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# Submerged-arc welding slags: Characterization and leaching strategies for the removal of aluminum and titanium

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# HIGHLIGHTS

- ► Submerged-arc welding slags were characterized by a variety of methods.
- ► The residue contain aluminum (10–14%) and titanium (up to 10%) to be reused.
- Spinel structures associated to Al species were identified in the slag.
- ▶ 80% Al was leached after calcination of slag followed by H<sub>2</sub>SO<sub>4</sub> leaching.

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# ABSTRACT

In the present study, submerged-arc welding slags were characterized by applying a variety of methods, including X-ray fluorescence, X-ray diffraction, particle size, Raman spectroscopy, and scanning electron microscope with energy dispersive X-ray analysis. The content of Al proved to be quite similar within neutral and acid slags (10–14%), while that of Ti proved to be much higher in acid slags (approximately 10%) than in neutral slags (<1%). The presence of spinel structures associated with Al species could also be identified in the analyzed samples. This characterization study was accompanied by leaching tests performed under changing operating conditions in an attempt to evaluate to what extent the Al and Ti bearing components could be removed from the slags. The leaching (HCl and H<sub>2</sub>SO<sub>4</sub>) using oxidizing/reducing agents, and (iii) slag calcination followed by H<sub>2</sub>SO<sub>4</sub> leaching. In the best result, 80% of Al was extracted in one single leaching stage after calcination of the acid slag with NaCl + C at 900 °C. By contrast, the removal of Ti proved to be unsatisfactory.

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## 1. Introduction

Submerged-arc welding is a well-established process capable of producing quality welds in a wide range of thicknesses in ferrous, stainless steels, and even some non-ferrous metals. The process consists of an arc that is formed when an electric current passes continuously between a welding wire and the workpiece. The arc, the tip of the welding wire, and the weld joint are fully covered by a layer of a powdered flux, which protects the welding operation from atmospheric contamination, prevents flash and glare, and makes it so that smoke and fumes are virtually nonexistent. During the welding process, the flux is partially melted, resulting in a liquid protective slag layer that is solidified during the sequence, generating a waste material known as submerged-arc welding slags (SAWS).

The slags, and the fluxes that originate them, are classified according to neutral, acid, or basic type basicity indexes. A higher level of basicity produces better impact values, but reduces such features as the welding speed, the parameter envelope, or the fine rippling of the weld bead. The basicity index can be calculated according to the following empirical formula, based on the chemical composition of the flux (in the percent weight of the species), independently of the wire [1]:

$$Basicity index = \frac{CaO + MgO + Na_2O + K_2O + CaF_2 + MnO + FeO/2}{SiO_2 + Al_2O_3 + TiO_2 + ZrO_2/2}$$
(1)

The chemical composition of SAWS may change considerably depending on the given basicity of the flux as well as on the metal transfer during a specific welding application [2,3].

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Fig. 1. Neutral SAWS as received used in this work.

In Brazil, it is estimated that the submerged-arc welding process currently generates about 1200 tons of SAWS per month. Such residues are fully land-disposed. Thus, the development of recycling technology to reuse these residues could be advantageous from both economic and environmental perspectives. Some researchers have explored the possibility of using a mixture of fresh flux and slag [4,5]. Nevertheless, despite the amount of SAWS generated, only a few recent works can be found in the literature that attempt to defend this recycling process.

Laboratory scale tests have shown that SAWS could be recycled after having performed the necessary modifications. In these studies, the satisfactory appearance of welding beads with no visual defects could be observed, and the mechanical properties of welded metal deposited with recycled slag were accepted as per ASME SFA 5,17-89. However, as the chemical composition of the flux may change depending on the welding work, such a reuse of SAWS may be a complex operation to be implemented in large scale. In addition, as the most expensive raw materials of flux are consumed during welding, the incorporation of SAWS into civil construction materials without any kind of pre-treatment has also been considered. Morete et al. [6] evaluated the chemical properties of ceramic bodies produced by adding SAWS in quantities of up to 10%, including the use of SAWS mixed with sand for the production of cement and concrete blocks. According to these studies, the resistance of the materials improved when SAWS were added. However, in such applications, the metal content of SAWS is lost, so hydrometallurgical methods could be applied to recover them. Hence, such treatment could reduce the volume of material to be discharged or reused through their incorporation within civil construction materials [7–9]. However, no reports on this issue have been found in the literature.

