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# Characterization of the fine fraction of the argon oxygen decarburization with lance (AOD-L) sludge generated by the stainless steelmaking industry

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# Abstract

The argon oxygen decarburization with lance (AOD-L) sludge generated by the stainless steelmaking industry is a hazardous waste due to the presence of chromium. While its coarse fraction is usually recycled into the own industrial process, the fine fraction is normally disposed in landfills. Techniques such as briquetting or magnetic separation were found to be inadequate to treat it for reuse purposes. So, in this work, the fine fraction of the AOD-L sludge was characterized aiming to find alternative methods to treat it. This sludge consists of a fine powder (mean diameter of 1  $\mu$ m) containing  $34 \pm 2\%$  (w/w) of iron,  $10.2 \pm 0.9\%$  (w/w) of chromium and  $1.4 \pm 0.1\%$  (w/w) of nickel. The main crystalline phases identified in this study were chromite (FeCr<sub>2</sub>O<sub>4</sub>), magnetic (Fe<sub>3</sub>O<sub>4</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>) and calcite (CaCO<sub>3</sub>). In the digestion tests, the addition of HClO<sub>4</sub> has favored the dissolution of chromite which is a very stable oxide in aqueous media. Nickel was found in very fine particles, probably in the metallic form or associated with iron and oxygen. The sludge was classified as hazardous waste, so its disposal in landfills should be avoided. © 2007 Elsevier B.V. All rights reserved.

Keywords: Argon oxygen decarburization with lance process sludge; Heavy metals; Hazardous wastes; Characterization

# 1. Introduction

The treatment of industrial wastes constitutes an eco-friendly alternative action that promotes the conscious use of the natural resources with consequent minimization of the environmental impact. As pointed out by Conard [1], the recycle of wastes is important since it may contribute to the benefit of future generations and also to the preservation of raw materials.

Nowadays, the increasing demand for metals has stimulated the development of new technologies worldwide to treat secondary resources like industrial wastes, mainly for those materials that present risks to the public health and/or to the environment if managed in an incorrect way. According to FEAM [2] (the environment agency of the Minas Gerais state, in Brazil), around 830,000 tonnes of hazardous industrial wastes were gen-

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erated in Minas Gerais in a period of 12 months between 2001 and 2002. From this amount, 66.0% was disposed in landfills and only 8.7% was sent to recycling, recovery or any reuse process. In addition, it was reported that 95.0% of the hazardous industrial waste produced in Minas Gerais was generated by the metallurgical sector.

It is well known that industrial plants for the production of primary and stainless steels normally generate a significant amount of wastes such as slag, sludge and dust. In the primary steelmaking production, the dust generated in electric furnaces is classified as hazardous waste due to the presence of chromium and lead [3]. Around 15–20 kg of dust is generated per ton of primary steel produced in the electric arc furnace [4]. In order to reuse it, dust can be incorporated into components for civil construction or used as an additive material for the production of ceramics. Additional application includes agglomeration of dust to charge furnaces. Some works have been found in the literature on the characterization of primary steel dusts and alternatives routes aiming to treat such wastes using pyro and/or

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hydrometallurgical processes in order to recover iron, zinc and lead were also proposed [5–10].

Considering the hazardous wastes generated by the stainless steelmaking processes, around 10-20 kg of dust is generated per ton of stainless steel produced in the electric arc furnace [11]. Such material contains iron, chromium and nickel, and it is normally classified as hazardous waste due to the presence of chromium. Magnetite (Fe<sub>3</sub>O<sub>4</sub>) was found to be the main phase present in such material together with chromite (FeCr<sub>2</sub>O<sub>4</sub>), while nickel was identified as Fe–Ni oxide [11] or mainly in the metallic form [12]. Treatment routes based on physical methods (gravity and magnetic separations) and pyrometallurgical processes aiming to recover metal values from stainless steel dusts were also found elsewhere [11–17]. Nickel recoveries up to 40% were obtained by gravity separation and up to 50% by magnetic separation. However, nothing has been found on the recovery of chromium from such wastes.

