

## Effect of MgO and CaO/SiO<sub>2</sub> on the immobilization of chromium in synthetic slags

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**Abstract** This work investigated the chemical and mineralogical properties of CaO–SiO<sub>2</sub>–Cr<sub>2</sub>O<sub>3</sub>–CaF<sub>2</sub>–MgO slags. Synthetic slags were prepared and the effect of the slag basicity (mass ratio CaO/SiO<sub>2</sub>) and MgO contents on the stability of the mineralogical species formed was analyzed. The morphology and composition of the slags were analyzed by X-ray powder diffraction (XRD) and scanning electron microscope-energy dispersive spectroscopy (SEM–EDS), whilst their chemical stability was evaluated by leaching with an aqueous acetic acid solution. It was found that in slags with CaO/SiO<sub>2</sub> = 1, the main Cr-compound was MgCr<sub>2</sub>O<sub>4</sub> spinel, which forms octahedron crystals. Small amounts of CaCr<sub>2</sub>O<sub>4</sub> and CaCrO<sub>4</sub> were also observed. It was found that with increasing the slag basicity from 1 to 2 the compounds MgCr<sub>2</sub>O<sub>4</sub> and CaCr<sub>2</sub>O<sub>4</sub> were formed together with the Cr(V)-containing compound complex Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F which forms hexagonal crystals. The results

showed that the highest Cr concentration levels in the leaching liquors corresponded to slags with CaO/SiO<sub>2</sub> = 2, probably owing to the formation of CaCrO<sub>4</sub> and Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F, whilst the lowest chromium concentration levels corresponded to MgO-based slags owing to the stable binding of chromium in spinel with MgO. Additionally, potential–pH diagrams for the Ca–Cr–H<sub>2</sub>O and Mg–Cr–H<sub>2</sub>O systems at 25 °C were calculated.

**Keywords** Chromium oxide · Magnesium oxide · Slag · Waste management

### Introduction

The slags are attractive as construction material due to their excellent technical material properties. However, environmental concerns have been raised about the content and leachability of heavy metals of stainless steel and ferrochrome slags, especially chromium [1, 2]. Kilau and Shah [3] reported that the critical slag composition factors to control the chromium leachability were the CaO/SiO<sub>2</sub> ratio and MgO content. It was reported that adding MgO to slags reduced the refractory wear and modified the slag composition, lowering the Cr-contents in the leachate [4, 5], whereas Eriksson and Björkman [6] showed that increasing the MgO in the stainless steel slags can change the mineral composition towards formation of merwinite (3CaO•MgO•2SiO<sub>2</sub>) which prevents disintegration of the slag.

Stabilization and solidification are very effective tools and are becoming standard processes in hazardous waste treatment and disposal. These processes aim to attain mineralogical control of the metals to be stabilized. In previous works we have studied the effect of several slags

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forming agents, mainly  $\text{Al}_2\text{O}_3$ , on the leaching behavior of Cr [7, 8]. We found that  $\text{CaCr}_2\text{O}_4$  and  $\text{CaCrO}_4$  were present in slags of the system  $\text{CaO-SiO}_2\text{-CaF}_2\text{-Cr}_2\text{O}_3$ . Gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) and the Cr(VI)-containing oxide complex  $\text{Ca}_4\text{Al}_6\text{CrO}_{16}$  were present when  $\text{Al}_2\text{O}_3$  was added to the slag. It was observed in the  $\text{Al}_2\text{O}_3$ -based slags that in increasing the slag basicity (mass %  $\text{CaO}$ /mass %  $\text{SiO}_2$ ) from 1 to 2 the leachability of the slags were notably increased. It was also shown that slags with MgO produced  $\text{MgCr}_2\text{O}_4$  as the main mineralogical species.

In this work, chromium containing slags were prepared and the effects of slag basicity and MgO content on the stability of the mineralogical species formed were evaluated. The morphology and composition of the slags were analyzed by X-ray powder diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS). The chemical stability of chromium was evaluated analyzing the leaching levels of chromium according to the Mexican Waste Norms [9]. Additionally, the potential-pH diagrams for the  $\text{Ca-Cr-H}_2\text{O}$  and  $\text{Mg-Cr-H}_2\text{O}$  systems at 25 °C were constructed using the FACTSage thermodynamic software [10].

## Materials and experimental procedure

The slag was prepared with laboratory reagent-grade compounds ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{CaF}_2$ ,  $\text{SiO}_2$  and  $\text{Cr}_2\text{O}_3$ ) which were previously ground into fine powder whose particle size was between 45 and 74  $\mu\text{m}$ . The MgO content ranged from 0 to 9 mass %,  $\text{Cr}_2\text{O}_3$  and  $\text{CaF}_2$  were 10 % and the slag basicity B, defined as the ratio of CaO content to the  $\text{SiO}_2$  content (all mass %), was held at 1 and 2. In order to observe clearly the effect of chromium on the environmental behavior of the slags, the  $\text{Cr}_2\text{O}_3$  contents tested were higher than those actually found in ferrochrome or stainless steel production. Table 1 shows the mixtures compositions used for the experiments.

