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REVIEW ARTICLE

Background and perspectives on the use of reducing additives in carbonate-ammonia technology for lateritic ores

Antecedentes y perspectivas del uso de aditivos reductores en la tecnología carbonato-amoniacal para menas lateríticas

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Abstract

Reducing agents are considered key variables for ensuring the metallurgical and energy efficiency of the Caron process during the roasting/reduction of lateritic ores. This study reviewed the state of the art regarding the main advances associated with the use of reducing agents in ammonia-carbonate technology. Based on a comprehensive review of high-visibility academic sources, the main findings directly related to the subject of study were synthesized narratively, combining retrospective and current approaches. In general, it was identified that the main objective of reducing agents is to utilize the saprolitic zone of the lateritic profile, where the use of pyrite and sulfur is most significant. Furthermore, the need to replace oil-based additives, which are implemented on a commercial scale, with solid reducing agents was demonstrated. The main limitations of oil-based additives are their increasing cost in the international market and the low efficiency they guarantee in the reduction zone of multiple-hearth furnaces. Finally, although significant progress has been made with the substitution of oil with bituminous coal, the evaluation of charcoal as a technological alternative is recommended to ensure the sustainability of the roasting/reduction process.

Keywords: reducing additives, roasting/reduction, Caron process, metallurgical sustainability

Resumen

Los aditivos reductores se consideran variables clave para garantizar la eficiencia metalúrgico-energética del proceso Caron durante la tostación/reducción de menas lateríticas. En este estudio se realizó una revisión del estado del arte sobre los principales avances que se asocian al uso de aditivos reductores en la tecnología carbonato-amoniacal. A partir de una revisión exhaustiva, en sitios académicos de alta visibilidad, se sintetizaron de forma narrativa los principales hallazgos con relación directa al tema objeto de estudio, mediante la combinación de enfoques retrospectivos y actuales. En general, se identificó que el objetivo principal de los aditivos reductores consiste en aprovechar la zona saprolítica del perfil laterítico, donde el empleo de la pirita y el azufre son los más significativos. Además, se demostró la necesidad de la sustitución del petróleo aditivo, que se implementa a escalas comerciables, por reductores sólidos porque este presenta como principales limitaciones el incremento de su costo en el mercado internacional y el bajo aprovechamiento que garantiza en la zona de reducción de los hornos de solera múltiples. Finalmente, aunque se evidencian avances significativos con la sustitución del petróleo por el carbón bituminoso, se recomienda la evaluación del carbón vegetal como alternativa tecnológica para garantizar la sostenibilidad del proceso de tostación/reducción.

Palabras clave: aditivos reductores, tostación/reducción, proceso Caron, sostenibilidad metalúrgica

1. INTRODUCCIÓN

Carbonate-ammonia technology, internationally known as the Caron process, is one of the established variants currently used for the extraction of nickel (Ni) and cobalt (Co) on a commercial scale (Rojas-Vargas *et al.,* 2022; Xiong *et al.,* 2024; Rojas-Vargas *et al.,* 2025; Acquah *et al.,* 2026; Chi *et al.,* 2026). To date, all industrial plants are characterized by combining pyro-hydrometallurgical processes for the processing of lateritic ores, with the roasting/reduction stage being key to guaranteeing economically competitive operating costs and the metallurgical-energy efficiency of the technology (Zevgolis & Daskalakis, 2022; Angulo-Palma *et al.,* 2025 a and b).

Historically, the roasting/reduction process is carried out in multiple-hearth furnaces of the Nichols-Herreshoff type (Miranda-López, 2025). In general, it is a complex stage in which the lateritic ore, with a moisture content of less than 5 % and a predominance of particle size fractions below 74 μm (84%-88%), is brought into direct contact with reducing gases in a countercurrent flow to selectively metallize Ni and Co, thus achieving strict control of metallic iron (Fe) formation with values below 5 % (Rojas-Vargas *et al.*, 2021; Angulo-Palma et al., 2022).

Different researchers recognize that the main variables that directly affect the roasting/reduction stage are the particularities of the lateritic ore fed to the process, the operational characteristics of the furnace, and the use of reducing additives (Ramírez-Pérez & Ramírez-Serrano, 2021; Angulo-Palma, 2024).