Particularly for the stainless steelmaking industry, the waste generated in the argon oxygen decarburization with lance converter (AOD-L) is also classified as a hazardous material [12]. Such converter is equipped with a gas-cleansing system and dust is removed from the exhausted gases during the atmospheric emissions control by a wet scrubber. A considerable amount of sludge is normally generated which is typically classified into a coarse fraction (around 40%, w/w) and a fine fraction (around 60%, w/w) with mean particle diameters of 100 and  $1 \,\mu m$ , respectively. The coarse fraction can be fed back into the smelting furnace after agglomeration by briquetting but the fine fraction does not agglomerate efficiently due to the small size of its particles. In addition, the use of magnetic separation technique to recover iron, chromium and nickel from the fine fraction did not show feasibility [12]. Consequently, the fine fraction of the AOD-L sludge generated in the Minas Gerais state, in Brazil, is fully disposed in landfills [18]. No others works have been found in the literature on the treatment and/or disposal methods of the fine fraction of the AOD-L sludge.

In this context, the purpose of the present study is to characterize the fine fraction of the AOD-L sludge in order to recover metals by a hydrometallurgical processing route. The recovery of iron, chromium and nickel from this material is relevant not only for the environment viewpoint but also important for economical reasons because such metals are widely used in industry. So, in this paper, the investigation was carried out by analyzing the moisture content, granulometry, mineralogical and chemical composition, and toxicity of the AOD-L sludge. A detailed study on the hydrometallurgical route to treat such waste is devoted to a future paper.

# 2. Experimental

#### 2.1. Preliminary treatment of the AOD-L sludge

Wet AOD-L sludge samples generated by a stainless steel company located in the Minas Gerais state, in Brazil, were withdrawn using a proper sampler and according to the proceedings of collecting samples from wastes as recommended by the legislation [19]. After the collection step, the following procedures were adopted to obtain representative samples for the characterization study. Firstly, the AOD-L sludge was dried at 60 °C for 24 h and the moisture content was assessed by weight difference using an analytical balance. Afterwards, the dry sludge was thoroughly homogenized resulting in a fine brown powder. Finally, the powder was successively quartered using a Quantachrome siewing rifler (model SRR5) in order to get samples containing around 1.0 g of the dried powder.

# 2.2. Characterization of the AOD-L sludge

#### 2.2.1. Granulometric analysis

The particle size distribution of the AOD-L sludge was assessed by laser diffraction method using a CILAS (model 1064) Granulometer. Aiming to minimize the magnetic agglomeration of particles present in the sample and to obtain representative particle size, tests A and B were carried out according to the following procedures: (A) granulometric analysis after a preliminary ultrasonic bath for 5 min; and (B) granulometric analysis after a preliminary ultrasonic bath for 5 min and use of the dispersing agent 0.05% (v/v) (NaPO<sub>3</sub>)<sub>6</sub> during the analysis. The results were expressed according to the cumulative percent diameters ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ ) and the mean diameter ( $d_m$ ) calculated by the Eq. (1):

$$d_{\rm m} = \sum_{i} \left[ (c_i - c_{i-1}) \left( \frac{d_i + d_{i-1}}{2} \right) \right] \tag{1}$$

where  $c_i$  is the cumulative percentage for particles with diameter *i* and  $d_i$  is the diameter of particles in microns.

#### 2.2.2. Mineralogical analysis

The mineralogical analysis of the AOD-L sludge was carried out by X-ray diffraction (XRD) using a Philips (model PW 1710) X-ray Diffractometer, and also by scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS) using a JEOL (model JSM 5410) Microscopy and Noram (model 648C-1SSS) Energy Dispersive Spectrometer. The main crystalline phases were identified by XRD analysis, while the morphology and size of particles and their chemical composition were determined by SEM/EDS analysis.

#### 2.2.3. Chemical analysis

The qualitative chemical composition of the AOD-L sludge was obtained by X-ray fluorescence (XRF) using a Philips (model PW 2400) X-Ray Fluorescence Spectrometer. The quantitative chemical composition of the AOD-L sludge was assessed by atomic absorption spectrometry (AAS) using a GBC (model 932 plus) Atomic Absorption Spectrometer.