**Table 1** Mixture compositions used for experiments in mass % (%  $\text{Cr}_2\text{O}_3 = 10$ , %  $\text{CaF}_2 = 10$ )

Slag number	CaO/SiO <sub>2</sub>	MgO	CaO	SiO <sub>2</sub>
1	1	0	40.0	40.0
2	1	3	38.5	38.5
3	1	6	37.0	37.0
4	1	9	35.5	35.5
5	2	0	53.3	26.7
6	2	3	51.4	25.7
7	2	6	49.4	24.7
8	2	9	47.4	23.7

100 g of each slag system were prepared as follows. The powders were homogeneously mixed and placed in an MgO crucible which was placed in a graphite protecting crucible inside an open induction furnace. The slags were heated between 1600 and 1650 °C and the temperature was measured with an R-type thermocouple (Pt-Pt, 13 %Rh). It is worth noting that there are not reliable melting temperature values for the slags of the  $\text{CaO-MgO-CaF}_2\text{-SiO}_2\text{-Cr}_2\text{O}_3$  system; then, to be sure that the system were completely melted at the furnace temperature, X-ray diffraction analysis were carried out after cooling the slags to verify the absence of free  $\text{Cr}_2\text{O}_3$ . The case where Cr formed complex compounds ( $\text{CaCr}_2\text{O}_4$ ,  $\text{Ca}_5(\text{CrO}_4)_3\text{F}$ , etc.) instead of free  $\text{Cr}_2\text{O}_3$ , was taken as evidence that the system was completely liquid.

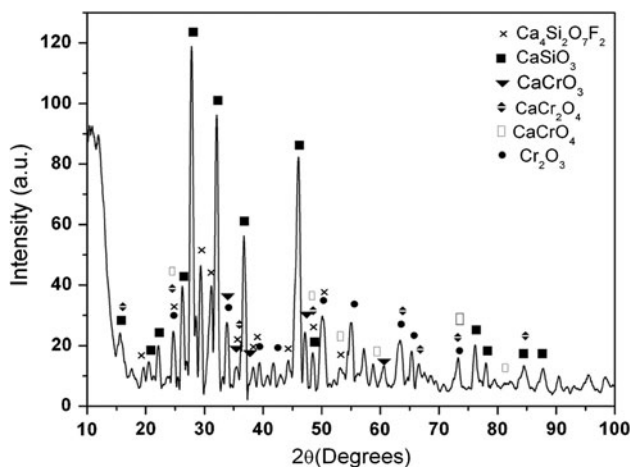
The slags were left inside the furnace to cool down slowly until room temperature, to promote the formation of well defined crystalline structures. The cooling rate from the melting point to complete solidification was about 8 °C/min. Attention was given to the morphology, shape and compositions of the solid crystallized phases: the presence of crystals homogeneous in composition, with well-developed facets was taken as indication of the attainment of equilibrium.

Samples of each slag were crushed into fine powders and characterized by X-ray diffraction (XRD Bruker D8 Focus) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS, Jeol 6300). The chemical stability of the Cr-containing species present in the materials was evaluated by the following leaching technique, according to the Mexican environmental regulations [9]. Twenty-five g of each slag were crushed below 74  $\mu\text{m}$  and contacted with 500  $\text{cm}^3$  of an aqueous acetic acid solution at  $\text{pH } 2.88 \pm 0.05$  in a rotary system during 20 h at  $30 \pm 2$  rpm and  $23 \pm 2$  °C. The solid residues were filtered through ashless filter paper (Whatmann 542) and the chromium present in the leachate was determined by atomic absorption spectrophotometry.

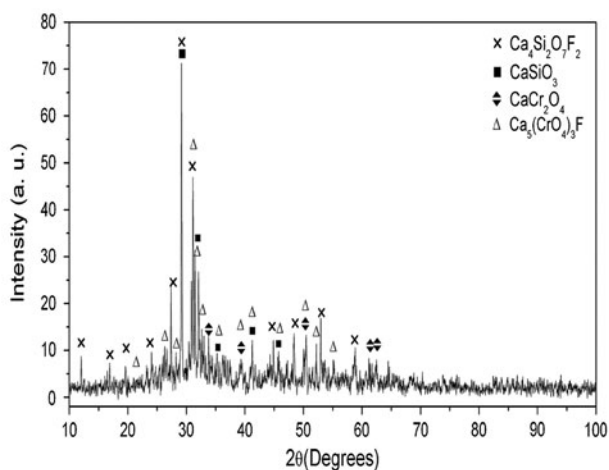
## Results and discussion

### Identification of species

The XRD patterns for slags with 0 % MgO are shown in Fig. 1. Cuspidine ( $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$ ) and wollastonite ( $\text{CaSiO}_3$ ) are the main species for the slags with  $\text{CaO/SiO}_2 = 1$  and 2. Calcium chromite ( $\text{CaCr}_2\text{O}_4$ ) is also present in both cases. Calcium chromate ( $\text{CaCrO}_4$ ) was observed in slags with  $\text{CaO/SiO}_2 = 1$ , whereas a Cr(V)-containing compound,  $\text{Ca}_5(\text{CrO}_4)_3\text{F}$ , was detected in slags with  $\text{CaO/SiO}_2 = 2$ .