In this context, the present investigation aims to characterize SAWS according to their chemical and mineralogical composition, as well as evaluate distinct leaching strategies linked to the recovery of Al and Ti bearing components from such slags.

# 2. Experimental

#### 2.1. Characterization of SAWS

Samples of submerged-arc welding slags, generated by various metallurgical companies located in the state of Minas Gerais, Brazil (Fig. 1), were collected and supplied by ESAB. These slags were classified according to the type of flux used in the welding process: neutral, acid, and basic. Basic slags were removed from the study due to their relatively lower content of Al and Ti (7.34% and 0.10%, respectively). Thus, only neutral and acid slags were

considered in the present investigation. The samples were crushed (jaw crusher Viatest, model BB 100 Mangan) and grounded in a disc mill. The powder was then sieved through a vibratory screening system. To assess the differences in the Al and Ti grades of distinct size fractions, each powder was divided according to their respective particle size:  $38-74 \,\mu\text{m}$  and  $74-149 \,\mu\text{m}$ . The finest and coarsest fractions of both powders were discharged from the study. After sieving, the powders were dried at 50 °C for two days and then quartered, using a Dialmática riffle splitter with 16 grids and 2 collecting plates.

The chemical compositions of the neutral and acid SAWS were obtained by X-ray fluorescence (XRF), using a Panalytical spectrometer, model Axios. The identification of main crystalline phases was performed by X-ray diffraction (XRD), using a Philips diffractometer, model PW1710. The morphological and chemical compositions of the particles were obtained by means of scanning electronic microscopy with energy dispersive spectroscopy (SEM-EDS), using a Jeol microscope, model JSM 5410. Finally, the structure analysis of SAWS was carried out by Raman spectroscopy, using the Jobin-Yvon/Horiba Raman laser system, model Labran HR800, coupled with a transference optical microscopy.

#### 2.2. Leaching of SAWS

Three distinct leaching strategies under changing operating conditions were evaluated in an attempt to maximize the dissolution of Al and Ti bearing components from neutral and acid SAWS: (i) alkaline leaching followed by acid leaching, (ii) acid leaching in the presence of oxidizing/reducing agents, and (iii) slag calcination followed by acid leaching.

In the first leaching strategy, samples were placed in contact with NaOH, followed by  $H_2SO_4$  solutions, at changing concentration levels. The following operating conditions were investigated: leaching agent concentration (1.5 and 6.0 M NaOH or  $H_2SO_4$ ), type of SAWS (neutral and acid), and particle size (38–74 and 74–149  $\mu$ m). In these tests, the following conditions remained constant: time=24 h, agitation speed=250 rpm, temperature=55 °C, and solid to liquid ratio=1:10 g mL<sup>-1</sup>.

In the second leaching strategy, samples were placed in contact with acid solutions containing oxidizing/reducing agents. The following operating conditions were evaluated: type of leaching agent ( $H_2SO_4$  and HCl), leaching agent concentration (1.5 and 6.0 M), type of oxidizing/reducing agent (0.75 g Fe/g sample and 1.67 mL  $H_2O_2$  30%), type of SAWS (neutral and acid), and particle size (38–74 and 74–149  $\mu$ m). The remaining operating conditions remained constant at the same levels of the previous leaching strategy.

Finally, in the third leaching strategy, slag samples were calcined in a laboratory electric resistance furnace for 30 min in the presence of NaCl+C or NaCl+Fe, followed by leaching with 6.0 M of H<sub>2</sub>SO<sub>4</sub>. The following operating conditions were investigated in the calcination: reagents [NaCl + C(2.31 g NaCl/g sample + 0.41 g C/g]sample), NaCl+Fe (2.31g NaCl/g sample+2.21g Fe/g sample)], and temperature (500 °C and 900 °C), using acid slags only with particle sizes of 38-74 µm. The weight of reagents used in the calcination tests was calculated according to reactions (2)-(5). All reagents were of analytical grade. The calcined samples were analyzed by XRD, using a PANalytical diffractometer, model X'Pert PRO MRD. In the leaching tests, time varied up to 120 min under the following operating conditions: agitation speed = 300 rpm, temperature = 80 °C, and solid to liquid ratio = 1:40 g mL<sup>-1</sup>. Such conditions were defined after preliminary tests, using acid slags that had not previously been submitted to calcination.