For the quantitative analysis, the following procedure was adopted to dissolve the AOD-L sludge in aqueous media. Firstly, samples of the AOD-L sludge were digested in a hot plate at 150 °C for 5 h. In this step, the following acid solutions were investigated: aqua regia, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 50% (v/v), and mixtures of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 50% (v/v) and perchloric acid (HClO<sub>4</sub>) 70% (v/v). After digestion, the solutions were vacuum filtered and properly diluted; then, the main elements identified

by XRF analysis were analyzed by AAS. The remaining solid phase not dissolved in the previous step (normally silica) was then roasted in a furnace at 1000 °C for 1 h in a platinum crucible. Later, the residue was digested in a 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.

The digestion procedure was repeated also to evaluate the annual variability on the content of iron, chromium and nickel in the AOD-L sludge generated by the industrial plant. For this attempt, 30 samples were collected in the period of August 2005 to August 2006. All samples were fully dissolved and their metal contents determined by AAS.

## 2.2.4. Toxicity analysis

The standard leaching test toxicity characteristics leaching procedure (TCLP) [20] was adopted in this study to assess the toxicity degree of the AOD-L sludge. It was classified as hazardous or non-hazardous waste based on the overall concentration of chromium in the extract solution.

# 3. Results and discussion

The AOD-L sludge was characterized according to its moisture content, granulometry, metal content, mineralogy and toxicity. The results are shown as follows.

## 3.1. Moisture of the AOD-L sludge

In this study, the mean moisture content of the AOD-L sludge was determined as  $33 \pm 2\%$  (w/w), thus corroborating previous investigations [12,13].

## 3.2. Granulometric analysis of the AOD-L sludge

The particle size distribution results of the AOD-L sludge obtained in tests A and B are shown in Table 1. The use of procedure test B resulted in considerably smaller particle sizes. It can be possibly attributed to the minor magnetic agglomeration of mineral phases presents in the AOD-L sludge such as magnetite (see mineralogical results, Section 3.3). A typical diagram for the particle size distribution of the AOD-L sludge obtained in test B is shown in Fig. 1. According to the cumulative curve, around 90% of the particles are smaller than 2.6  $\mu$ m and 10% are smaller than 0.1  $\mu$ m. The median size (i.e., the diameter value for which the cumulative results are 50%) is 0.5  $\mu$ m, while the mean size calculated for this analysis is 1.0  $\mu$ m.

Contrary to the coarse fraction of the AOD-L sludge, the small size of the fine fraction makes briquetting or agglomeration a difficult task if one desires to reuse such material to load furnaces.

Table 1 Cumulative percent diameters  $(d_{10}, d_{50} \text{ and } d_{90})$  and mean diameter  $(d_m)$  of the AOD-L sludge according to tests A and B

Test	d <sub>10</sub> (μm)	d <sub>50</sub> (μm)	d <sub>90</sub> (µm)	$d_{\rm m}$ (µm)
A	$0.26\pm0.07$	$1.97\pm0.03$	$515\pm0.09$	$2.38\pm0.07$
В	$0.12 \pm 0.01$	$0.57\pm0.03$	$2.63\pm0.02$	$1.04\pm0.02$



Fig. 1. Particle size distribution of the AOD-L sludge (test B).

However, it might be advantageous for leaching operations in order to dissolve the metal content using adequate aqueous solutions because leaching rate is favored by large contact areas as normally found in very fine materials. In addition, no grinding steps are also required. However, filtration difficulties must be taken into account.