(a) CaO/SiO<sub>2</sub> = 1

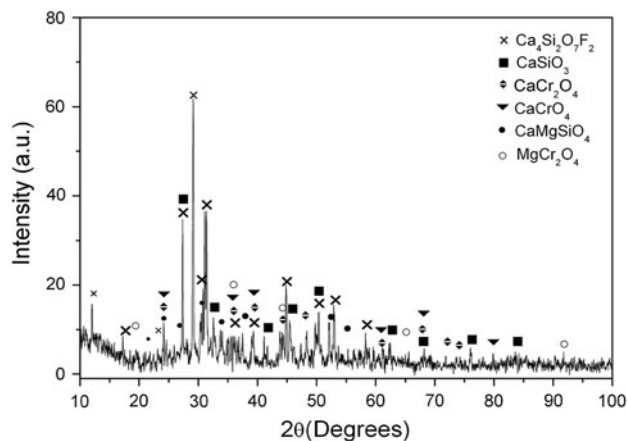


(b) CaO/SiO<sub>2</sub> = 2

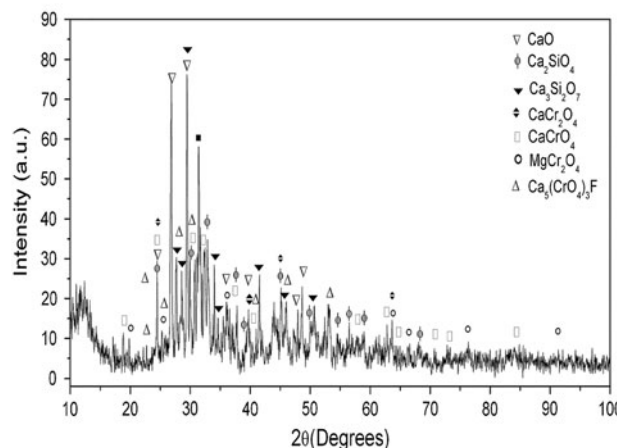
**Fig. 1** XRD patterns of slags with 0 % MgO and **a** CaO/SiO<sub>2</sub> = 1, **b** CaO/SiO<sub>2</sub> = 2

Wollastonite (CaSiO<sub>3</sub>) and cuspidine (Ca<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>F<sub>2</sub>) are again the main species present in the slag with 3 % MgO and CaO/SiO<sub>2</sub> = 1; magnesium chromite (MgCr<sub>2</sub>O<sub>4</sub>), CaCrO<sub>4</sub> and CaCr<sub>2</sub>O<sub>3</sub> are also obtained, as can be observed in the XRD patterns shown in Fig. 2a. Increasing the slag basicity from 1 to 2, new calcium silicate are produced (Ca<sub>2</sub>SiO<sub>4</sub> and Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>) and the main chromium compounds are MgCr<sub>2</sub>O<sub>4</sub>, CaCrO<sub>4</sub> and Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F. Peaks corresponding to free CaO are also observed.

Figure 3 shows the scanning electron microscope (SEM) micrograph, X-ray spectra and the composition obtained by this semiquantitative method for the slab-shaped crystals observed in the slag with 3 % MgO and CaO/SiO<sub>2</sub> = 1. These crystals, containing almost the same atom % of Ca and Cr, probably correspond to CaCrO<sub>4</sub>, identified by XRD (see Fig. 2). Figure 4 shows the micrographs of the crystalline phases of the slag with 3 % MgO and CaO/SiO<sub>2</sub> = 2. Octahedron crystals (labeled S) have high



(a) CaO/SiO<sub>2</sub> = 1

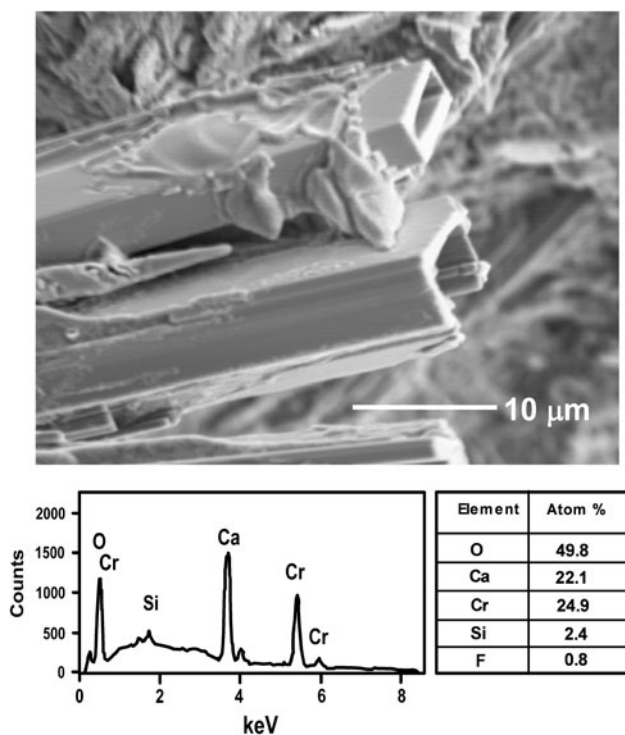


(b) CaO/SiO<sub>2</sub> = 2

**Fig. 2** XRD patterns of slags with 3 % MgO and **a** CaO/SiO<sub>2</sub> = 1, **b** CaO/SiO<sub>2</sub> = 2

contents of chromium, magnesium and oxygen; then, they correspond to MgCr<sub>2</sub>O<sub>4</sub> spinel. It has been reported [11] that magnesium chromite (MgCr<sub>2</sub>O<sub>4</sub>) crystallizes in cubes or octahedrons, such as those observed in this sample. Monoclinic crystals, labeled C, correspond to cuspidine (Ca<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>F<sub>2</sub>), according to the EDS analysis. The hexagonal crystals (CF) contain calcium, chromium, fluorine and oxygen which probably is the complex compound Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F.