In the case of the use of reducing additives, despite the existence of previous research (Caron, 1950; Ilyas *et al.,* 2021; Angulo-Palma *et al.,* 2024), to date there is no current study analyzing their main background and possible future perspectives to consider to make the technology more attractive from an economic-energy point of view; a reason that justifies the present study.

This article presents the results of a review of the use of reducing additives in the Caron process. For better understanding, the study was divided into two parts: historical evolution of the main background, and the analysis of the current situation and perspectives of reducing additives in the Caron process.

2. MATERIALS AND METHODS

To carry out the state-of-the-art review, high-visibility academic databases (Web of Science, Scopus, and SciELO) were used, as well as the repositories of some Cuban and foreign universities.

From a search of more than 4,830,000 results in Google Scholar on reducing additives, studies that specified in their title and keywords some of the fundamental constructs to ensure that the research was directly linked to the proposed general objective were selected. To select the most relevant studies, several filtering processes were carried out (by indexing, alignment with the subject matter, and importance of the contribution). After the filtering process, 296 publications were selected for final analysis. It was ensured that the bibliographic references ultimately cited were updated within the last 10 years, with a percentage exceeding 65%.

During the preparation of the study, the following theoretical methods were used:

- Historical-logical: To study the evolution of the phenomena linked to the roasting/reduction process and the use of reducing additives for processing lateritic ores in Caron technology.
- Analysis-synthesis: To break down the different parts of the lateritic ore roasting/reduction process and establish the essential relationships concerning the use of reducing additives.
- Inductive-deductive: To make generalizations based on the singular findings identified during the research.
- Hypothetical-deductive: To establish particular conclusions based on the deductions proposed in the study.

It is also important to highlight that its development followed the recommendations proposed by Grant & Booth (2009); see Table 1.

Table 1. Recommendations used to carry out the state-of-the-art review

Criteria	**Methods**
Description	The current state of the use of reducing additives in the Caron process is addressed, combining retrospective and current approaches. Finally, the main perspectives for ensuring the sustainability of the process are presented
Search	An exhaustive search of the current literature associated with reducing additives is carried out
Evaluation	No formal quality assessment is performed
Synthesis	Narrative
Analysis	The current state of knowledge of reducing additives is analyzed, and priorities for future research are recommended

3. RESULTS AND DISCUSSION

3.1. Main background of the use of reducing additives in the Caron process

Since Caron (1924) patented the carbonate-ammonia technology, he recognized that liquid, solid, or gaseous reducing agents could be used during the roasting/reduction stage. Although the patent was novel in its early days, it did not include details of the type of reducing agent, mass percentage, preparation method, or incorporation into the process. Due to this limitation,

in subsequent years a new line of research was developed to evaluate the effect of different reducing additives during the processing of different zones of the lateritic profile.

Regarding the use of reducing additives, Caron (1950) published the first studies evaluating pyrite (FeS_2), sodium chloride (NaCl), and calcium chloride ($CaCl_2$). His research showed that the addition of FeS_2 is more effective when processing hydrated nickel silicate ores, as it increases extractions by more than 10%, with a tendency to decrease as the mass percentage of Fe increases. His evaluations with NaCl showed a decrease in the reduction temperature from 800 °C to 725 °C when feeding ores with 26% manganese dioxide (MnO_2), with the possibility of achieving Ni and Co extractions between 88.8% and 98.3%. In the case of using $CaCl_2$, he concluded that Ni extractions increased by 4.3%; without generating changes in the reduction temperature.

From 1968 to 1980, different studies were reported with new evidence on the benefits of using elemental sulfur (S) and FeS_2 as reducing additives in carbonate-ammonia technology during the processing of serpentinitic ores and the transition zone with mass percentages of the sum of magnesium-aluminum-silicon (Mg-Al-Si) between 15.38% and 20.19 % (De Graaf, 1979; Chandra *et al.*, 1980). In general, these works managed to identify that:

- The addition of 0.8% S in the roasting/reduction of saprolitic ores guarantees Ni extractions of 89%.
- The use of 1.25% FeS_2 during the processing of lateritic ores from the transition zone guarantees Ni extractions above 90%, at reduction temperatures between 600°C and 660°C, due to the additive contributing to the formation of easily leachable porous structures and the ability to delay the formation of refractory silicates.

