Utilisation of Residues of Nickel Production in EAF Steelmaking Route

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A stock of over 100 Mt of residues (colas or tailings) from metallurgical production of nickel exists presently in Cuba with concentrations of around 0.4 wt% Ni, 42 wt% Fe and 2.0 wt% Cr. The annual production of colas in year 2005 will be about 10 Mt/year.

The aim of this study is to develop a sustainable recycling concept in EAF steelmaking route for utilising a part of those residues, thus reducing impact on the environment and recycling valuable materials.

Experiments have been carried out in suitably equipped 50 kg lab-scale electric induction furnace by adding, inserting or injecting of tailings at 1600 °C with or without reducing agents (e.g. coal) to study recovery of the metals contained to the steel melt. The experiments were carried out under equilibrium, quasi-equilibrium and non-equilibrium conditions.

Thermodynamical calculations at RWTH lab-scale conditions had shown nearly complete reducibility of the compounds NiO, Fe3O4 and Cr2O3 from the colas. The experimental conditions have confirmed this, resulting in about 90% recovery of Ni, 80% of Cr and 99% of Fe.

Industrial tests at Antillana de Acero in Cuba in a 1.5 ton EAF with the injection of tailings in combination with coal have presented around 75% of recovery of chromium, 100% of nickel and 85% of iron.

KEY WORDS: recycling of tailings; recovery of nickel; thermodynamic calculation; industrial tests.

1. Introduction

In Cuba the recovery of nickel from the lateritic mineral is carried out by the technologies: acid leaching under pressure and use of ammonia carbonate. In a study in the Siderurgic Research Centre of Nicaro1) an endothermic reaction and a heat absorption resulted in the range between 300 °C and 700 °C were obtained, carried out by thermal analysis (TDA) of those colas. This analysis demonstrated, that in the colas not only internal humidity exists, but also the crystalline humidity and in addition carbonic salts in small amounts.

In a further existing report of the Steelmaking Research Centre of Nicaro2) in cooperation work with specialists of the ex-USSR, 68.6% recovery of iron from the fresh colas was obtained in the process with separation by humid route concentrates and 67.0–71.1% from the deposited colas. The humidity of cake during the filtration of the concentrates reached 29%. It was noticed, that one amount of petroleum existed in the solid and liquid phases on the colas, which exert a detrimental influence in the stability of the processes of separation and filtration, as well as in the corresponding technological indices.

1.1. Characterisation of the Colas

From several investigations3,4) was demonstrated that the colas of Nicaro are a complex waste for their industrial operation, due to its characteristic physical-chemistry and mineralogy. The Table 1 shows the chemical composition of the colas.

In 1977 investigations of the mineralogical composition of colas from Nicaro5) have been carried out in which the following mineralogical phases were confirmed by X-ray diffraction (see Table 2).

The Table 3 shows the grain sized composition of a sample of colas of Nicaro, the content and the distribution by

Table 1. Chemical composition of the colas in wt%.

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<tbody>
<tr>
<td>C</td>
<td>P</td>
<td>CaO</td>
<td>NiO</td>
<td>Cr2O3</td>
<td>CoO</td>
</tr>
<tr>
<td>1.34</td>
<td>0.017</td>
<td>0.10</td>
<td>0.381</td>
<td>2.70</td>
<td>0.0127</td>
</tr>
<tr>
<td>FeO</td>
<td>SiO2</td>
<td>MgO</td>
<td>Al2O3</td>
<td>MnO</td>
<td>Na2O</td>
</tr>
<tr>
<td>62.41</td>
<td>14.1</td>
<td>8.4</td>
<td>5.85</td>
<td>2.22</td>
<td>0.270</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>1.81</td>
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is classes of Fe, Cr$_2$O$_3$ and Al$_2$O$_3$.

It can be observed, that the colas are a powder mineral of fine grain size, this is given so that the head mineral that is processed in the nickel plant previously is crushed up to 80% of smaller particles to 0.074 mm. The content and the distribution of the Fe increases with the diminution of the particles, whereas for chromium the greater contents and distribution are between 0.125 mm and 0.030 mm; the contents of Al$_2$O$_3$ do not present a defined affluent regularity, but the distribution shows a variation very similar to the chromium.

The pignometrical analysis of the colas done earlier show that they have a 42.50% of pores, the same has a capillar molecular humidity of 42.40%. From this result follows that in the furnaces of the nickel production plant the hematite (fundamental ferrous phase) is reduced to magnetite, product of this reduction escapes part of oxygen content of the mineral, leaving small pores in magnetite grains, which causes a spongy configuration in the grains.