## 3.3. Mineralogical analysis of the AOD-L sludge

The XRD results for the mineralogical analysis of the AOD-L sludge are shown in Fig. 2. According to this figure, species are predominantly found as crystalline matter and the following main phases were identified: chromite (FeCr<sub>2</sub>O<sub>4</sub>), magnetite  $(Fe_3O_4)$ , hematite  $(Fe_2O_3)$  and calcite  $(CaCO_3)$ . Such result corroborates previous studies carried out by Correa [12]. Chromite and magnetite are minerals belonging to the spinel group, and chromite has a crystalline structure that is normally difficult to leach [21,22]. The peaks reported for the chromite and magnetite on the diffractogram are overlapped which may be explained by their similar crystalline net. Thus, both phases are present in the analyzed sample and any phase of intermediate composition of the chromite-magnetite solid solution series may be present as well. Peaks of nickel phases were not very clear by XRD analysis, thus indicating that nickel content is relatively low in the analyzed sample. Moreover, the detection of Ni-Fe



Fig. 2. XRD analysis for the AOD-L sludge.

or Ni–Cr oxides was not possible probably due to the overlap of peaks from  $FeCr_2O_4$  and  $Fe_3O_4$  species. Therefore, the presence of nickel phases in the AOD-L sludge could not be assessed by XRD analysis. On the other hand, nickel was identified by SEM/EDS analysis.

Typical micrographs of AOD-L sludge obtained by SEM are shown in Fig. 3. According to these micrographs, the sludge contains very fine particles (smaller than 1  $\mu$ m), thus corroborating the results from the granulometric analysis (Section 3.2). The presence of agglomerates of ultra fine particles possibly due to the magnetic agglomeration of phases such as magnetite, and the presence of agglomerates of fine particles likely formed by low-



Fig. 3. SEM analysis of the AOD-L sludge and the selected areas.

temperature agglomeration (e.g., in filters), were also observed by MEV analysis. The predominance of spherical particles is shown in Fig. 3. This shape is in agreement with the main generation mechanism of dusts inside the AOD-L converter, i.e., the ejection of metal droplets due to the impact of the oxygen bubble jet from the lance at the liquid metal surface [23]. Some irregular particles (more coarse particles) were identified in the micrographs as well. These particles may be stainless steelmaking materials not processed in the electric arc furnace or even directly sucked into the off gas pipe line during its loading into the converter.

Table 2 presents the EDS analysis of areas 1–8 as identified in Fig. 3. Oxygen is practically distributed along all the selected particles, which may suggest the presence of metal–oxygen structural form species. In areas 1 and 7, the particles contain predominately iron and chromium, and their composition is similar to the majority of the particles analyzed by EDS. In area 2, the small particle which covers the larger one is very fine and nickel is present in a high amount, probably in the metallic form. SEM/EDS analysis also showed that nickel is present in the analyzed sample associated with iron and oxygen (area 3), which may suggest the presence of Ni–Fe oxide.

With respect to the irregular particles (areas 5 and 8), these generally constituted of chromium and iron, probably as Fe–Cr alloy. By EDS analysis, it can be observed that calcium also seems to be present in the AOD-L sludge in two types of particles: (i) in association with iron and oxygen as shown in area 6, which may suggest the presence of Fe–Ca oxide; and (ii) in association with magnesium and oxygen as shown in area 4, which may suggest the existence of Ca–Mg oxide. The presence of particles with a high content of iron and silicon was also observed by EDS analysis. However, phases containing such associated elements (Fe–Ca–O, Ca–Mg–O, and Fe–Si) were not detected by XRD analysis possibly due to their low concentration in the analyzed sample.

# 3.4. Chemical analysis of the AOD-L sludge

The chemical analysis by XRF indicated that iron and oxygen are the main elements present in the AOD-L sludge, followed by chromium which was 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 calcium, magnesium, manganese, silicon and nickel. The XRF analysis indicated also traces of aluminum, copper, sodium, potassium, molybdenum, cobalt and vanadium in the sample.

The quantitative composition was assessed by AAS analysis and results are shown in Table 3 in the elemental form. It can be observed that the AOD-L sludge contains mainly iron and chromium (around 34.0% (w/w) and 10.2% (w/w), respectively), thus corresponding to approximately 45% (w/w) of the analyzed samples. The nickel content is comparatively lower, around 1.4% (w/w), but it is similar to the content of nickel normally verified in the Brazilian lateritic nickel ores [24], which are iron-rich nickel limonite ore containing 1–2% (w/w) of nickel bound in goethite.