At the beginning of the 1980s, Canterford (1983) reported the use of 2.5% fuel oil (PT-25) with high sulfur content as a reducing additive at the Queensland Nickel Process plant in Australia, to achieve Ni extractions close

to 80%. Its feed into the industrial furnaces was implemented by direct addition to the ore in mixers.

The effect of using FeS_2 and NaCl additives in the selective roasting/reduction process of Cuban saprolitic ores was evaluated by Castellanos-Suárez (1984a). His study shows that the use of 10% NaCl does not generate any benefit in the pyrometallurgical process, while the incorporation of 10% concentrated pyrite allows for an increase in Ni recovery between 15% and 17%.

Castellanos-Suárez (1984b; 1985) determined the effectiveness of using additive oil as a reducing agent for Cuban lateritic ores from Nicaro in the Caron process on a pilot scale. To verify the influence of the additive incorporation method, he evaluated three variants: direct addition to the ore before the grinding process (3% additive), oil injection into hearth nine (H-9) using a lance (2.1% and 3% additive), and the use of poor gas (conventional scheme with CO percentages between 18% and 26%). The highest Ni extractions were achieved using the first variant, with an increase between 4% and 5%, compared to the findings reported with the conventional scheme.

With the aim of reducing the production of reducing gas at the Nicaro plant, in 1986 the effect of using asphaltite with a particle size between 1.5 mm and 3.0 mm and a mixture of bagasse and NaCl was analyzed. By adding 4.0% asphaltite, an increase in the extractable Ni from 70.8% to 82.2% and Co from 56.7% to 59.7% was reported in the reduction of a Cuban serpentinitic ore with Fe mass values between 15% and 18%; this allowed replacing up to 11.0% of the reducing gas consumption in the furnace and a decrease in anthracite coal consumption for poor gas production. With the use of 4.0% bagasse and 1.0% NaCl in addition to the reducing gas, it was demonstrated that it is possible to increase Ni extractions by 3.5%, compared to using only reducing gas (Sánchez-Guillén *et al.*, 2020).

In 1992, the possibility of extracting Ni from a low-grade ore with a high amount of Si was examined. The findings demonstrated that the optimal

reduction temperature is 750 °C, regardless of the reducing agents analyzed (fuel oil and its combinations with NaCl and FeS_2). The highest Ni extractions were obtained with the combination of 10% fuel oil, 10% NaCl, and 1% FeS_2, with increases in Ni production between 6% - 8%, compared to those achieved with fuel oil without additives. The author justified his findings by the catalytic effect of NaCl on the reduction kinetics of NiO and its combination with the rapid dehydration at lower temperatures generated by the addition of FeS_2 (Yang, 2014).

Between 1991 and 1996, reducing gas was replaced by 2.5% PT-25 at the Punta Gorda plant, Moa-Cuba. Although unlike the Queensland Nickel Process plant, the additive addition is performed directly to the ore before grinding; its implementation allowed for improved process operability, increased plant production capacity, and improved working conditions for workers (Llansana *et al.,* 2009).

Valix & Cheung (2002a and b) analyzed the influence of using S as a reducing additive to process three types of lateritic ores: limonite, weathered serpentine, and fresh serpentine. They concluded that adding 5% sulfur improves Ni recoveries for all types of laterites under study. In the case of saprolites, they reported Ni conversion increases between 5% and 8% with reduction temperatures lower by 100 and 200 °C, compared to those used without additive (700 °C and 800 °C). During limonite reduction, they obtained a recovery increase of 51.6% during reduction at 600 °C. In general, all experiments reported Fe recovery increases between 8% and 10%.

From 2015 onwards, the effect of replacing additive oil with bituminous coal (BC) in the Caron process on a laboratory scale was evaluated. In general, it was demonstrated that:

- 4% BC as a reducing additive can replace PT-25 without affecting Ni and Co extractions, with a decrease in process costs of more than 23.55 million USD/year, an estimate reflecting the price difference of the additives (Angulo-Palma *et al.,* 2018).