2. Objectives

The investigations were carried out with the following objectives:

1) to prepare EAF recycling route of treatment for colas, 
2) to adapt a metallurgical condition in order to obtain upgrade steels with Cr and Ni alloying from the colas.

3. Experimental Work and Results

The basic experiments were carried out in an electric induction furnace (alumina crucible, 17 cm diameter, 40 cm height) with capacity of 50 kg (Fig. 1) at RWTH Aachen University, equipped with porous plug for gas stirring, inert atmosphere and injection of cored wire. For the inert atmosphere inside the furnace, 10 ml/min of argon was blown through one chamber (cover). The materials were 30 kg of technical pure iron, 30 kg of a low-alloyed steel grade, 100 g of colas, 100 g of 50 wt% CaO-50 wt%Al$_2$O$_3$-slag, 100 g of Ca-Al-alloy (30 wt% Ca), 100 g anthracite (coal) and 100 g metallic aluminium. The chemical composition of the technical pure iron, the low-alloyed steel, the anthracite and its ash are presented in Tables 4–7 respectively. The metallic samples were analysed through the optical emission spectrometry method.

3.1. Experiments with Technical Pure Iron

In this group of experiments, 30 kg of technical pure iron were smelted in the induction furnace and superheated up to 1600°C, after that it was killed with 100 g aluminium, and 100 g of CaO-Al$_2$O$_3$-slag were brought onto the surface of the melt. Then two meters of a cored wire with mixture of
50% colas-50% anthracite or 50% colas-50% Ca-Al-alloy were submerged in the melt. The samples were taken at 1 600°C, and every five minutes after the addition of the cored wire. During the experiment a gas flow of 1 liter/min of argon was blown through the bottom porous plug. The whole treatment time was 25 minutes.

4. Results

a) Results of application of cored wire with mixture of colas and anthracite.

Figure 2 presents the results of application of cored wire with mixture of 100 g colas-100 g anthracite at 1 600°C. The diagram shows that the recovery at this method is about 90% of chromium and nickel and 80% of iron after 25 minutes of treatment.

b) Results with the utilisation of cored wire with a mixture of colas and Ca-Al-alloy.

Figure 3 shows the results of the treatment with the method or cored wire with mixing of 100 g colas-100 g Ca-Al-alloy at 1 600°C. By that treatment about 90% of chromium and nickel and 80% of iron can be recovered.

4.1. Experiments with Low Alloyed Steel

In this group of experiments, 30 kg of low-alloyed steel were smelted in the induction furnace, also superheated up to 1 600°C, and killed with 100 g aluminium. Subsequently, 100 g of CaO-Al₂O₃-slag were given onto the melt surface. Two meters of cored wire with mixing of 50% colas-50% Ca-Al-alloy or 100 g aluminium (experiment on equilibrium) were added into the melt. The samples were taken at 1 600°C and every five minutes after the addition of cored wire and aluminium. Like before, 1 liter/min of argon-gas was blown through the bottom porous plug. The whole treatment time was 25 minutes.

a) Results with the utilisation of aluminium (experiment on equilibrium)

Figure 4 presents the results of the treatment with the utilisation of 100 g aluminium and 100 g colas at 1 600°C. The diagram shows that the recovery with this method is about 90% of nickel and iron and 70% of chromium after 25 minutes of the treatment.

b) Results with the utilisation of cored wire with mixing of colas-Ca-Al-alloy

Figure 5 presents the results of the treatment with the utilisation of cored wire with mixing of 100 g colas-100 g Ca-Al-alloy at 1 600°C. With this method about 90% of nickel, 80% of iron and 60% of chromium can be recovered after 25 minutes of the treatment.

Figure 6 presents the summary of the experiments with different mixings of colas with others compounds. The figure expresses that the recovery of nickel obtained in all of the experiments is about 90%. Chromium presents the highest recovery by 90% on the system anthracite-colas and colas-Ca-Al-alloy in pure iron. Finally, iron can be recovered by 90% on the system colas-aluminium in low alloyed steel (experiment on equilibrium).
5. Thermodynamical Calculations

To clarify the influence of the aluminium, of added Ca-Al-alloy and of calcium-aluminate slag on the recovery treatment with low alloyed steel, thermodynamical calculations with the Equilib7 program have been carried out. The procedure of the calculation was done as follows. The quantities of low alloyed steel or technical pure iron and the additions of anthracite, CaO–Al2O3 slag, aluminium and Ca-Al-alloy were set up at 1600 and 25°C respectively. The quantities of Ca-Al-alloy, aluminium and anthracite were considered as variables in the calculation. Moreover in the software, databases were selected for the prediction of the three phases presented in the treatment: gas, liquid iron or liquid steel and slag.

a) Results with cored wire of mixing of colas-aluminium.