Figure 5 shows the X-ray diffraction patterns for slags with 6 % MgO and CaO/SiO<sub>2</sub> = 1, 2. As in the previous case, the slag with CaO/SiO<sub>2</sub> = 1 contains cuspidine (Ca<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>F<sub>2</sub>), MgCr<sub>2</sub>O<sub>4</sub> and wollastonite (CaSiO<sub>3</sub>). Figure 5b shows that the number of chemical species is increased by increasing the slag basicity. In this case calcium and magnesium silicates are formed together with the Cr-based compounds (MgCr<sub>2</sub>O<sub>4</sub>, CaCr<sub>2</sub>O<sub>4</sub>, CaCrO<sub>4</sub> and Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F).

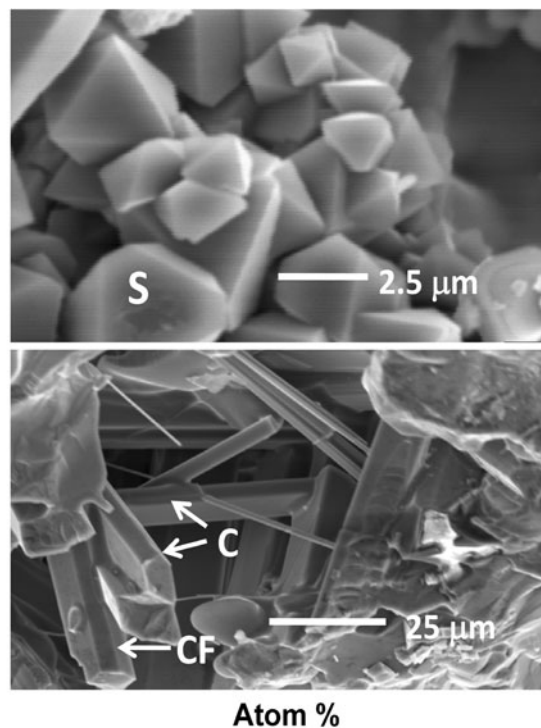


**Fig. 3** SEM micrographs of the slag with 3 % MgO and CaO/SiO<sub>2</sub> = 1. Elongated crystals are CaCrO<sub>4</sub>

The SEM–EDS analysis confirm the XRD results, as can be observed in the micrographs shown in Fig. 6, corresponding to slag with 6 % MgO and CaO/SiO<sub>2</sub> = 2. Hexagonal and monoclinic crystals were observed in this system. According to the EDS analysis, the hexagonal crystal (labeled CF) corresponds to Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F, whereas elongated crystals (labeled C) contain fluorine, calcium and silicon, which might correspond to cuspidine. EDS analysis and XRD results indicate that crystals labeled C<sub>3</sub>S are calcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>).

Cuspidine (Ca<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>F<sub>2</sub>), calcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>) and the spinel structured compound (MgCr<sub>2</sub>O<sub>4</sub>) are present in the slags with 9 % MgO and CaO/SiO<sub>2</sub> = 1 and 2, as can be observed in the XRD patterns shown in Fig. 7. Besides, the slag with CaO/SiO<sub>2</sub> = 1 contains magnesium silicates (MgSiO<sub>3</sub> and Mg<sub>2</sub>SiO<sub>4</sub>) and in the slag with CaO/SiO<sub>2</sub> = 2 three Ca–Cr compounds were formed; CaCr<sub>2</sub>O<sub>4</sub>, CaCrO<sub>4</sub> and Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F, where chromium has an oxidation state of 3+, 6+, and 5+, respectively.

Figure 8 shows micrographs of the crystalline structures obtained in the slag with 9 % MgO and CaO/SiO<sub>2</sub> = 2. There were obtained as tetragonal crystals (labeled C<sub>2</sub>S), which contained mainly calcium, silicon and oxygen, probably corresponding to Ca<sub>2</sub>SiO<sub>4</sub>, identified by XRD (see Fig. 7). The octahedron crystals (labeled S) correspond again to magnesium chromite (MgCr<sub>2</sub>O<sub>4</sub>). The



Crystal	Ca	Si	Cr	Mg	O	F
S	3.8	1.3	34.8	13.7	43.2	3.2
C	23.0	7.3	2.7	0.0	53.5	13.5
CF	47.5	0.4	11.8	0.0	31.5	8.8