- With a mixture of 2% BC and 1.25% fuel oil (BC20-PT12.50), maximum Ni and Co extractions (values of 90.7% and 68.3%, respectively) are achieved in the roasting/reduction stage of the Caron process, with a decrease in process costs of approximately 15.52 million USD/year, which can be attributed to the price difference of the additives (Angulo-Palma *et al.,* 2020).

- The use of a BC percentage below 4% does not generate increases in the specific energy consumption in the grinding process (Angulo-Palma *et al.,* 2020, 2021).

- The use of BC percentages below 2.52% does not cause decreases in the settling rate in the first stage of the Leaching and Washing circuit (Angulo-Palma *et al.,* 2025c).

Tittle-Basulto (2018) analyzed the influence of using anthracite coal fines as a reducing additive on bench and industrial scales. He observed that as the anthracite coal percentage increases up to 12%, extractions increase; while using a higher proportion, extractions begin to decrease. The highest Ni and Co extraction was obtained using the mixture of 2.0% fuel oil and 1.1% anthracite coal at 770 °C, with values of 86.7% and 58.9% for Ni and Co, respectively. Finally, the study proved economically unviable due to the price of anthracite coal; a situation that remains current.

De Alvarenga-Oliveira *et al.* (2019) evaluated by thermogravimetry the hydrogen reduction and thermal decomposition of a nickel silicon laterite ore under Caron process conditions using NaCl as a reducing additive. Their results show that Ni extraction can be increased from values below 3% to 90% with the incorporation of 1% additive, regardless of the reduction temperature used (up to 850 °C), after leaching the reduced ore with the ammoniacal solution.

Sánchez-Guillén *et al.* (2020) investigated the effect of using petcoke as a reducing additive in the Caron process on a laboratory scale. They concluded that its use is profitable with percentages equal to and greater than 10%. The

best extraction yields were achieved with 12% additive, with maximum Ni and Co extractions of 81.40% and 64.30%, respectively.

Ilyas and colleagues-initiated studies of carbothermic roasting/reduction, followed by ammoniacal leaching, of a Ni laterite ore from Bajaur-Pakistan to determine its possible exploitation through the Caron process. They observed that the optimal reduction condition was mixing the laterite ore with 10% by weight of bituminous coal and 9% by weight of Na_2SO_4, reduced at 800 °C for 120 minutes. Although the research proved technically feasible, it presented as a limitation the use of a considerable Residence Time (RT) and ammonia concentrations (150 g/L) much higher than those established in industrial-scale plants (60 g/L -100 g/L) during the leaching stage (Ilyas *et al.*, 2020, 2021).

A comprehensive analysis of the historical evolution of the use of additives in the roasting/reduction process of lateritic ores allows identifying that their main objective is to facilitate a better utilization of the different zones of the lateritic profiles, which under normal operating conditions cannot be used due to the low profitability they generate. It is striking that, except for the use of PT-25, the main studies were carried out on a laboratory scale, which limits the full reproduction of the impact of the main operational variables of the roasting/reduction stage; where the low availability of commercial-scale facilities (pilot and industrial) is the most determining factor.

3.2. Current situation and future perspectives of the use of reducing additives in the Caron process

Despite the different studies reported on the use of reducing additives in the Caron process, commercial plants implemented PT-25 (Reid & Fittock, 2004; Rodríguez, 2004; Angulo-Palma *et al.,* 2021, 2025c; Rojas-Vargas *et al.,* 2025) as an alternative to avoid the costs associated with the preparation of other reducing agents (e.g., anthracite coal gasification).

In general, the use of additive oil in the Caron process currently causes two major drawbacks. The first is associated with the low profitability generated by the high price increases of this energy carrier in the international market. The second is because the additive provides the main reducing agents in the heating zone of the furnaces upon contact with temperatures above 300 °C, which causes a waste of its calorific potential in the reduction zones of the furnace (from H-7 to H-16).

In the specific case of the Caron process in Cuba, in addition to the aforementioned limitations, the negative effect generated by the additive in the grinding facilities is added (Figure 1). In this regard, Coello-Velázquez *et al.* (2020) recognize that the feeding of PT-25 before the grinding process causes:

- Increase in the + 0.149 mm class in the ore after grinding.
- Increased fuel oil consumption in the process to counteract fuel losses adhered to the balls and mill walls.
- 12% decrease in mill productivity.
- Increase of more than 6 kWh/t in the specific energy consumption of the grinding process.

