



## Leaching of the fine fraction of the argon oxygen decarburization with lance (AOD-L) sludge for the preferential removal of iron

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### ABSTRACT

The fine fraction of the argon oxygen decarburization with lance (AOD-L) sludge is a hazardous waste generated by the stainless steel industry which is normally disposed in landfills. Due to the relative high content of Fe, Cr and Ni as well as its low granulometry, a hydrometallurgical route based on sequential leaching steps is being investigated to treat it. In this paper, an attempt made to remove Fe from the sludge and concentrate Cr and Ni in the solid is highlighted. Leaching was carried out at atmospheric pressure using  $H_2SO_4$  and HCl at varying temperature (25, 40, 55 and 70 °C) and acid concentration (3, 6 and 12%, v/v). For both acids, leaching rate increased with temperature and acid concentration, and higher dissolutions of Fe and Ni were obtained in comparison with that of Cr. HCl was found more selective for Fe over Ni and Cr. The content of Fe was reduced nearly 50% (w/w) at 70 °C and HCl 12% (v/v), while Cr remained mostly in the solid; however, around 40% (w/w) of Ni was dissolved and it may hinder such leaching step in the studied route. The study points out that total metal leaching of sludge under high temperature and pressure conditions must be considered.

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### 1. Introduction

Significant quantities of industrial hazardous wastes are generated everyday worldwide. Such materials may represent a potential source of contamination to the environment and also to the human health if managed in an inappropriate way. According to FEAM [1] (the environment governmental agency of the state of Minas Gerais, in Brazil), approximately 830,000 tons of industrial hazardous wastes was generated in Minas Gerais in a period of 12 months between 2001 and 2002. From this amount, around 790,000 tons (or 95%) was generated by the metallurgical sector which has a significant economic importance for the state of Minas Gerais. The metallurgical wastes normally contain a high content of metals, which might be reused as secondary raw materials. Nowadays, the increasing demand for metals stimulates the development of alternative methods for recycling such materials in order to reduce or even avoid the loss of valuable metals mainly if the residues are disposed in landfills. Also according to FEAM [1], around 550,000 tons (or 66%) of the industrial hazardous waste generated in the previously mentioned period was disposed in landfills and only 725,000 tons (or 9%) was sent for recycling, recovery and any other reuse process.

In fact, the disposal of hazardous wastes in landfills is a common but non-sustainable and expensive industrial practice. It represents perhaps the immediate solution when no proper treatment method is available. The development of processing routes aiming to treat hazardous industrial wastes is extremely important not only to protect the environment and to conserve mineral resources (because their supply is finite) but also for economic reasons. Particularly in the production of stainless steel, significant quantities of wastes such as slags, sludges and dusts are annually generated. These materials usually contain valuable and toxic metals, which may contaminate the soil and groundwater if released to the environment. For example, the electric arc furnace dust, which is a particulate matter removed from the exhausted gases during the atmospheric emissions control, was classified as hazardous waste since the total chromium concentration exceeded the Toxicity Characteristic Regulatory Level [2]. By similar reason, the sludge generated by the argon oxygen decarburization with lance (AOD-L) converter during the removal of particulate matter from the exhausted gases by a wet scrubber was also classified as hazardous waste [3,4]. Therefore, the recovery of chromium and many other metals like iron, lead, nickel, zinc, cadmium, etc., which are generally found in such type of wastes, may contribute to reduce the quantity and toxicity of many materials that are normally disposed in landfills, thus incorporating the concept of environmental quality and sustainability.

Around 20–30 kg of AOD-L sludge is generated per ton of stainless steel produced. The AOD-L sludge is normally divided into

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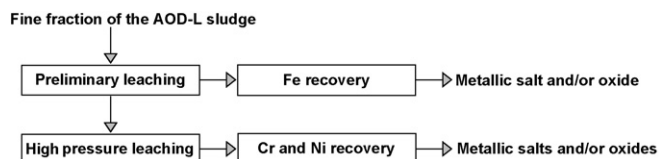


Fig. 1. Simplified hydrometallurgical treatment route of the AOD-L sludge.

coarse (40%, w/w) and fine (60%, w/w) fractions with mean particle diameters of 100 and 1  $\mu\text{m}$ , respectively. The coarse fraction is commonly recycled into the own stainless steelmaking process after briquetting, but its fine fraction does not agglomerate efficiently [5]. In addition, the use of magnetic separation technique was also found to be inadequate to treat it for reuse purposes [3] as well as gravity separation technique. Consequently, due to the inexistence of feasible alternatives methods to treat the fine fraction of the AOD-L sludge, this hazardous waste, particularly in Minas Gerais state, is currently disposed in landfills [5]. However, taking into account that the AOD-L sludge is a very fine material, it is reasonable to consider the use of hydrometallurgy as an alternative method to treat it in order to recover chromium (which is a toxic but valuable element) as well as other metals like iron and nickel. The recovery of these metals as oxides and/or metallic salts from the AOD-L sludge seems to be very attractive as these compounds are normally used in a number of industrial processes.

In a study carried out by Conard [6], it has been pointed out the advantages of using hydrometallurgical processing routes in contrast to pyrometallurgical ones to treat the wastes generated by the industrial activities. In fact, hydrometallurgy may offer a more eco-friendly alternative of treatment but the success of the aqueous processing depends on the specific characteristics of the waste to be processed as, for example, the particle size, solubility of the mineral phases, impurities content, etc. Currently, several hydrometallurgical routes were proposed to recover valuable and heavy metals such as iron, zinc and lead from wastes generated by the steelmaking processes [7–12] and zinc from wastes generated by the stainless steelmaking process [13], but no work using hydrometallurgical methods to recover iron, chromium and nickel from the AOD-L sludge was found in the literature. The chemical composition of particular AOD-L sludge samples generated in the state of Minas Gerais consists basically of 24–42% (w/w) of iron, 6–13% (w/w) of chromium, and up to 2.5% (w/w) of nickel [4]. Such metal composition may change according to the type of stainless steel produced. Although the content of nickel is relatively low, recover it may be attractive due to its high demand and economic value. Actually, the content of nickel in the fine fraction of the AOD-L sludge is similar to those normally verified in the Brazilian lateritic nickel ores—on the average 1–2% (w/w) Ni [14].

In this context, a hydrometallurgical processing route schematically shown in Fig. 1 is being under investigation in order to treat the fine fraction of the AOD-L sludge aiming to recover chromium, nickel and iron as oxides and/or metallic salts. Due to the relatively higher content of iron in this material, the investigation of the operational leaching conditions for the preferential removal of iron is highlighted in this paper (named preliminary leaching step), aiming to concentrate chromium and nickel in the solid phase. These metals can be recovered in a posterior leaching step. The preliminary leaching tests were carried out under atmospheric conditions using hydrochloric and sulfuric acids as leaching agents and at moderate temperature levels. The study of this step may be interesting because the presence of iron into the leaching liquor may affect the successive step of chromium and nickel recovery and it would be advantageous to keep it to a minimum concentration. Nonetheless, it is important to mention that if the preliminary leaching step is

not successful, high pressure leaching of iron, chromium and nickel from the AOD-L sludge must be considered.