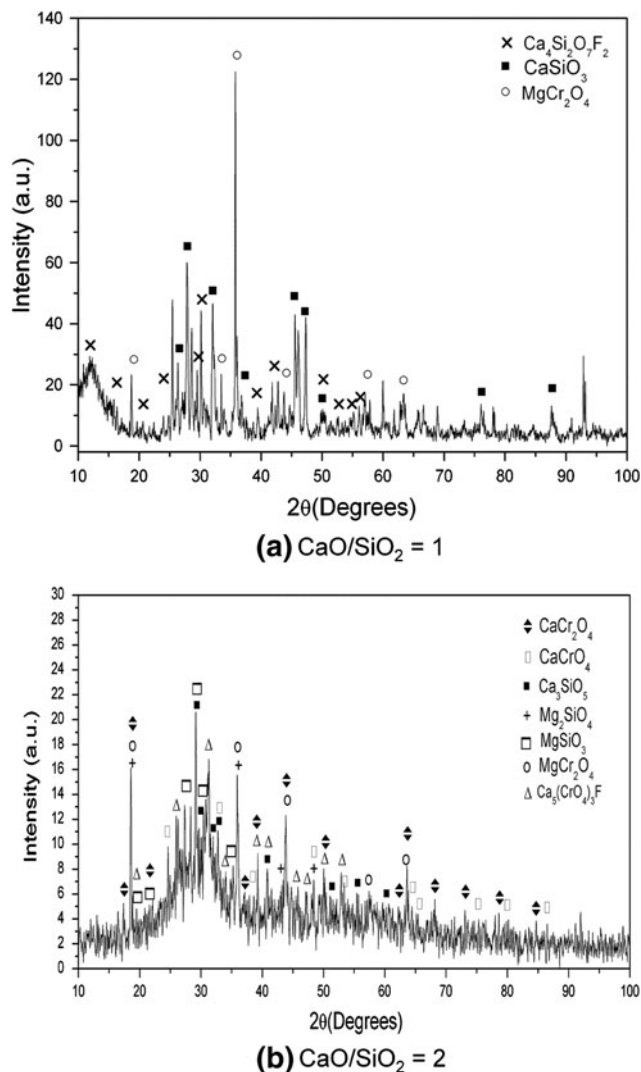
**Fig. 4** SEM micrographs of the crystalline phases of the slag with 3 % MgO and CaO/SiO<sub>2</sub> = 2. CF, Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F; C, cuspidine (Ca<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>F<sub>2</sub>); S, MgCr<sub>2</sub>O<sub>4</sub> spinel

crystal labeled C corresponds to cuspidine, according to the EDS analysis.

Finally, elongated crystals (labeled CC) correspond to calcium chromite (CaCr<sub>2</sub>O<sub>4</sub>). Hashimoto et al. [12] also obtained needle-like CaCr<sub>2</sub>O<sub>4</sub> crystals by heating a powder mixture of CaCO<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>, which are very similar to the crystals shown in Fig. 8.

Spinel-type compounds, such as MgCr<sub>2</sub>O<sub>4</sub>, are very resistant to oxidation and dissolution in acid environments; low chromium levels of leaching are expected in the MgO modified slags from stainless steelmaking. Therefore, it can be said that the presence of MgO leads to the formation of MgCr<sub>2</sub>O<sub>4</sub> instead of CaCrO<sub>4</sub> or Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F in these slags, diminishing the formation of leachable chromium compounds; however, the CaO/SiO<sub>2</sub> ratio must be maintained in a low level to avoid the formation of the Ca–Cr compounds, which may be leached in acid environments.



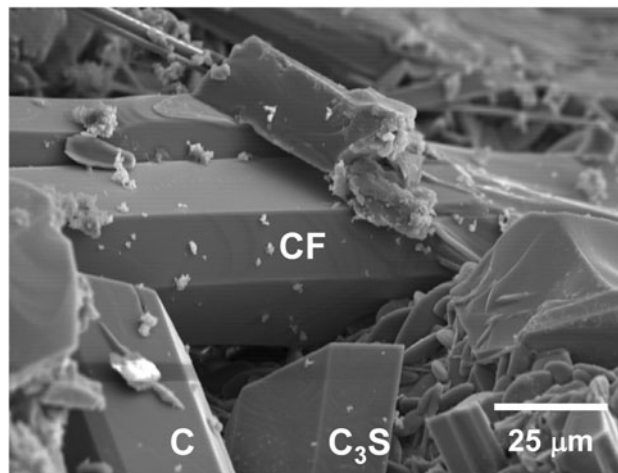


**Fig. 5** XRD patterns of slags with 6 % MgO and **a**  $\text{CaO/SiO}_2 = 1$ , **b**  $\text{CaO/SiO}_2 = 2$

**Leaching trials**

Figure 9 shows the effect of MgO and the  $\text{CaO/SiO}_2$  ratio in the slags on the leaching behavior of chromium. As can be seen, the maximum chromium extraction, 40 mg/l Cr and 98 mg/l Cr, are reached when MgO is not added in the slag and the basicity is 1 and 2, respectively; whilst 29 mg/l Cr and 68 mg/l Cr are leached from slags with 9 %MgO and  $\text{CaO/SiO}_2$  equals 1 and 2, respectively. These results showed that the lowest chromium concentration levels in the leaching liquors corresponded to MgO-based slags and low slag basicity ( $\text{CaO/SiO}_2 = 1$ ) owing to the stable binding of chromium in spinel with MgO ( $\text{MgCr}_2\text{O}_4$ ).