The following procedure was adopted for the leaching tests. First, a given volume of the selected leaching solution was placed in the reactor and heated to the specific temperature of the test. At the initial time, a 10g slag sample (neutral or acid) was added

Table 1	1
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Composition of neutral and acid SAWS as viewed by XRF analysis.

Compounds Neutral (%) Acid (%)   Al <sub>2</sub> O <sub>3</sub> /Al 19.8/10.5 25.9/13.7   TiO <sub>2</sub> /Ti 0.8/0.5 11.0/9.5   CaO 13.6 6.6   F 4.9 1.7   Fe <sub>2</sub> O <sub>3</sub> 3.9 10.0   MgO 22.6 2.1   MnO 5.3 22.9   Na <sub>2</sub> O 3.8 2.5   SiO <sub>2</sub> 23.5 11.4   Others 1.9 6.0			
$\begin{array}{ccccc} Al_2 O_3 / Al & 19.8 / 10.5 & 25.9 / 13.7 \\ Ti O_2 / Ti & 0.8 / 0.5 & 11.0 / 9.5 \\ CaO & 13.6 & 6.6 \\ F & 4.9 & 1.7 \\ Fe_2 O_3 & 3.9 & 10.0 \\ MgO & 22.6 & 2.1 \\ MnO & 5.3 & 22.9 \\ Na_2 O & 3.8 & 2.5 \\ Si O_2 & 23.5 & 11.4 \\ Others & 1.9 & 6.0 \\ \end{array}$	Compounds	Neutral (%)	Acid (%)
TiO2/Ti 0.8/0.5 11.0/9.5   CaO 13.6 6.6   F 4.9 1.7   Fe2O3 3.9 10.0   MgO 22.6 2.1   MnO 5.3 22.9   Na2O 3.8 2.5   SiO2 23.5 11.4   Others 1.9 6.0	Al <sub>2</sub> O <sub>3</sub> /Al	19.8/10.5	25.9/13.7
CaO 13.6 6.6   F 4.9 1.7   Fe <sub>2</sub> O <sub>3</sub> 3.9 10.0   MgO 22.6 2.1   MnO 5.3 22.9   Na <sub>2</sub> O 3.8 2.5   SiO <sub>2</sub> 23.5 11.4   Others 1.9 6.0	TiO <sub>2</sub> /Ti	0.8/0.5	11.0/9.5
F 4.9 1.7   Fe2O3 3.9 10.0   MgO 22.6 2.1   MnO 5.3 22.9   Na2O 3.8 2.5   SiO2 23.5 11.4   Others 1.9 6.0	CaO	13.6	6.6
Fe <sub>2</sub> O <sub>3</sub> 3.9 10.0   MgO 22.6 2.1   MnO 5.3 22.9   Na <sub>2</sub> O 3.8 2.5   SiO <sub>2</sub> 23.5 11.4   Others 1.9 6.0	F	4.9	1.7
MgO 22.6 2.1   MnO 5.3 22.9   Na <sub>2</sub> O 3.8 2.5   SiO <sub>2</sub> 23.5 11.4   Others 1.9 6.0	Fe <sub>2</sub> O <sub>3</sub>	3.9	10.0
MnO 5.3 22.9   Na <sub>2</sub> O 3.8 2.5   SiO <sub>2</sub> 23.5 11.4   Others 1.9 6.0	MgO	22.6	2.1
Na2O 3.8 2.5   SiO2 23.5 11.4   Others 1.9 6.0	MnO	5.3	22.9
SiO2 23.5 11.4   Others 1.9 6.0	Na <sub>2</sub> O	3.8	2.5
Others 1.9 6.0	SiO <sub>2</sub>	23.5	11.4
	Others	1.9	6.0