Figures 7 and 8 present the results of the thermodynamical calculations of the system colas-aluminium. Figure 7 shows that with the addition of aluminium, the aluminium and nickel contents can be increased to 0.25 and 0.17%, respectively.

In according of the increasing of these elements, the iron and chromium contents can be diluted to 96% and 1.7%, respectively. With the addition of 100 g CaO-Al2O3-slag (without aluminium), the compounds NiO and Cr2O3 can be completely reduced (Fig. 8). Fe2O3 can react with manganese, aluminium and silicon from the melt and also with aluminium and it can be formed FeO. This compound can be reduced with a few addition of aluminium.

b) Results with cored wire with mixing of colas-Ca-Al-alloy.

Figures 9 and 10 present the results of the thermodynamical calculations of the system colas-Ca-Al-alloy. Figure 9 shows that with the addition of Ca-Al-alloy, the aluminium and nickel contents can be increased to 0.20 and 0.18%, respectively.

In according of the increase of those elements, the iron and chromium contents can be diluted to 96 and 1.69%, respectively. With the addition of 100 g CaO-Al2O3-slag (without Ca-Al-alloy addition), the compounds NiO and Cr2O3 can be completely reduced (Fig. 10). Fe2O3 can react with manganese, aluminium and silicon from the melt and also with calcium and aluminium from the alloy; FeO
can be formed. This compound can also be reduced with a few addition of aluminium.

Thermodynamic results calculated for pure iron have been similar than for the low alloyed steel grades.

6. Pilot Test

The pilot test was carried out at Antillana de Acero in Cuba in a 1.5 ton electric arc furnace (EAF) with the injection of 207 kg tailings together with 60 kg coal. The melt was 1.5 ton of one steel with the chemical composition 0.91%wt C-0.022%wt Si-0.22%wt Mn–0.043%wt P–0.0099%wt S–0.064%wt Cr–0.12%wt Ni. For the test some materials like 5 kg mill scale, 6 kg SiMn, 10 kg FeSi (with 75%wt Si) and 2 kg graphite dust were used. During the treatment metal and slag samples were taken at several times and the temperature was measured. Figure 11 shows that during the injection and the addition of the materials the contents of chromium and nickel were increased and the carbon content in the melt was diminished. In Fig. 12 the recovery of Cr, Ni and Fe during the treatment is presented. The values of recovery were 70% of chromium, 100% of nickel and 80% of iron.

7. Conclusions

It has been shown in the experiments at induction furnace, that Ni, Fe and Cr from colas can be recycled to a steel melt at 90%.

Thermodynamical calculations are supporting those results: The oxides NiO and Cr$_2$O$_3$ from the colas can be completely reduced with a slag. FeO$_2$ can react with silicon, aluminium and manganese from the melt and FeO will be formed. FeO can be post-reduced with increased additions of anthracite, aluminium or Ca-Al-alloy.

A pilot plant test at Antillana de Acero shows that the injection of tailings in combination with anthracite is feasible and a recovery of 75% Cr, 100% Ni and 85% Fe was obtained already at first approach.

Acknowledgment

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REFERENCES


Appendix

The recovery of nickel from colas which is contains 0.38 wt% NiO needs e.g. carbon:

\[
(NiO) + <C> = [Ni] + \{CO\}
\]

In the case of the above mentioned EAF trial anthracite with 91.2 wt% carbon was used. By stoichiometric estimation the specific amount of anthracite is:

\[
M_{NiO} = 74.7 \text{ kg/kmole}, M_{Ni} = 58.7 \text{ kg/kmole}, M_{C} = 12 \text{ kg/kmole}.
\]

In 1 ton of colas 0.381 wt% NiO or 3.81 kg/t colas are contained. That means a Ni met amount of 2.99 kg/t colas. At a recovery rate of 90% a nickel mass of 2.69 kg/t colas can be extracted into the steel melt. The specific mole number of recovered Ni is 2.69/58.7 = 0.046 kmole/t colas. For nickel extraction the same mole number of carbon is necessary at minimum so that the needed carbon mass amounts 0.044*12 = 0.550 kg/t colas or 0.55/91.2%/2.69 = 0.224 kg anthracite/kg nickel, respectively.

Estimation of the metallic extraction, anthracite consumption and gas production leads to the following Table 8. A \{CO\} gas production useable for stirring of melt and slag will be about 224 m$^3$ (STP)/t colas.

<table>
<thead>
<tr>
<th>Table 8. Estimation of the metallic extraction, anthracite consumption.</th>
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<tbody>
<tr>
<td>recovered metal, spec., kg/t colas</td>
</tr>
<tr>
<td>-----------------------------------</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Fe</td>
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