## 2. Experimental

### 2.1. Sample preparation and composition of the AOD-L sludge

The fine fraction of the AOD-L sludge used in this study was generated by a stainless steelmaking company located in the state of Minas Gerais, in Brazil. After sampling, the following procedures were adopted to obtain representative samples: (1) the AOD-L sludge was dried at 60 °C for 24 h; (2) the dry sludge was thoroughly homogenized resulting in a very fine powder (mean diameter = 1  $\mu\text{m}$ ); and then (3) the powder was successively quartered using a Quantachrome sieving rifler (model SRR5) in order to obtain samples weighting around 5 g of material. The granulometric analysis of the dry powder is shown elsewhere [4].

The chemical composition of the dry powder was assessed by the following dissolution procedure. Firstly, samples of the AOD-L sludge were digested in a hot plate at 150 °C ( $\pm 5$  °C sensitivity) for 5 h using a mixture of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) 50% (v/v) and perchloric acid ( $\text{HClO}_4$ ) 70% (v/v). After digestion, the solutions were vacuum filtered and properly diluted; then, the concentration of the metal ions in the acidic solution was analyzed by atomic absorption spectrophotometry (AAS) using a GBC Atomic Absorption Spectrophotometer (model 932 plus). The remaining solid phase not dissolved in the previous step (normally silica) was then roasted in a furnace at 1000 °C ( $\pm 50$  °C sensitivity) for 1 h in a platinum crucible. Later, the residue was digested in the hot plate at 150 °C for 1 h with hydrofluoric acid (HF) 40% (v/v); and the silica content was determined by weight difference using an analytical balance.

### 2.2. Leaching tests

All leaching tests were carried out in a covered 1 L Pyrex® reactor immersed in a controlled-temperature bath ( $\pm 1$  °C sensitivity) and provided with a mechanical stirrer using a glass impeller marine-type. The leaching of the AOD-L sludge was investigated under atmospheric conditions using hydrochloric acid (HCl) or sulfuric acid ( $\text{H}_2\text{SO}_4$ ) as leaching agents. The operating variables temperature (25, 40, 55 and 70 °C) and acid concentration (3, 6 and 12%, v/v) were investigated. Experiments were performed at low pulp density (solid/liquid ratio maintained constant at 1/30 g/mL). Tests were done in duplicate. The leaching time of these tests was defined in a preliminary investigation at 55 °C using 6% (v/v) of  $\text{H}_2\text{SO}_4$  and HCl as leaching solutions. All chemicals used in this study were of reagent grade and aqueous solutions were prepared using distilled water.

The following procedure was adopted for the leaching tests. Firstly, a volume of 150 mL of the selected leaching solution was placed into the reactor and heated to the specific temperature of the test. At the initial time, a sample weighting 5 g was added to the solution under constant stirring (420 rpm), and at the end of each test, a sample of 10 mL of liquor was withdrawn, properly diluted and then analyzed for iron, chromium and nickel by AAS. In the tests where the leaching residue was analyzed, the leaching solution was vacuum filtered while the solid phase was rinsed with distilled water and then dried at 60 °C for 24 h.

The concentration of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in the leaching solution was determined by volumetric titration with standard 0.1N potassium permanganate ( $\text{KMnO}_4$ ). The indicator ferroin was added and analysis was carried out in sulfuric acid solution at room temperature. As chloride ions interfere in the titration of  $\text{Fe}^{2+}$  with standard  $\text{KMnO}_4$ , the preventive solution of Zimmermann–Reinhardt was

**Table 1**  
Chemical composition of the AOD-L sludge

Element	Content (% w/w)
Fe	34.0 ± 2.0
Cr	10.2 ± 0.9
Ca	7.0 ± 0.8
Mg	3.7 ± 0.6
Mn	1.7 ± 0.4
Si	1.7 ± 0.1
Ni	1.4 ± 0.1

used [15]. The mean value of three successive titrations was used as the molar concentration.

### 2.3. Chemical and mineralogical characterization of the leaching residue

The qualitative chemical composition of the leaching residue was obtained by X-ray fluorescence (XRF) using a Philips X-ray Fluorescence Spectrometer (model PW 2400). The mineralogical analysis of the leaching residue was carried out by X-ray diffraction (XRD) using a Philips X-ray Diffractometer (model 115 PW 1710); and also by scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS) using a JEOL Microscopy (model JSM 5410) and a Noram Energy Dispersive Spectrometer (model 648C-1SSS). Analyses of the leaching residue were carried out to identify the main crystalline phases not dissolved in the leaching tests and to support the mineralogical composition of the AOD-L sludge.

## 3. Results and discussion

### 3.1. Chemical composition of the AOD-L sludge

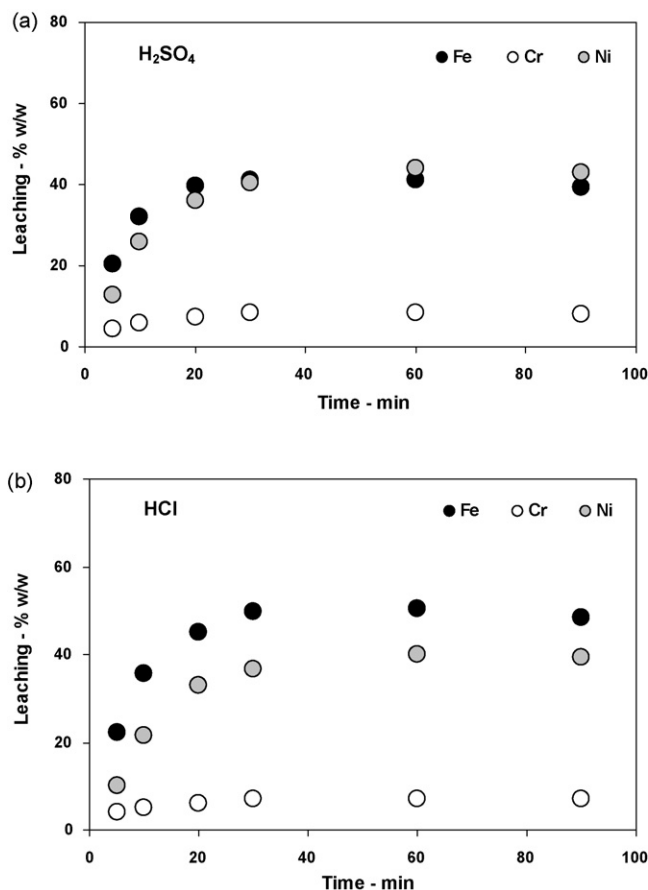
The chemical composition of the dry powder used in this study is shown in Table 1 (elemental form). Further analysis done in a previous work [4] revealed that the primary crystalline phases detected in the AOD-L sludge are chromite ( $\text{FeCr}_2\text{O}_4$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), calcite ( $\text{CaCO}_3$ ), wustite ( $\text{FeO}$ ) and metallic iron (Fe). The results show that there is a relatively high content of iron in the material, so the selective removal of iron over chromium and nickel may be an interesting task. As chromite has a stable lattice, powerful oxidizing agents are required to dissolve it; therefore, the efficiency of the chromium leaching will depend on the chromite dissolution efficiency. As presented in a previous work [4], nickel was found in very fine particles in the AOD-L sludge, probably in the metallic form or associated preferentially with iron and oxygen, which suggest the presence of Ni and Ni–Fe oxides in the material.