to the solution and mixed under constant stirring. In the first and second strategies, pulp mixing was carried out using a mechanical shaker (Nova Ética 109), while in the third strategy the pulp was mixed in a reactor immersed in a controlled-temperature bath ( $\pm 1$  °C sensitivity) and provided with a mechanical stirrer, using a marine-type glass impeller. At the given time intervals, 10 ml of the liquid sample was withdrawn, filtered, properly diluted, and analyzed for Al, Ti, and other metal species by AAS or ICP-OES. At the end of the test, the pulp was filtered and the volume of residual leaching liquor was measured in order to specify the loss of leaching solution due to evaporation and sample withdrawn during the experiment.

# 3. Results and discussion

#### 3.1. Characterization of SAWS

The compositions of neutral and acid SAWS obtained by XRF are shown in Table 1. No significant difference concerning particle size (38–74 and 74–149  $\mu$ m) could be verified in the metal composition of the analyzed samples. The content of Al is relatively similar for neutral and acid slags, approximately 10–14%. However, those of Ti proved to be much higher in acid slags (approximately 10%) when compared to neutral slags (<1%). Hence, the removal of Ti from neutral SAWS does not appear to be economical. Significant variations in the chemical composition of SAWS are expected and depend on the specific welding service. Such a variation in the chemical composition of raw materials may require some flexibility in the operations of the recycling process of the residue.

The XRD pattern of neutral and acid SAWS is shown in Fig. 2. The following phases were identified for both slags, thus corroborating a previous analysis carried out on agglomerated fluxes [10]: CaF<sub>2</sub>, Fe and/or Cr, M<sub>x</sub>O<sub>y</sub>·Al<sub>2</sub>O<sub>3</sub> (where M could be, for example, Fe or even Mg, Ca, and Mn), and Al<sub>2</sub>O<sub>3</sub> and/or Al<sub>1.98</sub>Cr<sub>0.02</sub>O<sub>3</sub>. This last phase was identified also by Raman analysis. The presence of metal spinel crystalline structures in SAWS is expected, given that welding processes are conducted under high oxidizing conditions and high temperature levels. In fact, such phases were identified and found to be in association with Al. It is also well-known that spinel phases are normally very stable and difficult to leach [11]. Phase MgO was detected in neutral SAWS, while phases TiO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub> were detected in acid SAWS, where the content of such metals were found to be more abundant. Again, no difference in the phase composition could be verified at the distinct particle sizes analyzed in this work (38-74 and  $74-149 \mu m$ ). The main phases, therefore, seem to be either FeAl<sub>2</sub>O<sub>4</sub> type compounds, or Al<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, and CaF<sub>2</sub> type compounds. From point of view of the slag's chemical composition, it is evident that some phases based on Si should also be present; however, these were difficult to determine due to heterogeneity, chemical complexity of the sample, structural similarity, and the overlapping of individual phase diffractions. However, the mineralogical analysis of

Table 2			
EDS analysis of areas 1-6	(in %, w/w	) identified in	Fig. 2(a).

2				0 ( )		
Elements	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	6 (%)
Al	34.1	33.5	3.8	2.8	82.6	3.6
Ca	7.6	7.9	0.7	0.6	1.7	81.5
Fe	2.5	5.4	74.7	31.7	1.8	2.4
Mn	21.1	19.9	6.7	8.9	4.8	3.0
Si	15.8	14.9	4.1	1.2	5.3	4.5
Ti	13.3	12.3	1.0	54.8	2.8	2.1

leaching residue (milled sample leached in 6 M H<sub>2</sub>SO<sub>4</sub> for 2 h) showed that slag could also contain silicates, such as CaSiO<sub>3</sub> (and/or similar type compounds, namely MgSiO<sub>3</sub>) and SiO<sub>2</sub>. Moreover, in addition to TiO<sub>2</sub> in the leaching residue, FeTiO<sub>3</sub> diffractions also appeared. From the thermodynamic point of view, the formation of FeTiO<sub>3</sub> in SAWS is favorable within an oxidation atmosphere and in the presence of metallic iron during the welding process. In some cases, the diffraction pattern after leaching considerably changes. In fact, some patterns are even eliminated or reduced due to the leaching out of individual phases, and peaks which had been previously lost in the background or overlapped become more "visible". Based on this finding, the XRD analysis of the leaching residue could be used to identify some probable additional phases in the input sample. Nonetheless, it still important to note that phases can also change or be created during leaching and that the qualitative analysis is always given considering some degree of probability.