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Area 7	Area 8
Fe	76.0	0.7	22.9	8.5	26.1	42.3	61.9	33.1
Cr	18.4	0.4	1.5	1.5	71.9	5.7	17.3	65.3
Ca	0.9	0.4	0.9	54.1	1.3	31.9	11.0	0.7
Mg	0.3	_	5.2	29.3	0.1	15.4	2.3	_
Mn	0.5	_	0.8	1.1	0.3	1.3	2.7	0.7
Si	0.7	0.3	0.5	5.5	0.3	2.3	1.4	0.1
Ni	2.9	98.1	68.1	-	-	1.1	3.3	_

Table 2 EDS analysis of areas 1-8 (in %, w/w) identified in Fig. 3

Fig. 4 shows the annual variability of the iron, chromium and nickel contents in the AOD-L sludge generated by the industrial plant from August 2005 to August 2006. According to these relative frequency diagrams, the annual variability of iron and chromium are nearly symmetrical. As shown in Fig. 4(A) and (B), around 80% of the analyzed samples contain iron ranging from 27 to 39% (w/w) and nearly 60% of the samples contain chromium ranging from 8.5 to 10.5% (w/w), respectively. From the statistical viewpoint, the annual variability for iron and chromium contents are  $33 \pm 9\%$  (w/w) and  $9 \pm 3\%$  (w/w), respectively, including 95% of the confidence interval. Thus, as the industrial plant produces stainless steels with a varied chemical composition, the contents of these metals in the AOD-L sludge changes according to the type and to the amount of stainless steel scrap used in the electric arc furnace, and also to the type of stainless steel produced. For the same type of stainless steel, the variation in metal composition can be small due to the use of standard stainless steelmaking materials and also to the operational stability.

On the other hand, as shown in Fig. 4(C), the annual variability of the nickel content in the AOD-L sludge was found to be asymmetrical. The content of nickel in a period of 12 months was found to behave as a bimodal curve, i.e., around 33% of the samples contain less than 0.4% (w/w) of nickel and nearly 30% of the samples contain nickel ranging from 1.2 to 1.6% (w/w). Actually, the content of nickel in the AOD-L sludge is strongly associated with the type of stainless steel produced and, therefore, the annual variability depends on the demand for materials that contain nickel, such as the austenitic stainless steels.

### 3.4.1. Digestion samples

Table 4 shows the results obtained in the digestion tests using aqua regia and  $H_2SO_4$  50% (v/v). It can be observed that the percent of dissolution (pd = mass of the residue obtained after

 Table 3

 Chemical analysis of the main elements present in the AOD-L sludge

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

the dissolution divided by mass of the initial sample) with aqua regia is quite low (57%, w/w). The dissolution of the AOD-L sludge with  $H_2SO_4$  50% (v/v) is considerably higher but it is still incomplete (92%, w/w). Table 4 also indicates that the use



Fig. 4. Relative frequency diagrams for the contents of iron (A), chromium (B) and nickel (C) nickel in the AOD-L sludge.

Table 4

Contents of iron, chromium and nickel (%, w/w) and the percent of dissolution pd (%, w/w) of the AOD-L sludge obtained with aqua regia and  $H_2SO_4$  50% (v/v).

Solution	Fe	Cr	Ni	pd
Aqua regia	$25\pm3$	$3 \pm 1$	$1.2 \pm 0.1$	$57 \pm 2$
H <sub>2</sub> SO <sub>4</sub> (50%, v/v)	$30\pm3$	$7 \pm 1$	$1.4 \pm 0.1$	$92 \pm 1$

of  $H_2SO_4$  50% (v/v) favors the dissolution of metals, mainly chromium. So aqua regia was found to be an inefficient leaching agent for the dissolution of chromium species contained in the AOD-L sludge.