### 3.2. Leaching tests

In this study, the AOD-L sludge was leached to preferentially remove iron aiming to reduce the volume of sludge to be treated, and also to concentrate chromium and nickel in the solid phase. The results were analyzed in order to identify the effects of the variables temperature and acid concentration ( $\text{H}_2\text{SO}_4$  and HCl) on the leaching of Fe, Cr and Ni from the AOD-L sludge. The discussion shown as follows is supported by the chemical and mineralogical composition of the leaching residue (Section 3.3).

#### 3.2.1. Leaching of iron, chromium and nickel from the AOD-L sludge

Firstly, the time of leaching was assessed in a preliminary investigation carried out at intermediate level conditions (6%, v/v, of  $\text{H}_2\text{SO}_4$  and HCl as leaching solutions, at 55 °C). The leaching of Fe,



**Fig. 2.** Leaching of iron, chromium and nickel from the AOD-L sludge with time at 55 °C: (a)  $\text{H}_2\text{SO}_4$  6% (v/v), and (b) HCl 6% (v/v).

Cr and Ni from the AOD-L sludge with time is shown in Fig. 2a and b for  $\text{H}_2\text{SO}_4$  and HCl leaching solutions, respectively. For both acids, the leaching rate of metals increased with time reaching a plateau within 30 min, approximately. Also for both acids, Fe and Ni were leached more easily than Cr. The low dissolution of Cr (below 9%, w/w) may be attributed to the low dissolution of chromite ( $\text{FeCr}_2\text{O}_4$ ) in the investigated experimental conditions. It can be noticed that the leaching of Fe was quite faster in the HCl solution. Therefore, according to these results and considering that tests were done at intermediate levels of temperature and acid concentration, it was selected a leaching time of 60 min for the continuing study.

The leaching of iron from the AOD-L sludge using  $\text{H}_2\text{SO}_4$  and HCl solutions as leaching agents are shown in Fig. 3a and b, respectively, as function of temperature and acid concentration. For both leaching agents, the increase on the temperature as well as on the acid concentration favored the leaching of Fe, which varied from 16.4 to 41.1% (w/w) with  $\text{H}_2\text{SO}_4$  and from 15.5 to 49.9% (w/w) with HCl solutions and, thus, the leaching of Fe was found relatively higher with HCl. The increase on temperature influenced positively the dissolution reaction kinetics of soluble iron phases present in the AOD-L sludge like wustite ( $\text{FeO}$ ) and metallic Fe (as evidenced in Sections 3.2.2 and 3.3.2), besides the dissolution of other Fe-bearing phases present in the material in minor amount. Also, the increase on the quantity of reagent into the solution favored the reaction rate. Both behaviors were expected being these however limited by the amount of soluble Fe phases in the AOD-L sludge. Possible dissolution reactions for the soluble Fe phases at the investigated experimental conditions, considering the low concentration

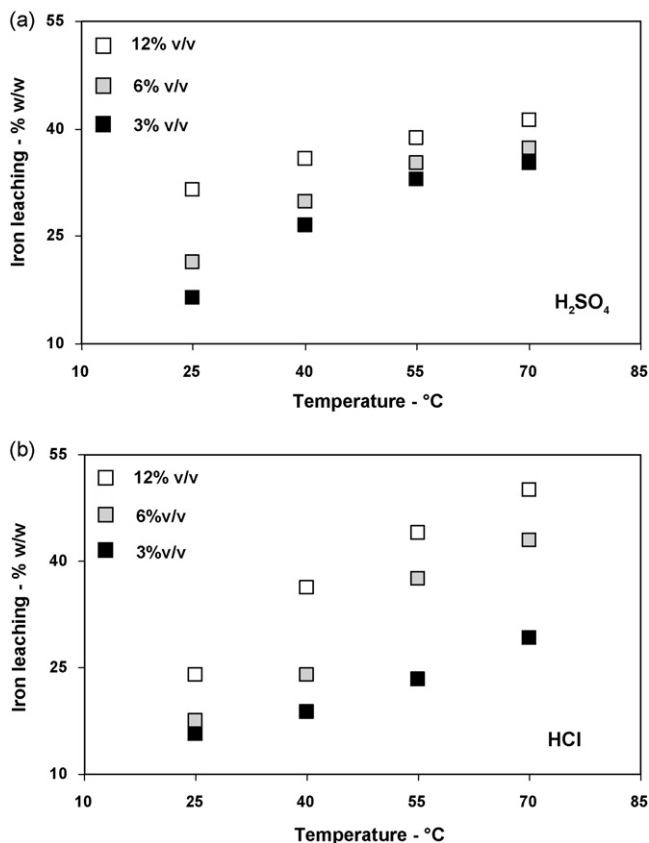
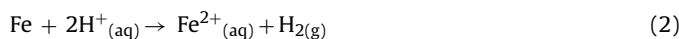
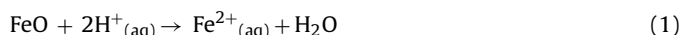


Fig. 3. Leaching of iron from the AOD-L sludge as a function of temperature and acid concentration ( $t = 1$  h): (a) H<sub>2</sub>SO<sub>4</sub> and (b) HCl.

of dissolved oxygen into the solution, may be expressed as:



As shown in Fig. 4a and b, a similar behavior was verified for the leaching of chromium from the AOD-L sludge with H<sub>2</sub>SO<sub>4</sub> and HCl leaching agents, respectively, for the temperature and acid concentration levels investigated in this study. However, the dissolution of Cr was comparatively lower than those obtained for Fe. In all cases, the leaching of Cr was below 9% (w/w): it varied from 3.4 to 8.3% (w/w) with H<sub>2</sub>SO<sub>4</sub> and from 2.7 to 6.9% (w/w) with HCl. Such results can be explained by the high stability of the FeCr<sub>2</sub>O<sub>4</sub> phase, which was not significantly dissolved at the studied experimental conditions (vide Section 3.3.2); and the small quantity of soluble Cr-bearing phases present in the material, which are not detected by XRD. The results still point out that relatively more Cr was leached with H<sub>2</sub>SO<sub>4</sub> solutions, so it seems more appropriate to use HCl to selectively remove Fe over Cr from the AOD-L sludge.