Typical micrographs of acid SAWS obtained by SEM are shown in Fig. 3, including views along the slag (top, central, and bottom regions). Table 2 presents the EDS analysis of areas 1 to 6 as identified in Fig. 3(a). Aluminum and titanium, as well as calcium, are disseminated throughout nearly the entire sample, but they predominate in the top region (see Fig. 3(b)). Iron, however, predominates in the bottom and central regions (Fig. 3(c) and (d), respectively). Closer to the welding bead, iron is evidenced in white circles of varying sizes (point 3). These regions seem to be quite uniform (points 1 and 2 present a similar composition), while a greater diversity of particles in terms of shape, color, and composition (see points 4, 5 and 6) can be viewed in the top region of the slag. The same conclusions were drawn by Raman analysis (spectra not shown), in which, in contrast to the bottom and central regions, the intensity of the peaks was much greater in the top region of the slag. Depending on the position of the point inside the slag, the temperature level to which the slags were exposed is quite different; as such the material suffered partial or complete fusion, which may well explain why Al and Ti bearing compounds are mainly concentrated in the top region of the slag.

# 3.2. Leaching of SAWS

Alkaline leaching with NaOH followed by acid leaching with H<sub>2</sub>SO<sub>4</sub> was evaluated as a starting point for the recovery of Al and Ti from neutral and acid SAWS. Results are summarized in Table 3. Despite the low extraction values obtained, alkaline leaching was considered to be quite selective for Al; in fact, no Ti, Mn, or Fe was leached. As expected, the removal of Al increased both when the finer powder was used and when the concentration of NaOH was increased. In addition, the content of Al extracted from the acid slags was comparatively higher than that from the neutral slags. It can therefore be inferred that there is a higher content of spinel Al species in neutral slags than in acid slags. Concerning acid leaching, all metals analyzed were leached at distinct levels. As expected, Al was easily leached from acid slags, whereas a contrary effect was found as regards Mn and Fe, and no effect was found regarding Ti extraction. Higher metal extraction levels were obtained when the concentration of H<sub>2</sub>SO<sub>4</sub> was increased, which unexpectedly rose in direct proportion to the increase in particle size, in some



Fig. 2. Pattern of neutral and acid SAWS as viewed by XRD analysis.

cases. However, as Al and Ti extractions were found to be low, this leaching strategy was considered to be ineffective.

In the second leaching strategy, acid and neutral SAWS were placed in contact with acid solutions ( $H_2SO_4$  and HCl) in the presence/absence of oxidizing/reducing agents ( $H_2O_2$  and Fe powder). Results depicted in Fig. 4 were classified into four regions:

(I) Ti extraction > 35% and Al extraction < 35%; (II) Al and Ti extractions > 35%; (III) Al and Ti extractions < 35%; and (IV) Al extraction > 35% and Ti extraction < 35%. Extractions of Al or Ti higher than 35% were obtained solely at higher concentrations of  $H_2SO_4$  or HCl. Al was again easily extracted from acid slags, whereas the opposite occurred in Ti extractions. Such a result demonstrates



Fig. 3. SEM analysis of the acid SAWS and EDS analysis of selected areas given in Table 2.