The effect of slag basicity on the leaching behavior of Cr was analyzed in the  $\text{Al}_2\text{O}_3$ -based slags in a previous work. It was shown that by using  $\text{Al}_2\text{O}_3$  instead of MgO to modify the slag, the slag basicity strongly affected the Cr



Atom %						
Crystal	Ca	Si	Cr	Mg	O	F
C	27.2	14.5	0.6	0.2	31.4	26.1
CF	22.5	4.30	9.10	0.0	55.2	8.90
$\text{C}_3\text{S}$	33.1	13.7	0.60	0.20	52.2	0.20

**Fig. 6** SEM micrographs and EDS analysis of the crystalline phases of the slag with 6 % MgO and  $\text{CaO/SiO}_2 = 2$ . C,  $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}$ ; CF,  $\text{Ca}_5(\text{CrO}_4)_3\text{F}$ ;  $\text{C}_3\text{S}$ ,  $\text{Ca}_3\text{SiO}_5$

extraction, when the  $\text{CaO/SiO}_2$  ratio was increased from 1 to 2. This behavior was mainly due to the formation of the Cr(VI)-containing compounds  $\text{CaCrO}_4$  and  $\text{Ca}_4\text{Al}_6\text{CrO}_{16}$ . In the MgO-based slags, the systems with high slag basicity ( $\text{CaO/SiO}_2 = 2$ ) produced compounds where chromium had a high oxidation state ( $\text{CaCrO}_4$  or  $\text{Ca}_5(\text{CrO}_4)_3\text{F}$ ), which increased the leachability of the slags.

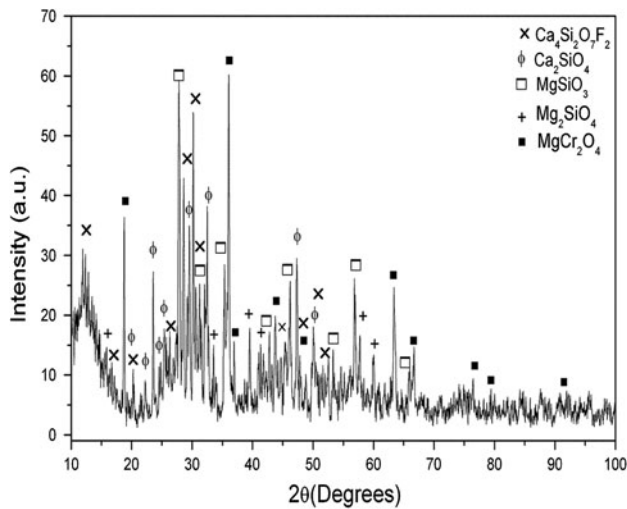
**Potential–pH diagrams**

Potential–pH diagrams can be used to identify the conditions required to dissolve a metallic compound in an aqueous solution at specific temperature and pressure. The FACTSage computational thermodynamic package [10] and its database were used to determine the potential–pH diagrams at 25 °C for the Ca–Cr– $\text{H}_2\text{O}$  and Mg–Cr– $\text{H}_2\text{O}$  systems. To complete the database of FACTSage we included the following thermodynamic information for the solid calcium chromate ( $\text{CaCrO}_4$ ) reported by Lee and Nassaralla [13].

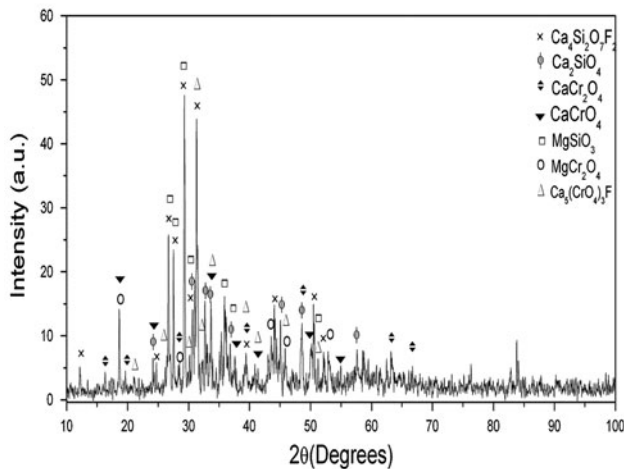
$$H_{298}^{\circ} = -1396.3 \text{ kJ mol}^{-1}; S_{298} = 130.9 \text{ J mol}^{-1} \text{ K}^{-1} \tag{1}$$

$$C_p = 127.92 + 35.73 \times 10^{-3} T - 2.257 \times 10^6 T^{-2} \text{ J mol}^{-1} \text{ K}^{-1} \tag{2}$$

Figure 10 shows the potential–pH diagrams at 298.15 K (25 °C) for the Ca–Cr– $\text{H}_2\text{O}$  and Mg–Cr– $\text{H}_2\text{O}$  systems



(a) CaO/SiO<sub>2</sub> = 1

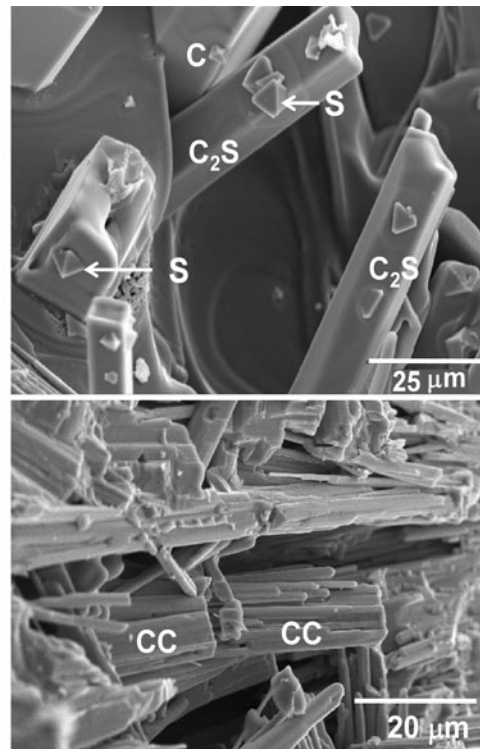


(b) CaO/SiO<sub>2</sub> = 2

**Fig. 7** XRD patterns of slags with 9 % MgO and **a** CaO/SiO<sub>2</sub> = 1, **b** CaO/SiO<sub>2</sub> = 2

calculated with the FAcTSage thermodynamic software [10]. Water is only stable in the region bounded by the dashed lines. The equilibrium conditions that can be utilized for the leaching of minerals or any solid compound in aqueous solutions at ambient temperature and pressure are constrained to those defined by the region of water stability.