The leaching of nickel from the AOD-L sludge with H<sub>2</sub>SO<sub>4</sub> or HCl is shown in Fig. 5a and b, respectively, at changing temperature and acid concentration. As verified to Fe and Cr, the leaching of Ni also increased with the increase of the temperature and acid concentration levels. The dissolution of Ni varied from 28.0 to 43.9% (w/w) with H<sub>2</sub>SO<sub>4</sub> and from 25.1 to 40.0% (w/w) with HCl solutions. It suggests that there are possibly two Ni phases in the AOD-L sludge: (1) soluble phases such as metallic Ni as well as other soluble Ni phases like nickel oxide (NiO); and (2) insoluble Ni-bearing phases probably found as Ni-Fe and/or Ni-Cr oxide, or even Ni-Fe and/or Ni-Cr alloys formed into the AOD-L converter. Similarly to Cr, relatively more Ni was leached with H<sub>2</sub>SO<sub>4</sub> solution, so HCl was found to

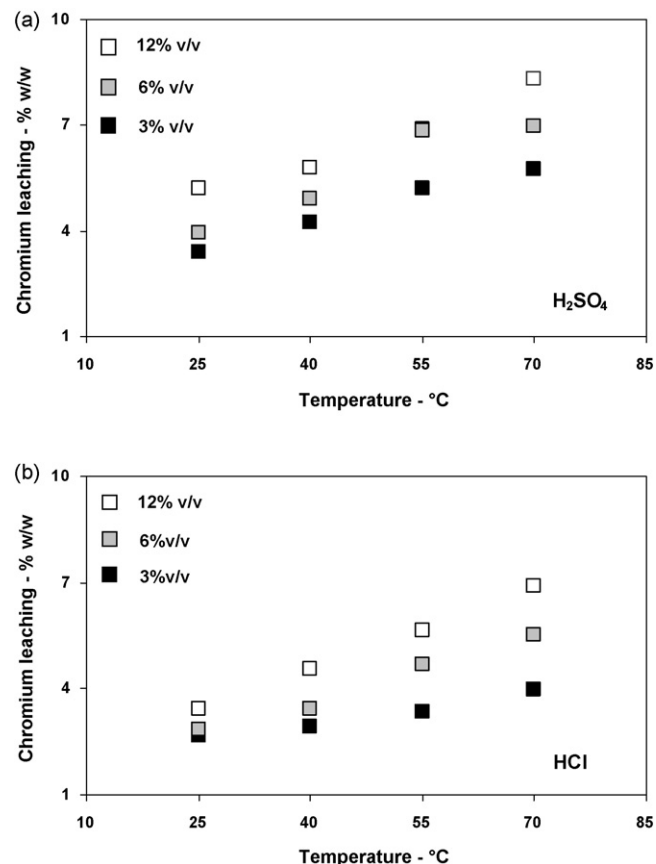
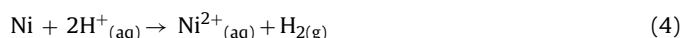
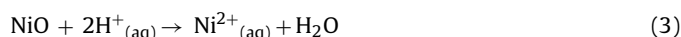


Fig. 4. Leaching of chromium from the AOD-L sludge as a function of temperature and acid concentration ( $t = 1$  h): (a) H<sub>2</sub>SO<sub>4</sub> and (b) HCl.

be more adequate to selectively remove Fe over Ni from the sludge. Possible dissolution reactions for the soluble Ni phases at the investigated experimental conditions, considering the low concentration of dissolved oxygen into the solution, may be expressed as:



In order to evaluate the effect of the variables temperature and acid concentration of H<sub>2</sub>SO<sub>4</sub> and HCl on the leaching of Fe, Cr and Ni from the fine fraction of the AOD-L sludge, the experimental results were fitted to the following empirical equation:

$$\%M = a + b \left( \frac{T}{T_{\text{max}}} \right)^c \left( \frac{C}{C_{\text{max}}} \right)^d \quad (5)$$

where %M represents the percent of metal leached (Fe, Cr, or Ni) (in w/w),  $T$  is the temperature (in °C),  $C$  is the acid concentration (in %, v/v), the subscript max represent the maximum value of operational variable, and the parameters  $a$ ,  $b$ ,  $c$  and  $d$  are constants to be obtained by data fitting. Table 2 summarizes the fitting results obtained using the software Statistica® (version 6.0), including the coefficient of determination  $R^2$ . In the calculations, the Quasi-Newton estimation method was used to minimize the loss function which was defined as the summation of the squared difference between experimental and calculated values. According to the fitting results shown in Table 2, the  $R^2$  values for Fe and Ni in the H<sub>2</sub>SO<sub>4</sub> medium and for Ni in the HCl system was somewhat lower than the expected level of 95% of confidence. The effect of temperature was found to be more significant than those exhibited by the acid concentration, as the  $c/d$  ratio was always higher than

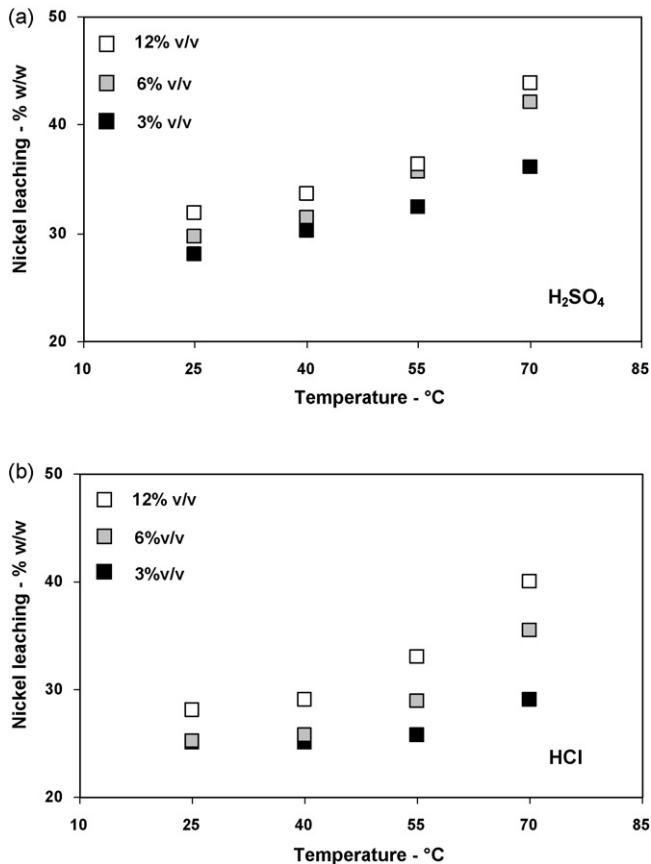


Fig. 5. Leaching of nickel from the AOD-L sludge as a function of temperature and acid concentration ( $t = 1$  h): (a) H<sub>2</sub>SO<sub>4</sub> and (b) HCl.

unity independently of the leaching agent used and for all metals evaluated. When the parameter  $c$  is evaluated separately it can be observed that the effect of the variable temperature on the leaching of iron is slightly higher with HCl. In addition, a higher amount of Fe was leached with HCl (see parameter  $b$ ), while more Cr and Ni were leached using H<sub>2</sub>SO<sub>4</sub> as leaching agent. Therefore, the use of HCl was found more adequate to obtain a better removal of Fe over Cr and Ni from the AOD-L sludge, as previously mentioned.