Type of SAWS	Particle size (µm)	Concentration (M)	Al extraction (%)		Ti extraction (%)		Mn Extraction (%)		Fe Extraction (%)	
			Alkaline	Acid	Alkaline	Acid	Alkaline	Acid	Alkaline	Acid
Acid	74–149	1.5	7.8	23.1	0.0	7.5	0.0	61.0	0.0	12.6
		6.0	17.4	25.1	0.0	10.1	0.0	63.0	0.0	14.0
	38-74	1.5	9.2	20.1	0.0	7.1	0.0	45.4	0.0	12.1
		6.0	23.8	23.8	0.0	10.3	0.0	51.2	0.0	14.5
Neutral	74-149	1.5	3.2	_	0.0	-	0.0	_	0.0	-
		6.0	5.3	14.1	0.0	10.2	0.0	93.1	0.0	30.4
	38-74	1.5	3.5	6.8	0.0	7.4	0.0	39.5	0.0	14.6
		6.0	5.3	12.4	0.0	9.7	0.0	75.5	0.0	26.9

Sequential leaching of SAWS with NaOH followed by leaching with  $H_2SO_4$  (t=24 h; agitation speed = 250 rpm; T=55 °C; solid to liquid ratio = 1:10 g mL<sup>-1</sup>).

the existence of distinct phase contents in acid and neutral SAWS. No significant effect could be observed regarding the use of  $H_2SO_4$  or HCl as leaching agents, regardles of using  $H_2O_2$  or Fe powder. This strategy was also considered ineffective, despite the relatively better results obtained (maximum extraction of 44% for Al and 42% for Ti from neutral slags, and 22% for Ti from acid slags) when compared to the sequential leaching tests.

Table 3

In the third leaching strategy, acid SAWS were leached in  $H_2SO_4$ 6 M after calcination with NaCl+C or NaCl+Fe. Fig. 5 shows a considerable improvement in the leaching of Al when SAWS were treated at 900 °C with NaCl+C (from 40% to approximately 80%). By contrast, calcination seemed to be less effective in the leaching of Ti, although a slightly higher extraction was achieved when acid SAWS were calcined with NaCl+Fe (around 30%) as compared to the use of the second strategy (approximately 20%) under similar leaching conditions. Calcination more often affected the leaching of Al due to the fact that the spinel structures in SAWS identified in this study were found to be associated with Al species. Tests at 500 °C did not improve the leaching results for either metal, and the effect of time proved to be insignificant for the evaluated period (extraction was practically constant after 20 min of leaching).

The aim of the calcination of SAWS was to verify if it is possible to change the metal phases in the slag under given conditions according to the proposed reactions (2)-(5) and make them more

leachable in water or acidic solutions:

$$TiO_{2(s)} + 4NaCl_{(s)} + 2C_{(s)} + 2O_{2(g)} = TiCl_{4(s)} + 2Na_2CO_{3(s)}, \quad \Delta G_{900 \circ C} = -198.552 \text{ kJ mol}^{-1}$$
(2)

$$TiO_{2(s)} + 4NaCl_{(s)} + 4Fe_{(s)} + 3O_{2(g)} = TiCl_{4(s)} + 4NaFeO_{2(1)}, \quad \Delta G_{900 \circ C} = -419.705 \text{ kJ mol}^{-1}$$
(3)

$$\begin{aligned} Al_2O_{3(s)} &+ 6NaCl_{(s)} + 3C_{(s)} + 3O_{2(g)} = 2AlCl_{3(s)} \\ &+ 3Na_2CO_{3(s)}, \quad \Delta G_{900^{\circ}C} = -126.068 \text{ kJ mol}^{-1} \end{aligned}$$
(4)

$$Al_2O_{3(s)} + 6NaCl_{(s)} + 6Fe_{(s)} + 4.5O_{2(g)} = 2AlCl_{3(s)} + 6NaFeO_{2(s)}, \quad \Delta G_{900 \circ C} = -291.933 \,\text{kJ} \,\text{mol}^{-1}$$
(5)

It should be also mentioned that  $TiO_2$  is generally a problematic substance to leach due to its character. Depending on the leaching temperature and the acid concentration, species, such as  $Ti^{3+}$ ,  $TiO_2^+$ ,  $TiSO_4^+$ ,  $Ti(SO_4)_2^-$ ,  $TiO(SO_4)_2^{2-}$ ,  $Ti(SO_4)_3^{2-}$ , among others, could rehydrolyze as  $TiO_2$  [12].