Furthermore, the combination of these limitations with periods of decreases in the price of Ni and Co in the international market and loss of funding has led to the closure of the main plants according to research consulted in high-prestige journalistic sources in Australia and Brazil (ABC-News, 2024; Excelência-Notícias, 2024), leaving only the Punta Gorda plant in Moa-Cuba in operation.

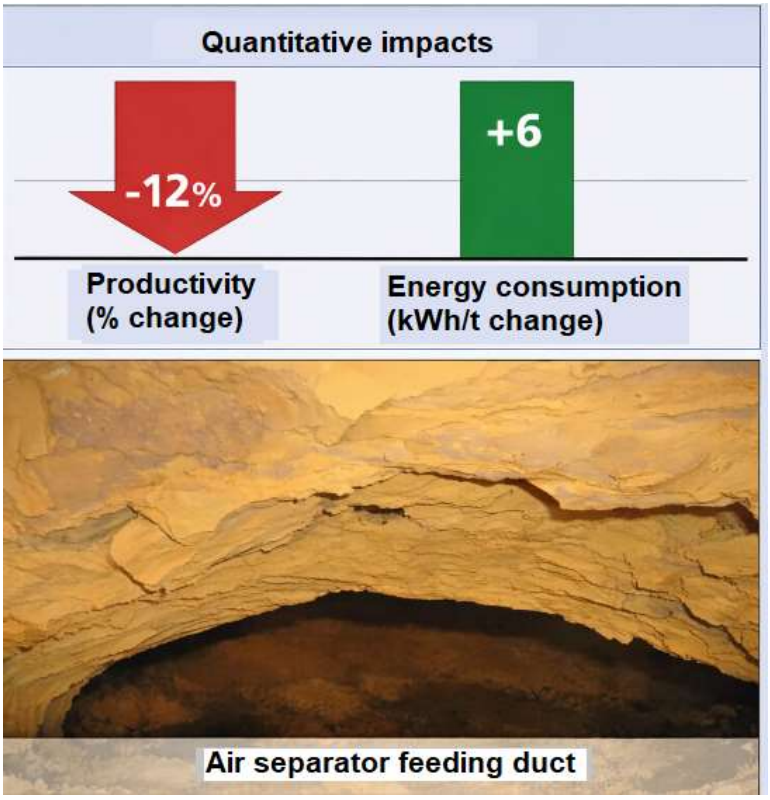


Figure 1. Adherence of lateritic ore in the grinding circuit due to the incorporation of additive oil.

Although the Caron process tends to disappear globally, the proper implementation of reducing additives on an industrial scale in the coming years will be decisive to guarantee its continuity in a more sustainable and economical way. For this purpose, in the last 10 years, research has continued to address the use of solid additives as a technological alternative to counteract the negative effects generated by the use of PT-25 as a reducing additive.

Under this perspective, the most significant studies were aimed at evaluating the use of asphaltite on a laboratory scale and demonstrating the benefits of using the BC20-PT12.50 mixture on a pilot scale (Angulo-Palma et al., 2024, 2025a, 2025b, 2026). Although recent advances with the use of these additives were promising, the investigations only evaluated non-renewable reducing agents, which constitutes a limitation. Therefore, future studies are needed to evaluate the roasting/reduction of lateritic ores using

charcoal (CH) as an additive. The comprehensive comparison of the results obtained for CH (technical, economic, and environmental advantages and disadvantages) with those previously reported for other additives (Figure 2) will be the basis for decision-making regarding the selection of the additive to be used in the coming years in the Cuban nickel industry (Retirado-Mediaceja *et al.,* 2026).