However, it is essential to note that the acid concentration levels discussed here (volumetric concentrations) are not comparable when molar concentrations are considered (e.g., in the leaching tests carried out at 6%, (v/v) solutions, the molar concentration of H<sub>2</sub>SO<sub>4</sub> and HCl is around 0.6 and 1.7 mol/L, respectively). Thus, the higher dissolution of Fe phases (primarily Fe oxides, the most abundant phases) with HCl could be associated to the higher concentration of free hydrogen ions into the solution and a greater dependence of the Fe oxides reaction rate with the hydrogen ion activity in HCl media than in H<sub>2</sub>SO<sub>4</sub> media. In addition, it is well known that sulfuric acid is diprotic and ionizes to bisulfate (HSO<sub>4</sub><sup>-</sup>)

Table 2  
Fitting coefficients of Eq. (5)

Acid medium	Metal	$a$	$b$	$c$	$d$	$R^2$
H <sub>2</sub> SO <sub>4</sub>	Fe	0	43.6	0.5	0.2	0.88
	Cr	0	8.2	0.5	0.2	0.95
	Ni	0	41.9	0.3	0.1	0.88
HCl	Fe	0	52.6	0.7	0.4	0.96
	Cr	1.8	5.2	1.1	0.6	0.98
	Ni	24.5	16.0	2.4	0.8	0.94

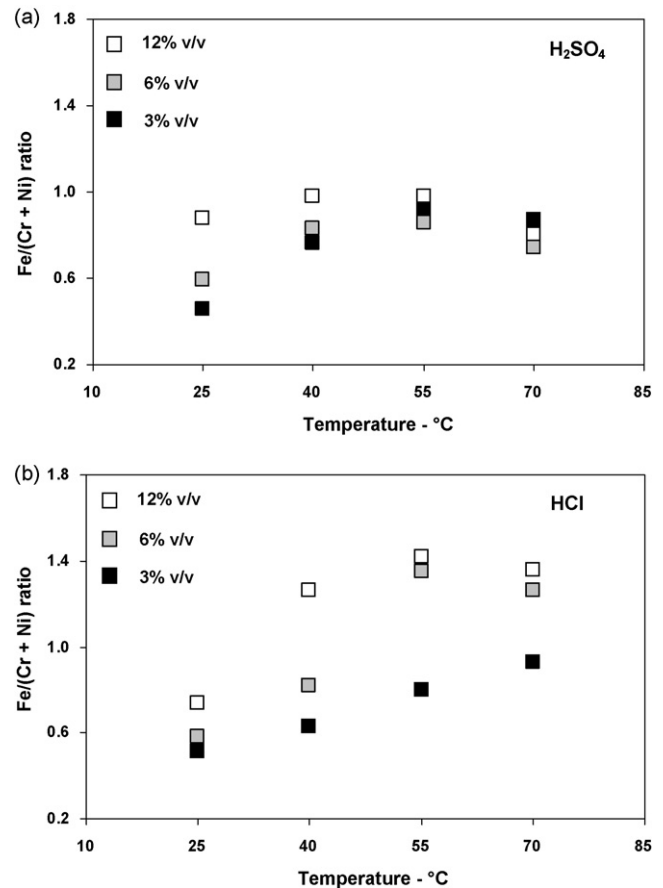
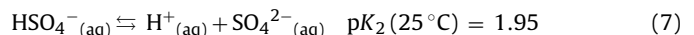
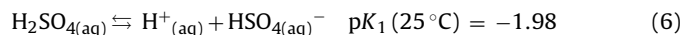


Fig. 6. Variation of the Fe/(Cr + Ni) ratio as a function of temperature and acid concentration ( $t = 1$  h): (a) H<sub>2</sub>SO<sub>4</sub> and (b) HCl.

and sulfate (SO<sub>4</sub><sup>2-</sup>) ions. While the first ionization is almost complete (Eq. (6)) in the acid conditions of the preliminary leaching tests (for all tests, the pH varied between 0 and 1), the second ionization (Eq. (7)) is incomplete.



The efficiency of the leaching step for the selective removal of Fe over Cr and Ni from the AOD-L sludge can be also evaluated using the parameter Fe/(Cr + Ni) ratio. In this case, the leaching operation will be as more selective for Fe as higher is the value of the Fe/(Cr + Ni) ratio. Fig. 6 shows the variation of this parameter as function of the temperature and acid concentration levels for H<sub>2</sub>SO<sub>4</sub> and HCl solutions. As verified previously, leaching is not feasible to separate Fe when H<sub>2</sub>SO<sub>4</sub> is used as reagent because the Fe dissolution is relatively lower compared to those obtained with HCl, while the dissolution of Ni and Cr are relatively higher. The opposite behavior was verified with HCl, so higher Fe/(Cr + Ni) ratios were obtained thus indicating that a more selective removal of Fe is obtained with HCl. For this reagent, the selectivity for Fe increased with temperature and acid concentration, reaching a maximum value at 55 °C and 6–12% (v/v) of HCl. The decrease of the Fe/(Cr + Ni) ratio at 70 °C with both leaching solutions occurred due to the increase on the leaching of Ni at this condition.

Hence, the preferential dissolution of Fe phases which are soluble in moderate operational conditions might be advantageous to reduce the volume of solid to be treated, and also to concentrate Cr and Ni in the solid phase. According to the results obtained in

this study with HCl 12% (v/v) and 70 °C, up to nearly 50% (w/w) of Fe was leached from the sludge in one single leaching step, with relatively low dissolution of Cr (around 7%, w/w). In this condition, the volume of sludge was reduced 2/3 from the initial one. However, Ni dissolution was considered high (around 40%, w/w) and it can possibly make this preliminary step not attractive from the economical viewpoint. Actually, nickel is the metal of higher commercial value contained in the AOD-L sludge and its separation from the Fe-rich liquor (around 0.2 g/L Ni and 6.0 g/L Fe) will require additional treatment. Another disadvantage that can be related to this leaching step for selective removal of Fe is the high consumption of acid for the investigated pulp density. Thus, aiming to reduce the acid consumption and to investigate the influence of the pulp density on the leaching of the AOD-L sludge, some investigative tests carried out at solid/liquid ratios of 1/15 and 1/5 g/mL were done. Basically, the process becomes more selective with the increase in the pulp density, but leaching of Fe decrease. Best results were 37.6% (w/w) Fe, 6.8% (w/w) Cr and 28.0% (w/w) Ni at 1/15 g/mL; and 20.5% (w/w) Fe, 1.8% (w/w) Cr and 11.5% (w/w) Ni at 1/5 g/mL.

### 3.2.2. Analysis of the leaching solution

The analysis of the leaching solution was done in the liquor obtained after leaching the AOD-L sludge with HCl 12% (v/v) at 70 °C. This operational condition was selected due to the relatively higher removal of Fe (nearly 50%, w/w) associated to low dissolution of Cr (around 7%, w/w). In addition, the weight of the AOD-L sludge residue was reduced 66% (w/w). The Fe speciation in the liquor (pH ≈ 1) was determined by titration with  $\text{KMnO}_4$  and it consists of around 83% of  $\text{Fe}^{2+}$  (or 5.0 g/L) and 17% of  $\text{Fe}^{3+}$  (or 1.0 g/L). The higher concentration of  $\text{Fe}^{2+}$  in this liquor suggests the dissolution of wustite ( $\text{FeO}$ ), which is present in the sludge in large amount, and metallic Fe (possibly according to Eqs. (1) and (2)), as well as other minor  $\text{Fe}^{2+}$ -bearing phases. On the other hand, the lower concentration of  $\text{Fe}^{3+}$  suggests the dissolution of  $\text{Fe}^{3+}$ -bearing phases present in the material in minor amount as hematite ( $\text{Fe}_2\text{O}_3$ ) and mixed phases containing Fe and Ca.