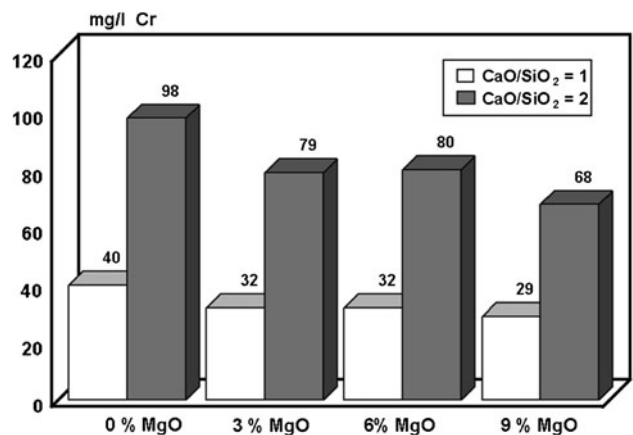
Figure 10 was constructed specifically to compare the domains of CaCr<sub>2</sub>O<sub>4</sub>, CaCrO<sub>4</sub> and MgCr<sub>2</sub>O<sub>4</sub> and in this way to establish which compound makes the slag more vulnerable to leaching. The molality of all the aqueous species in these systems have been fixed at *m* = 1. CaCrO<sub>4</sub> is not stable in acid solutions. CaCr<sub>2</sub>O<sub>4</sub> becomes unstable when the pH of the leaching solution is slightly acid, about pH < 6, where Ca<sup>2+</sup> and Cr(OH)<sup>2+</sup> ions are produced. The domain of MgCr<sub>2</sub>O<sub>4</sub> is larger than that corresponding to



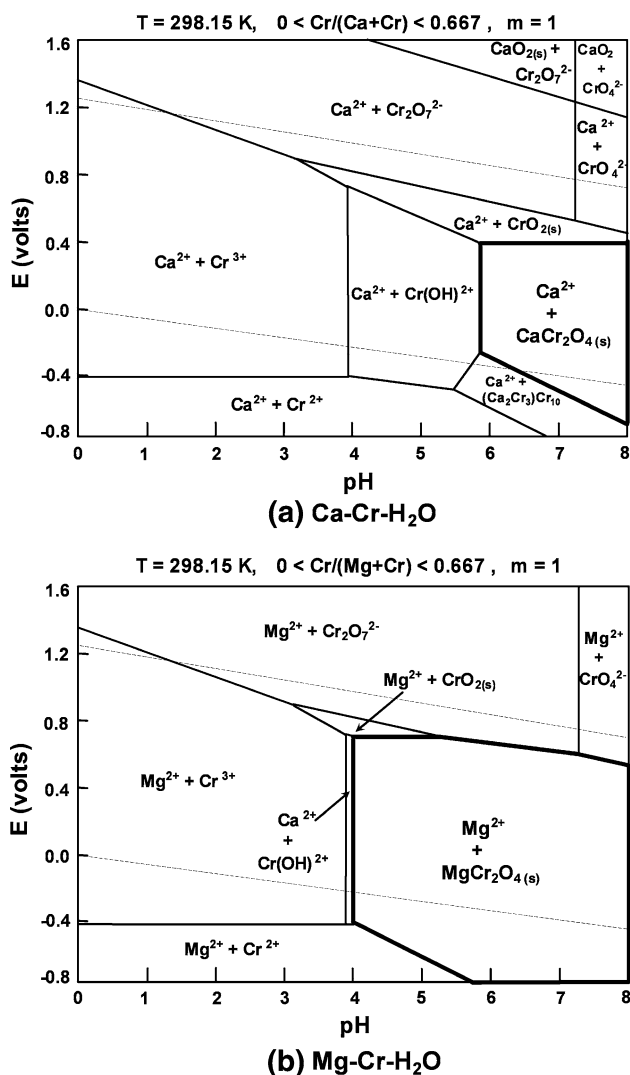
Atom %

Crystal	Ca	Si	Cr	Mg	O	F
S	2.9	3.3	33.0	15.2	42.1	3.5
C	28.1	13.7	0.7	0.9	42.7	13.9
C <sub>2</sub> S	29.6	7.9	0.9	1.0	60.6	0.0
CC	16.3	1.4	26.1	0.0	54.9	1.3

**Fig. 8** SEM micrographs of the crystalline phases of the slag with 9 % MgO and CaO/SiO<sub>2</sub> = 2. C, Ca<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>F; C<sub>2</sub>S, Ca<sub>2</sub>SiO<sub>4</sub>; S, MgCr<sub>2</sub>O<sub>4</sub>; CC, CaCr<sub>2</sub>O<sub>4</sub>



**Fig. 9** Effect of the CaO/SiO<sub>2</sub> ratio and MgO content on the leaching behavior of Cr



**Fig. 10** Calculated potential–pH diagrams for the Ca–Cr–H<sub>2</sub>O and Mg–Cr–H<sub>2</sub>O systems at 25 °C

CaCr<sub>2</sub>O<sub>4</sub> and it is stable in solutions with pH >4. Then, it is important to promote the stabilization of chromium in the slag using MgO. It is worth noting that the thermodynamic information for Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F was not available and this species was not included in the E–pH diagrams.