**Fig. 4.** Leaching of Al and Ti with  $H_2SO_4$  and HCl solutions from acid and neutral SAWS in the presence/absence of oxidizing/reducing agents  $H_2O_2$  and Fe powder (t=24 h; agitation speed = 250 rpm; T=55 °C; solid to liquid ratio = 1:10 g mL<sup>-1</sup>).



**Fig. 5.** Effect of the calcination of acid SAWS and time spent to leach Al and Ti ( $[H_2SO_4]=6M$ ; agitation speed=300 rpm; T=80 °C; solid to liquid ratio=1:40 g mL<sup>-1</sup>).

From the mineralogical analysis of the sample after calcination with NaCl+C, it could be concluded that the expected TiCl<sub>4</sub> (or TiCl<sub>3</sub>) phase could not be formed and that the only possible new Ti phase that did in fact occur was Na<sub>2</sub>Ti<sub>2</sub>Si<sub>2</sub>O<sub>9</sub>. The rest of TiO<sub>2</sub> phase (rutile) showed no reaction. By contrast, as possible new Al-based phase could be identified as sodalite-type compounds (Na<sub>4</sub>Al<sub>3</sub>Si<sub>3</sub>O<sub>12</sub>Cl), then AlCl<sub>3</sub>, NaAlCl<sub>4</sub>, and NaAlSiO<sub>4</sub> (or even Na<sub>3</sub>AlF<sub>6</sub>) could also be responsible for a more effective leaching of Al. The calcination of the slag mixture with NaCl+C under these conditions also caused changes in the Mn<sub>3</sub>O<sub>4</sub> phase to MnO<sub>2</sub>. Residual phases, such as Al<sub>2</sub>O<sub>3</sub>, spinel-type (FeAl<sub>2</sub>O<sub>4</sub>), SiO<sub>2</sub>, and CaF<sub>2</sub> presented no reaction within in the slag. In the slag sample after calcination with NaCl+Fe, in addition to Na2Ti2Si2O9, other soluble phases, such as Na<sub>0.54</sub>TiO<sub>2</sub> and CaTi<sub>21</sub>O<sub>38</sub>, also occurred. This fact could contribute to formulating a better extraction of Ti using this mixture. Moreover, chloride ions present in the leaching process influence the ionic strength and chemical potential of the solution and often aid in leaching out specific substances. The XRD patterns of calcined slag samples with NaCl + Fe and NaCl + C at 900 °C are shown in Fig. 6.

Proposed leaching reactions of suggested new Al-phases in  $H_2SO_4$  are described in Eqs. (6)–(9). The reaction of sodalite is not presented here due to a lack of thermodynamic data. All mentioned reactions proved to be favorable under given conditions.

$$\begin{aligned} \text{NaAlSiO}_{4(s)} + 4\text{H}_2\text{SO}_{4(aq)} &= \text{Al}_2(\text{SO}_4)_{3(aq)} + 2\text{SiO}_{2(s)} + \text{Na}_2\text{SO}_{4(aq)} \\ &+ 4\text{H}_2\text{O}_{(1)}, \quad \Delta G_{80\,^\circ\text{C}} = -304.350\,\text{kJ}\,\text{mol}^{-1} \end{aligned} \tag{6}$$

$$2\text{NaAlCl}_{4(s)} + 4\text{H}_2\text{SO}_{4(aq)} = \text{Na}_2\text{SO}_{4(aq)} + \text{Al}_2(\text{SO}_4)_{3(aq)} + 8\text{HCl}_{(aq)}, \quad \Delta G_{80^{\circ}\text{C}} = -518.563 \text{ kJ mol}^{-1}$$
(7)

$$2Na_{3}AIF_{6(s)} + 6H_{2}SO_{4(aq)} = Al_{2}(SO_{4})_{3(aq)} + 12HF_{(aq)}$$
  
+ 3Na\_{2}SO\_{4(aq)},  $\Delta G_{80\,^{\circ}C} = -65.730 \,\text{kJ}\,\text{mol}^{-1}$  (8)

$$2\text{AlCl}_{3(aq)} + 3\text{H}_2\text{SO}_{4(aq)} = \text{Al}_2(\text{SO}_4)_{3(aq)} + 6\text{HCl}_{(aq)}, \quad \Delta G_{80 \circ \text{C}}$$
$$= -514 \ 422 \ \text{kI} \ \text{mol}^{-1} \tag{9}$$