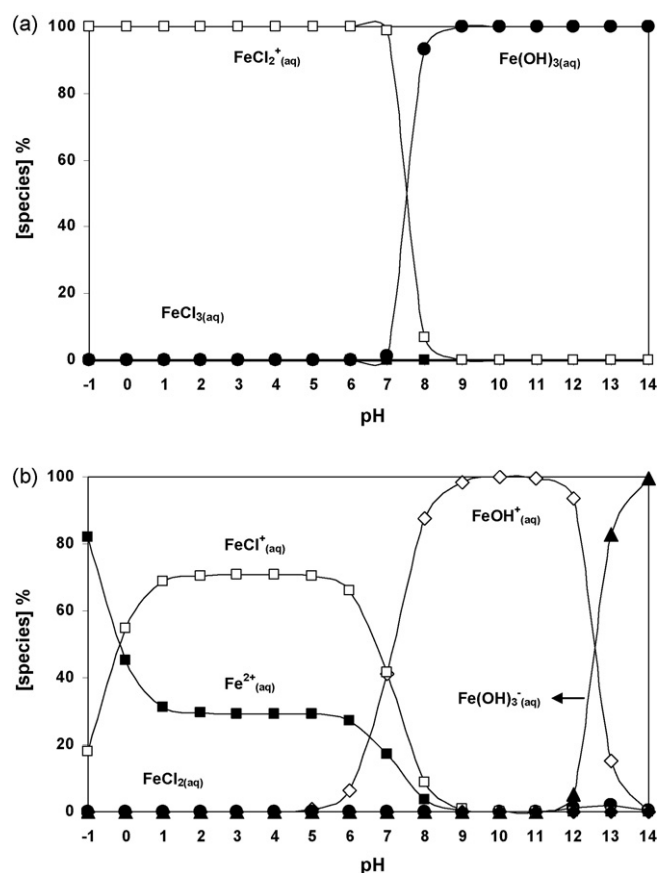
In function of the preferential dissolution of Fe phases with HCl 12% (v/v) at 70 °C may be advantageous to reduce the volume of solid to be treated, and to concentrate Cr in the solid phase, which can be recovered under pressure leaching conditions. Being interesting to include this preliminary step in the hydrometallurgical treatment route of the AOD-L sludge, it is necessary to consider the complexity of the liquor generated in order to treat it aiming to recover Fe. Thus, species distribution diagrams were evaluated in order to identify the most stable  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  aquo-complex species in the leaching solution and also to speculate how this metal can be recovered from it. The equilibrium constants used in this study are reported in Table 3. The formation of solid phases was not considered and the effects of the ionic strength were negligible. Species distribution diagrams for (a) Fe(III)-chloride-water, and (b) Fe(II)-chloride-water systems at 25 °C are shown in Fig. 7. The total concentration of chloride into the solutions was considered to be 3.5 mol/L (or HCl 12% (v/v) solution). As this solution was strongly acidic, the concentration of hydroxyl ions in the pH range studied (around 0 and 1) was negligibly small compared to that of dissociated ligands from the leaching agent, so no hydroxo-complex species exists in the solution (or it exists at negligible concentration). For the Fe(III)-chloride-water system (Fig. 7a), it can be seen that  $\text{FeCl}_2^+(\text{aq})$  is the predominant complex species in the pH range studied, and, except for  $\text{FeCl}_3(\text{aq})$  which may exist at very low concentrations, no other complex is supposed to co-exist in the liquor. For the Fe(II)-chloride-water system (Fig. 7b),  $\text{FeCl}^+(\text{aq})$  is the predominant complex species in the pH range studied; however,  $\text{Fe}^{2+}(\text{aq})$  ions can also exist mainly at very acidic conditions (pH < 0). Therefore, based on such calculations, it seems reason-

**Table 3**

Formation reactions of the Fe(III) and Fe(II) aquo-complexes and their complex formation constants at 25 °C (HSC Chemistry®, version 4.0)

Reactions	log k
$\text{Fe}^{3+}(\text{aq}) + \text{Cl}^-(\text{aq}) = \text{FeCl}^{2+}(\text{aq})$	1.48
$\text{FeCl}^{2+}(\text{aq}) + \text{Cl}^-(\text{aq}) = \text{FeCl}_2^+(\text{aq})$	12.75
$\text{FeCl}_2^+(\text{aq}) + \text{Cl}^-(\text{aq}) = \text{FeCl}_3(\text{aq})$	-16.37
$\text{Fe}^{3+}(\text{aq}) + \text{H}_2\text{O} = \text{Fe}(\text{OH})^{2+}(\text{aq}) + \text{H}^+(\text{aq})$	-4.38
$\text{Fe}^{3+}(\text{aq}) + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2^+(\text{aq}) + 2\text{H}^+(\text{aq})$	-9.39
$\text{Fe}^{3+}(\text{aq}) + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{aq}) + 3\text{H}^+(\text{aq})$	-9.02
$\text{Fe}^{3+}(\text{aq}) + 4\text{H}_2\text{O} = \text{Fe}(\text{OH})_4^-(\text{aq}) + 4\text{H}^+(\text{aq})$	-27.77
$\text{Fe}^{2+}(\text{aq}) + \text{Cl}^-(\text{aq}) = \text{FeCl}^+(\text{aq})$	-0.16
$\text{FeCl}^+(\text{aq}) + \text{Cl}^-(\text{aq}) = \text{FeCl}_2(\text{aq})$	-8.01
$\text{Fe}^{2+}(\text{aq}) + \text{H}_2\text{O} = \text{Fe}(\text{OH})^+(\text{aq}) + \text{H}^+(\text{aq})$	-6.62
$\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2(\text{aq}) + 2\text{H}^+(\text{aq})$	-20.48
$\text{Fe}^{2+}(\text{aq}) + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3^-(\text{aq}) + 3\text{H}^+(\text{aq})$	-31.88

able to assume that the more stable Fe aquo-complex species in the HCl 12% (v/v) solution are  $\text{FeCl}_2^+(\text{aq})$ ,  $\text{Fe}^{2+}(\text{aq})$  and  $\text{FeCl}^+(\text{aq})$ . The presence of the complexing ligand  $\text{Cl}^-$  modifies the solubility of ferric and ferrous ions in the aqueous phase. Theoretically, below the supersaturation condition, the larger is the concentration of chloride ions in solution the larger is the solubility of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions. It can be evidenced by the increase on the precipitation pH of solid compounds, e.g., ferric hydroxide  $\text{Fe}(\text{OH})_3$  and ferrous hydroxide  $\text{Fe}(\text{OH})_2$ . As a result, the recovery of Fe from the leaching solution as hydroxides is not interesting essentially due to (i) the largest consumption of precipitation agent to raise the aqueous pH, (ii) difficulty of recycle the hydrochloric acid in the leaching process, and (iii) the lower value of such compounds. However, the precipitation of iron as hematite [16,17] or ferric/ferrous chlorides by physical



**Fig. 7.** Species distribution diagrams for (a) Fe(III)-chloride-water and (b) Fe(II)-chloride-water systems, at 25 °C;  $[\text{Cl}]_{\text{T}} = 3.5 \text{ mol/L}$ ; and  $[\text{Fe}]_{\text{T}} = 0.1 \text{ mol/L}$ .

