%									ρ / kg m^{-3}	Magnetic fraction, %
		Ni	Co	Fe	Ni°	Fe°	Fe^{2+}	FeO	S	C		
FO-2.5	a	1.378	0.111	46.162	1.032	2.414	25.628	19.612	0.798	1.274	4690	59.584
	σ	0.022	0.003	0.277	0.034	0.213	1.387	0.543	0.036	0.053	8.843	1.268
BC2-FO1.25	a	1.344	0.112	46.534	1.067	2.782	25.058	19.896	0.604	1.368	4560	59.632
	σ	0.034	0.005	0.267	0.585	0.064	0.235	0.235	0.055	0.049	9.418	1.859

It is observed that regardless of the type of reducing additive used, chemical characteristics of the compounds correspond to an adequate reduction process where the conversion of NiO into metallic nickel (Ni°) is maximized, with contents of metallic iron (Fe^0) lower than 2.85 %. Also, Ni, Co, Fe, Fe^{2+}, FeO, and C contents, density and the magnetic fraction have shown similar values and were indicative that the substitution of the standard additive does not negatively affect the reducibility of the lateritic ores. It should be noted that the sulfur content was significantly lower when using the coal-oil mixture.

Different researchers [39,40] characterized the reduced ore when using FO-2.5 as a reducing additive and the reported values are close to those reported in this study.

Rojas *et al.* [41] recognized the negative effect caused by the increase in the sulfur content in the reduced ore in Ni and Co extractions due to the effect generated by passivation of the combined Fe-Ni-Co alloys during leaching. Therefore, implementation of the BC2-FO1.25 mixture on an industrial scale would benefit the leaching process.

3. 3. Effect of substituting the reducing additive FO-2.5 with BC2-FO1.25 on the CO/CO_2 profile in the furnace atmosphere

Figure 5 shows how the CO/CO_2 volumetric ratio varies in the even hearths of the pilot reduction furnace when using the reducing additives under analysis, see Supplementary Material Tables S-3 and S-4. The two zones described by Angulo *et al.* [25] were observed in correspondence with the content of reducing agents.

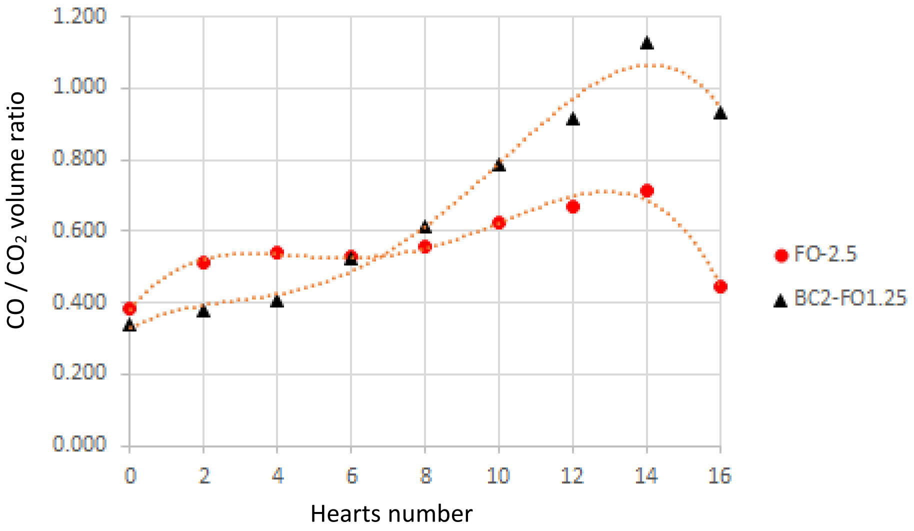

Figure 5. CO/CO_2 profile in the pilot furnace atmosphere

The first zone (from H-0 to H-6) is characterized by low CO/CO_2 volumetric ratios for both reducers resulting from the dilution generated by the post-combustion air supply in furnace hearths four and six. The average content of CO was higher by 16.4 % when using the FO-2.5 additive, justified by the fact that the temperatures in all furnaces are higher than the flash point of oil, while in the case of coal, the energy is not sufficient to provide the reductants from the dissociation process.