**Conclusions**

Slags samples of the system CaO–CaF<sub>2</sub>–SiO<sub>2</sub>–Cr<sub>2</sub>O<sub>3</sub>–MgO were prepared in order to analyze the effect of the CaO/SiO<sub>2</sub> ratio and MgO content on the stability of the mineralogical species and the leachability of slags. The following results were obtained:

- a. Slags with CaO/SiO<sub>2</sub> = 1 and low MgO content (3 %) contained magnesium chromite (MgCr<sub>2</sub>O<sub>4</sub>) together with CaCr<sub>2</sub>O<sub>4</sub> and the hexavalent chromium species

CaCrO<sub>4</sub>. Increasing the MgO content, the only Cr-containing compound formed was MgCr<sub>2</sub>O<sub>4</sub>, a spinel structured compound.

- b. Slags with CaO/SiO<sub>2</sub> = 2 contained MgCr<sub>2</sub>O<sub>4</sub> together with CaCr<sub>2</sub>O<sub>4</sub>, CaCrO<sub>4</sub> and the Cr(V)-containing compound complex Ca<sub>5</sub>(CrO<sub>4</sub>)<sub>3</sub>F which was formed with hexagonal crystals. However, the presence of MgO in the slag leads to the formation of MgCr<sub>2</sub>O<sub>4</sub>, diminishing the formation of leachable Ca–Cr compounds.
- c. The leaching trials results showed that the slags with high slag basicity produced the highest chromium extraction in the leachates. The presence of MgO in the slag diminished the formation of leachable chromium compounds; however, the CaO/SiO<sub>2</sub> ratio must be maintained in a low level to avoid the formation of Cr(V) and Cr(VI) compounds, which may be leached by acidic solutions. MgO helped to control the chromium leachability, which is due to the stable binding of chromium in MgCr<sub>2</sub>O<sub>4</sub>. The E–pH diagrams showed that the stability domain of MgCr<sub>2</sub>O<sub>4</sub> is larger than that corresponding to CaCr<sub>2</sub>O<sub>4</sub> and CaCrO<sub>4</sub>; therefore, the formation of the Mg-spinel minimizes the leachability of the slag.
- d. A topic of future research will be the stabilization and solidification as processes of hazardous waste treatment and disposal.

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**References**

1. Lind BB, Fällman A-M, Larsson LB (2001) Environmental impact of ferrochrome slag in road construction. Waste Manag (Oxford) 21:255–264
2. Hiltunen R, Hiltunen A (2004) Environmental aspects of the utilization of steel industry slags. VII international conference on molten slags, fluxes and salts, pp 357–361
3. Kilau HW, Shah ID (1984) Chromium-bearing waste slag: evaluation of leachability when exposed to simulated acid precipitation. Hazardous and industrial waste management and testing: third symposium, ASTM, pp 61–80
4. Kindness A, Macias A, Glasser FP (1994) Immobilization of chromium in cement matrices. Waste Manag (Oxford) 14:3–11
5. Duchesne J, Laforest G (2004) Evaluation of the degree of Cr ions immobilization by different binders. Cem Concr Res 34:1173–1177
6. Eriksson J, Björkman B (2004) MgO modification of slag from stainless steelmaking. VII international conference on molten slags, fluxes and salts, pp 455–459
7. Arredondo-Torres V, Romero-Serrano A, Zeifert B, Cruz-Rivera J, Flores P, Cruz-Ramírez A (2006) Stabilization of MgO•Cr<sub>2</sub>O<sub>3</sub> spinel in slags of the SiO<sub>2</sub>–CaO–MgO–Cr<sub>2</sub>O<sub>3</sub> system. Revista de Metalurgia de Madrid 42:417–424

8. García E, Romero-Serrano A, Zeifert B, Flores P, Hallen M (2008) Immobilization of chromium in slags using MgO and Al<sub>2</sub>O<sub>3</sub>. *Steel Res Int* 79:332–338
9. Mexican Official Norms. NOM-053-ECOL (1993). <http://www.Semarnat.gob.mx>
10. Thompson WT, Bale CW, Pelton AD (2010) FACTSage—facility for the analysis of chemical thermodynamics (FACTSage). Ecole Polytechnique, Montreal. <http://www.crct.polymtl.ca>
11. Chesterman CW, Lowe KE (eds) (1988) The Audubon Society. Field guide to North American rocks and minerals. Alfred A. Knopf, Inc., New York, pp 416–419
12. Hashimoto S, Yamaguchi A, Takahashi Y (1997) Growth and characterization of needle-like  $\beta$ -CaCr<sub>2</sub>O<sub>4</sub> crystals. *Mater Res Bull* 32:1593–1602
13. Lee YM, Nassaralla CL (2006) Standard free energy of formation of calcium chromate. *Mater Sci Eng* 437:334–339