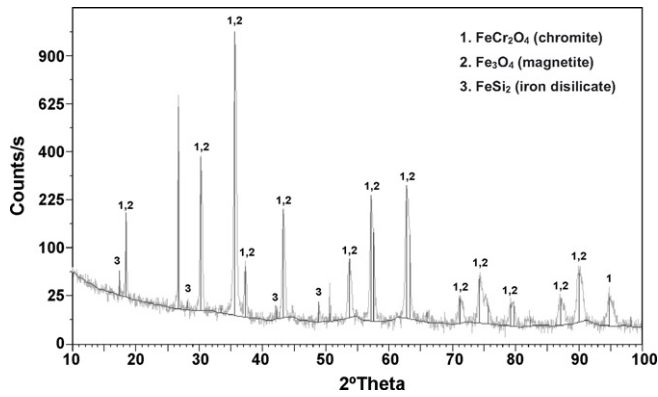


Fig. 8. XRD analysis of the leaching residue after dissolution of the AOD-L sludge with HCl 12% (v/v) at 70 °C ( $t=1$  h).

process (or crystallization) [18] from the chloride solutions may be an attractive operation because a final product having better quality and higher commercial value can be obtained. The application of such alternatives methods to recover Fe from the liquor requires further studies and the certainty that the preliminary step will be implemented.

### 3.3. Characterization of the leaching residue

Chemical and mineralogical analyses of the leaching residue were carried out after leaching the AOD-L sludge with HCl 12% (v/v) at 70 °C. As mentioned previously, the residue obtained on these operational conditions was chosen to be analyzed due to the relative high removal of Fe (nearly 50%, w/w) and low dissolution of Cr (around 7%, w/w). Thus, the weight of the AOD-L sludge was reduced 66% (w/w) and Cr was concentrated in the solid phase.

#### 3.3.1. Chemical analysis

The chemical analysis by XRF indicated that Fe, Cr and O are the main elements present in the leaching residue, followed by Ni and Mn which were identified with an intermediate intensity peak. Other species were found to be present in minor quantities as verified by lower intensity peaks in the XRF results such as Mg and Si. The XRF analysis indicated also traces of Ca, Al, Cu, Zn, Na, K, P, Mo, V and Cl in the sample. In comparison to the chemical analysis of the AOD-L sludge before leaching [4], a significant reduction in the intensity peak for Ca was verified and this is associated to the high solubility of calcite ( $\text{CaCO}_3$ ) in acidic solutions. The results obtained by XRD (vide Section 3.3.2) also support the dissolution of calcite in the experimental conditions studied.

#### 3.3.2. Mineralogical analysis

The XRD patterns of the leaching residue are shown in Fig. 8. The following crystalline phases were identified: chromite ( $\text{FeCr}_2\text{O}_4$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and iron disilicate ( $\text{FeSi}_2$ ). The peaks reported for  $\text{FeCr}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  on the diffractogram are overlapped which may be explained by their similar crystalline net. These spinel group minerals are predominant in the analyzed sample and this suggests that these are chemically stable in the leaching conditions. Chromite has a crystalline structure that is normally difficult to leach [19–21] and, therefore, the results obtained in the leaching tests for the dissolution of Cr are due to the resistance of this mineral phase to the acid attack. The presence of  $\text{Fe}_3\text{O}_4$  and  $\text{FeSi}_2$  (reducing agent used during the refining of the stainless steel in the AOD-L converter) in the leaching residue may be associated to its low dissolution in the conditions studied. The peak at 26.5° corresponds to the main peak of graphite, but as only this peak

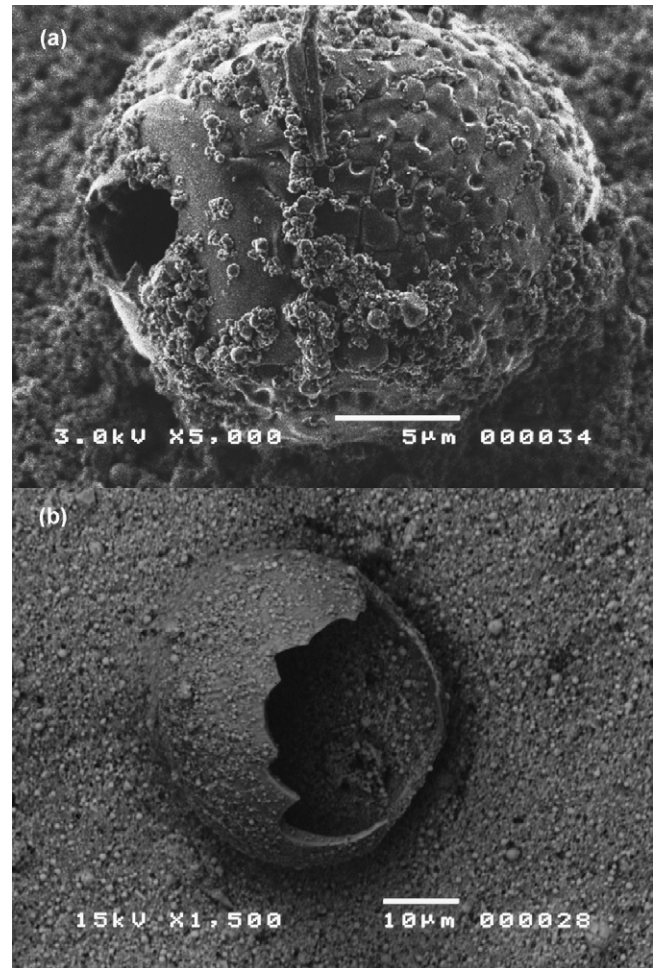


Fig. 9. SEM analysis of the leaching residue.

was identified it was not possible to confirm the presence of this phase by XRD. As mentioned earlier, no peak of the  $\text{CaCO}_3$  phase was detected in the leaching residue. Likewise, the characteristic peaks of wustite ( $\text{FeO}$ ) and metallic iron ( $\text{Fe}$ ) were not identified. Thus, the Fe removal from the AOD-L sludge during the leaching tests could be explained by the solubility of these phases in the leaching solutions, besides the dissolution of others Fe-bearing phases present in minor amount. Also, peaks of Ni phases were not identified by XRD analysis in the leaching residue. The detection of Ni–Fe and Ni–Cr phases (also classified as spinel group minerals) was not possible, probably due to the overlap of peaks from  $\text{FeCr}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  phases as well as their low concentration in the analyzed sample. Therefore, the presence of nickel in the leaching residue could not be assessed by XRD analysis, but particles containing Ni were identified by SEM/EDS analysis.