The second zone (from H-8 to H-16) is characterized by a gradual increase in the concentration of reducing gases. In all the hearths of the reduction zone (from H-8 to H-16) when using the BC2-FO1.25 additive, the average CO formation is increased by 22.4 % ($\sigma < 0.08$) compared to that achieved with the additive that is implemented currently on the industrial scale (FO-2.5).

Angulo *et al.* [11] report the average contents of CO in the chimney and the H-10 of the pilot furnace of 5.10 and 8.70 % respectively ($\sigma < 0.105$), values close to those achieved in this investigation (5.30 and 7.80 % for the H-0 and H-10, respectively). In the case of the BC2-FO1.25 mixture, no research was found to date that would allow comparisons to be made.

3. 4. Effect of replacing the reducing additive FO-2.5 for BC2-FO1.25 on nickel and cobalt extractions

During the evaluation of both additives, extraction content ranged from 78 to 84 % and 34 to 46 % for Ni and Co, respectively (Table 3 and Supplementary Material Tables S-5 and S-6). Different studies [11,13,16,25,37,39,40] reported values that coincide with those achieved in this investigation.

The average extraction of Ni and Co were higher by ~3 and ~8 %, respectively, when using the BC2-FO1.25 mixture as a reducing additive (Table 3), an aspect that is directly related to chemical and physical characteristics of the resulting reduced ore and the reducing atmosphere in the furnace in the process with this additive. The increases in Ni and Co extraction yields indicate that the used technological modification ensures more efficient operation of the reduction roasting process. These results confirm the values reported by Angulo *et al.* [23,24] for the laboratory scale experiments.

Table 3. Nickel and cobalt extraction results

Additive		Content, wt.% (Reduced and leached)			Extraction, wt.%	
		Ni	Co	Fe	Ni	Co
FO-2.5	*a*	0.295	0.077	48.11	79.22	35.74
	σ	0.004	0.001	0.598	0.428	1.130
BC2-FO1.25	*a*	0.254	0.069	48.37	82.30	43.90
	σ	0.015	0.002	0.253	1.104	1.388

5. CONCLUSIONS

The BC2-FO1.25 additive can reasonably increase the degree of recovery of nickel and cobalt from the laterite ore in the roasting/selective reduction process. The results of this study suggest that using this technological modification guarantees proper transformation of goethite in limonite to magnetite and serpentine minerals to olivine phases in saprolite. The use of this additive at a pilot scale showed that the industrially used additive fuel oil (FO-2.5) can be replaced since the main technological indicators of the process were improved. It should be stressed that the average formation of carbon monoxide in all hearths in the furnace reduction zone increased by ~22 % while the average extraction yields of Ni and Co were higher by ~3 and ~8 % respectively.

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

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Upotreba smeše uglja i nafte kao aditiva za selektivnu redukciju lateritne rude Caron procesom

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Izvod

Lateritne rude predstavljaju glavni izvor sirovine za ekstrakciju Ni i Co po Caron procesu. Potrošnja ulja u redukcionoj peći jedan je od ključnih pokazatelja da li je metalurški proces ekonomičan. Do danas nije bilo moguće zameniti aditiv lož ulje koji se koristi u komercijalnim razmerama, stoga je cilj ove studije bio da se delimično zameni nafta bitumenskim ugljem na pilot skali korišćenjem mešavine 2 % uglja i 1,25 % nafte kao redukcionog aditiva. Faze redukovanih/luženih ruda analizirane su difrakcijom rendgenskih zraka praha, dok je metalno stanje rude određivano luženjem izreagovanih uzoraka rastvorom brom-etanola nakon čega je usledila analiza atomske apsorpcione spektrometrije. Ekstrakcije Ni i Co potvrđene su luženjem redukovane rude rastvorima amonijum-amonijum karbonata. Uočeno je da smeša koja se koristi kao redukcioni aditiv može da zameni mazut jer omogućava adekvatnu transformaciju glavnih mineraloških faza lateritne rude tokom procesa redukcije i prosečne prinose ekstrakcije Ni i Co za ~3 i ~8. %, redom. Iako efekat veličine čestica bitumenskog uglja u procesu nije analiziran, redukciona smeša je obezbedila da je Caron proces efikasniji.

Ključne reči: ekstrakcija nikla i kobalta, rad peći, pirometalurgija