In order to identify the mineral phases which were not dissolved in the digestion tests carried out with  $H_2SO_4$  50% (v/v), the residue after filtration was analyzed by XRD. Results shown in Fig. 5 reveal the main crystalline phases identified were chromite (FeCr<sub>2</sub>O<sub>4</sub>) and quartz (SiO<sub>2</sub>). Chromite was not completely dissolved with H<sub>2</sub>SO<sub>4</sub> 50% (v/v) but it can be digested by a mixture of concentrated H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> as oxidizing agent [21,22]. Therefore, HClO<sub>4</sub> was used at changing concentrations in the digestion experiments according to the following HClO<sub>4</sub>/AOD-L sludge ratios (volume of HClO<sub>4</sub> divided by mass of AOD-L sludge): 0, 2 and 4 mL/g. Fig. 6 shows the contents of iron, chromium and nickel after the dissolution of the sludge with H<sub>2</sub>SO<sub>4</sub> 50% (v/v) and HClO<sub>4</sub> 70% (v/v), including a confidence interval of 95%. Leaching of iron and nickel were found to be quite similar from the statistical viewpoint but the presence of HClO<sub>4</sub> seems to affect the average contents of iron and chromium. The higher leaching efficiency was obtained at HClO<sub>4</sub>/AOD-L sludge ratio of 4, so the addition of HClO<sub>4</sub> favors the dissolution of chromite. With respect to the nickel content, its dissolution is practically not affected by the presence of HClO<sub>4</sub>. A comparison between metal contents in Tables 3 and 4 indicates that nickel species was fully dissolved with H2SO4 50% (v/v). The percent of dissolution with  $H_2SO_4$  50% (v/v) and HClO<sub>4</sub>/AOD-L sludge ratio equal to 4 was around 99% (w/w). By XRF, only metal traces were detected in the residue and the silicon was found as the main component. As silica is insoluble in sulfuric acid media, their silicon content was determined after dissolution with HF.



Fig. 5. XRD analysis for the residue obtained in AOD-L sludge dissolution using  $H_2SO_4$  50% (v/v).



Fig. 6. Contents of iron (A), chromium (B) and nickel (C) of the AOD-L sludge obtained after dissolution with  $H_2SO_4$  50% (v/v) and HClO<sub>4</sub> 70% (v/v).

#### 3.5. Toxicity analysis of the AOD-L sludge

According to the TCLP test, the AOD-L sludge investigated in this study is a toxic waste. The overall concentration of chromium in the extract solution  $14 \pm 4$  mg/L was found to be much higher than the limit value of the toxicity characteristic regulatory level (TCRL), i.e., 5.0 mg/L. Therefore, the AOD-L sludge was classified as a hazardous waste. Based on the XRD analysis, chromium was identified mainly as FeCr<sub>2</sub>O<sub>4</sub>. This specie is very stable and quite difficult to be leached in the conditions of the TCLP test (extract solution pH  $\approx$ 2.8). Hence, it is pointed out that chromium extracted in the TCLP conditions is probably associated to some other mineral phases which are easier to leach.

According to the results obtained in this study, the disposal of the AOD-L sludge in landfills may cause environmental impact due to the mobility of chromium. If the landfill waterproof system is inefficient and no preliminary treatment (such as stabilization methods) is accomplished, chromium could contaminate the soil and ground water. The chromium, mainly on its hexavalent form, is highly toxic, mutagenic and potentially carcinogenic to human beings [25].

# 4. Conclusions

The fine fraction of the AOD-L sludge from the stainless steelmaking industry has been characterized in this study and the main conclusions are as follows:

- The predominance of spinel group minerals such as chromite and magnetite were identified by XRD analysis. Chromite has a very stable structure in aqueous media, so the recovery of chromium will depend on the chromite leaching efficiency. The addition of perchloric acid seems to favor the dissolution of chromite;
- The SEM analysis indicated that nickel is present in very fine particles, possibly in the metallic form or associated with iron and oxygen. The content of nickel is relatively low, but its recovery may be attractive due to high demand and high economic value of this metal;
- The annual variability of iron and chromium contents in the AOD-L sludge was determined as  $33 \pm 9$  and  $9 \pm 3\%$  (w/w), respectively. With respect to nickel content (up to 2.5%, w/w), its content depends on the type of stainless steel produced;
- The AOD-L sludge was classified as hazardous waste according to TCLP test.

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