By analyzing the leaching residue of the milled sample (without calcination, T=80 °C;  $[H_2SO_4]=6$  M; solid to liquid ratio = 1:40 g mL<sup>-1</sup>; t=2 h), it could also be concluded that spinel phase is more leachable in  $H_2SO_4$  than  $Al_2O_3$ . In fact, according to thermodynamics (see Eqs. (10)–(11)), the preference should be to leach the spinel phase. Furthermore, according to Eq. (12), CaF<sub>2</sub> appears to have been completely leached out of the milled slag without calcination.

$$\begin{aligned} \text{FeAl}_2\text{O}_{4(s)} + 4\text{H}_2\text{SO}_{4(aq)} &= \text{FeSO}_{4(aq)} + \text{Al}_2(\text{SO}_4)_{3(aq)} \\ &+ 4\text{H}_2\text{O}_{(1)}, \quad \Delta G_{80\,^\circ\text{C}} = -228.438\,\text{kJ}\,\text{mol}^{-1} \end{aligned} \tag{10}$$

$$\begin{aligned} Al_2O_{3(s)} &+ 3H_2SO_{4(aq)} = Al_2(SO_4)_{3(aq)} + 3H_2O_{(l)}, \quad \Delta G_{80 \circ C} \\ &= -154.943 \text{ kJ mol}^{-1} \end{aligned} \tag{11}$$

$$CaF_{2(s)} + H_2SO_{4(aq)} = CaSO_{4(aq)} + 2HF_{(aq)}, \quad \Delta G_{80 \circ C}$$
  
= -61.664 kJ mol<sup>-1</sup> (12)

Gibbs free energy of proposed reactions (2)-(12) was calculated with the help of HSC Chemistry 6 software.



Fig. 6. Pattern of calcined SAWS with NaCl+Fe and NaCl+C at 900 °C as viewed by XRD analysis.

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# 4. Conclusions

In this study, neutral and acid SAWS were characterized in detail and submitted to distinct leaching strategies in an attempt to remove Al and Ti from the residue for recycling purposes. The main conclusions drawn are as follows:

- Metal composition: (i) the content of Al was similar for neutral and acid slags (10–14%); (ii) acid slags contain more Ti (10%) than neutral slags (<1%); (iii) composition did not change with the distinct particle sizes evaluated in this study;
- Phase composition: (i) CaF<sub>2</sub>, Fe, and/or Cr, M<sub>x</sub>O<sub>y</sub>.Al<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> and/or Al<sub>1.98</sub>Cr<sub>0.02</sub>O<sub>3</sub>, were identified in neutral and acid slags; (ii) Metal spinel structures are associated with Al species; (iii) Phase MgO was identified only in neutral slags, while phases TiO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub> were found in acid SAWS;
- *Metal distribution*: SEM-EDS analysis revealed that Al and Ti, as well as Ca, can be found throughout the acid slag, but they are predominately found far from the welding bead. The opposite behavior was verified for iron;
- *Leaching strategies*: (i) NaOH leaching is very selective for Al, but proved to be inefficient (<24%), as did subsequent acid leaching with H<sub>2</sub>SO<sub>4</sub> or HCl for Al and Ti; (ii) The existence of distinct phases in acid and neutral SAWS may well explain why the extraction of Al is relatively higher when taken from acid slags; and, (iii) Al extraction doubled (from 40% to 80%) after the calcination of acid SAWS with NaCl + C at 900 °C, while those of Ti slightly improved (from 20% to 30%) after calcination with NaCl + Fe at 900 °C.

Although the experimental strategy adopted in this work is justifiable based on the characterization of SAWS, results of leaching tests have fallen short of expectation for Ti. Therefore, further investigations are warranted to improve recovery of Ti. One feasible approach may well be to include the leaching of SAWS in the presence of HF, or calcining them with Na<sub>2</sub>CO<sub>3</sub>, followed by alkaline or acid leaching to leach out Al and other impurities, thus leaving TiO<sub>2</sub> in the leaching residue.

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