A typical micrograph of particles present in the leaching residue obtained by SEM/EDS is shown in Fig. 9. Preferential sites of dissolution are observed in the particle shown in Fig. 9a, besides the presence of agglomerates of fine particles stuck on its surface. The presence of such agglomerates may indicate the existence of magnetic attraction of such particles, thus supporting the hypothesis of agglomeration of particles discussed in the granulometric analysis of the AOD-L sludge [4]. A micrograph of a large hollow particle whose composition corresponds to the stainless steel bath (mainly Fe and Cr) is shown in Fig. 9b. The constituent particles of the leaching residue have predominantly spherical format (similarly to the AOD-L sludge) and this shape is in agreement with the

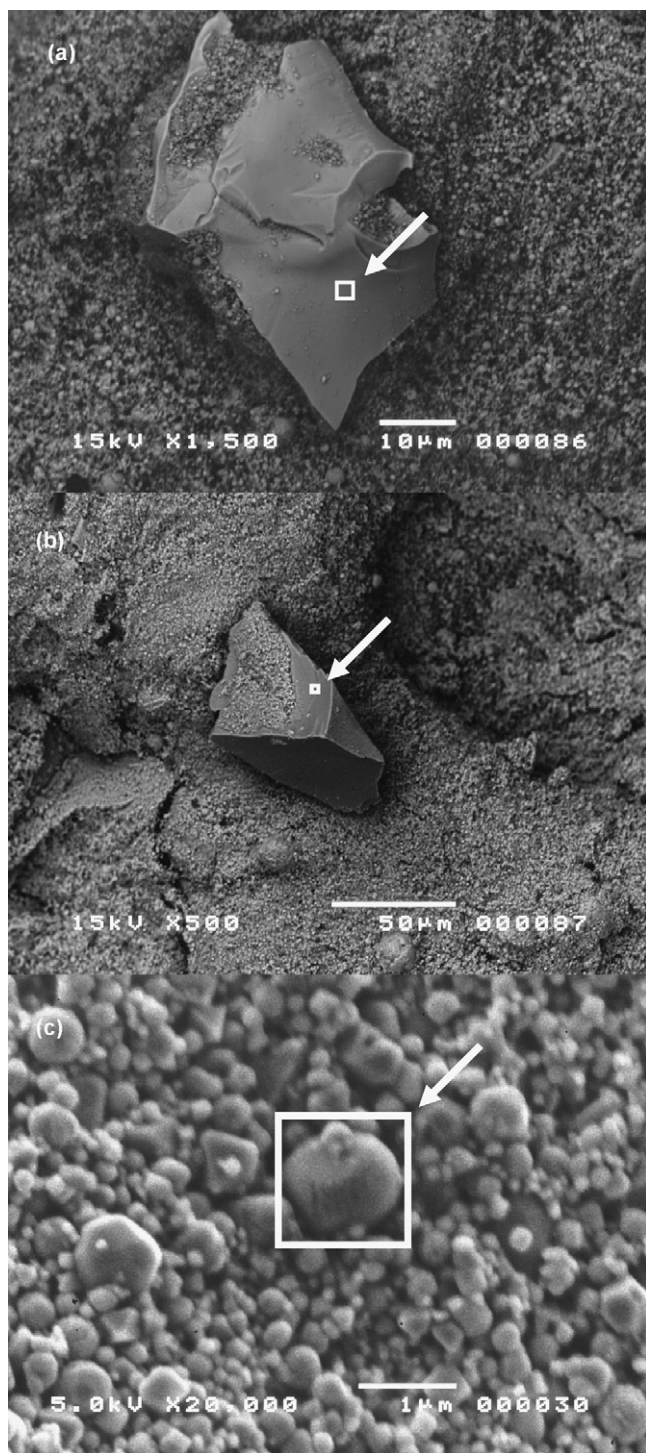


Fig. 10. SEM analysis of the leaching residue and selected areas.

main generation mechanism of dusts inside the AOD-L converter, i.e., the ejection of metal droplets by bursting of bubbles at the metallic bath surface [22]. A comprehensive discussion of the generation mechanism of dusts inside the AOD-L converter is beyond the scope of the present study, but we believe that the presence of such hollow particles (coarse or fine ones) in the leaching residue is associated to the generation mechanism of dusts. However, it would not be impossible that the presence of some hollow particles would be associated to the dynamics of their dissolution.

Table 4

EDS analysis of areas 1–3 (in %, w/w) identified in Fig. 10

Element	Area 1	Area 2	Area 3
Fe	23.7	42.7	67.1
Cr	75.9	1.0	12.3
Si	0.4	56.2	0.6
Ni	–	–	19.3

Others micrographs of particles present in the leaching residue are shown in Fig. 10. Some coarse irregular particles (Fig. 10a and b) were identified in the leaching residue as well, and according to these images these particles are resistant to the leaching conditions studied which can be observed by their smooth surfaces (not attacked). Table 4 presents the EDS analysis of areas 1–3 as identified in Fig. 10. In area 1 (Fig. 10a), the irregular particle contains predominately Fe and Cr, probably as Fe–Cr alloy. In area 2 (Fig. 10b), the irregular particle contains predominately Fe and Si, probably as  $\text{FeSi}_2$  or Fe–Si alloys. These particles are stainless steel-making materials not processed or even directly sucked into the off gas pipe line during its loading into the AOD-L converter. Finally, in area 3 (Fig. 10c), the small particle contains predominately Fe, Ni, Cr and O. In this study, Ni was again detected in fine particles (particle size around  $1\ \mu\text{m}$ ), and preferentially associated to Fe, Cr and O, probably as Ni–Fe and/or Ni–Cr oxides. In contrast, the presence of metallic Ni was not detected in the leaching residue what suggests its dissolution in the process.

#### 4. Conclusions

In this paper, the atmospheric leaching of the fine fraction of the AOD-L sludge was investigated using  $\text{H}_2\text{SO}_4$  and HCl as leaching agents in order to selectively remove iron in detriment of chromium and nickel. The main conclusions are:

- For both leaching agents, the leaching of Fe, Cr and Ni increased with the increase of temperature and acid concentration. Higher dissolution of Fe and Ni were obtained in comparison with the dissolution of Cr. This result is possibly associated to the larger dissolution of FeO, NiO, metallic Fe and metallic Ni, and low dissolution of  $\text{FeCr}_2\text{O}_4$  and Fe–Cr alloys;
- The largest selectivity for Fe was observed in the HCl media. At  $70^\circ\text{C}$  and HCl 12% (v/v) as leaching solution, the content of Fe initially present in the AOD-L sludge was reduced around 50% (w/w), while Cr was concentrated in the solid phase (around 110%, w/w). In addition, nearly 40% (w/w) of Ni was dissolved, which can hinder the inclusion of this preliminary step in the processing route of the AOD-L sludge;
- The mineralogical analysis of the leaching residue indicated the presence of  $\text{FeSi}_2$  and Ni associated to Fe, Cr and O, probably as Ni–Fe and/or Ni–Cr oxides, thus, complementing the mineralogical composition of the AOD-L sludge.

The goal of this study was to investigate the preferential removal of Fe from the AOD-L sludge in order to concentrate Cr and Ni in the solid phase, which can be recovered in a sequential leaching step. Based on the experimental results, the problem of sludge treatment still remains as the objectives were only partially fulfilled. Actually, the separation of Fe from the sludge by atmospheric acid leaching seems not interesting as shown by experimental data, so leaching Fe, Cr and Ni under high temperature and pressure conditions might be more promising. Exploratory experiments indicate it is possible to get high recoveries of Cr and Ni associated with low recovery of Fe which is precipitated into the system, but operational and investment cost is high.



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