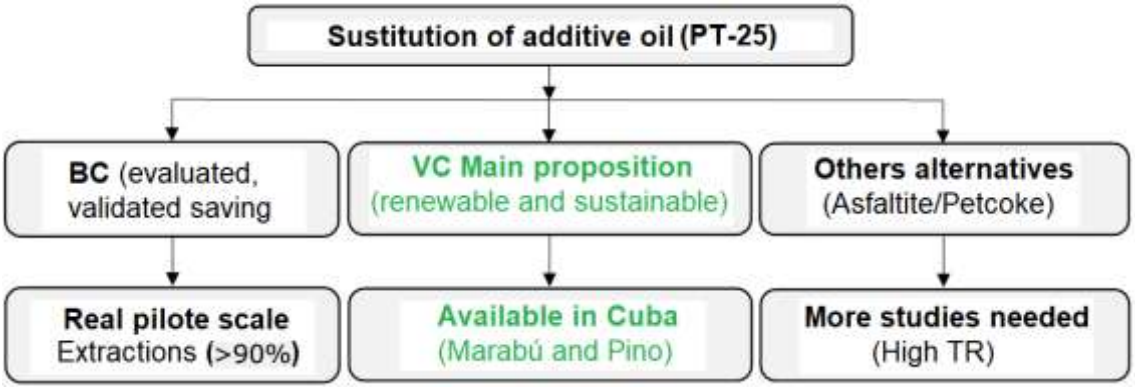


Figure 2. Perspectives for replacing PT-25 with CH or other additives.

In the specific case of Cuba, the large extensions of marabú (*Dichrostachys cinerea*) scattered mainly in the center of the country and the clearing of Cuban pine (*Pinus cubensis*) generated by the mining of carbonate-ammonia technology are the most available options to promote the sustainable development of the roasting/reduction process (Durán-Manual *et al.,* 2022; Méndez-Santos *et al.,* 2022; Valero-Jorge *et al.,* 2024; Baeza-Guzmán *et al.,* 2025; Fernández-Pedroso *et al.,* 2025; Gómez-Hechavarría *et al.,* 2025).

In the future, although charcoal presents an attractive potential as a renewable reducing agent in the Caron process, its effect on the technology must be rigorously analyzed. In this context, the most important aspects to consider are:

- **Fixed carbon**: Since CH has higher values than BC, it will be necessary to evaluate whether it can partially or totally replace the amount of coal present in the BC20-PT12.50 mixture without affecting the metallurgical efficiency of the process.

- **Ash formation**: CH can have a variable ash and volatile matter content, so in future studies special attention should be paid to the effect that the introduction of impurities into the leaching and washing system may generate and its possible impact on the quality of the final Ni and Co products.

- **Risk of Fe over-reduction**: The high reactivity of CH can hinder the selectivity of the process, with an increase in the metallization of a significant fraction of Fe, which hinders subsequent leaching and reduces product quality. To this end, it will be necessary to evaluate whether it guarantees the same control as BC with the use of different thermal profiles.

- **Low density**: This characteristic implies a greater volume to handle and transport, as well as a possible increase in furnace entrainment, an aspect to consider due to possible negative repercussions on logistics and the energy efficiency of the process.

4. CONCLUSIONS

- Reducing additives are fundamentally used in the Caron process as technological alternatives to guarantee the utilization of zones of the lateritic profile that are traditionally difficult to exploit, where pyrite and sulfur show the most significant effects concerning metallurgical efficiency.

- The replacement of additive oil with solid reducing agents, such as bituminous coal, is essential to eliminate the current limitations of the technology, associated with operating costs and the comprehensive utilization of the lateritic ore entering the process.

- The future evaluation of charcoal as a reducing additive is a technological alternative to consider to guarantee the sustainability of the roasting/reduction stage of the Caron process, given the wide availability of the raw material and the proven quality of this type of coal in other industrial applications. The practical implication of this technological innovation for the Cuban nickel industry will be the subject of future research.

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Additional information

Conflict of interest

The authors declare that there are no conflicts of interest.

Author contributions

YHB: Conceptualization, formal analysis, investigation, writing of the original draft, and writing review and editing. **RSAR**: Conceptualization, formal analysis, investigation, project administration, supervision, writing of the original draft, and writing review and editing. **JAPH:** Formal analysis, investigation, methodology, writing of the original draft, and writing review and editing. **EMP**: Formal analysis, investigation, writing of the original draft, and writing review and editing. **CHP**: Formal analysis, investigation, methodology, writing of the original draft, and writing review and editing. **HJAP**: Conceptualization, formal analysis, funding acquisition, investigation, project administration, supervision, writing of the original draft, and writing review and editing. **YRM**: Conceptualization, formal analysis, investigation, methodology, supervision, writing of the original draft, and writing review and editing of the final manuscript.

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