TECHNICAL PAPER

Stabilization of Chromium in Synthetic Slags with $FeSO_4$ and FeS_2

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Abstract In this work, the effects of the slag basicity (mass ratio CaO to SiO_2) and the addition of $FeSO_4$ or FeS_2 into the slag on the stability of the mineralogical species in the slag containing chromium compounds were studied. The chemical stability was evaluated by leaching the slags with an acid solution. The main Cr-compounds in slags with low basicity ($CaO/SiO_2 = 1$) and $FeSO_4$ were $FeCr_2O_4$ and $Ca_3Cr_2Si_3O_{12}$, while Cr_3S_4 and $Ca_3Cr_2Si_3O_{12}$ were formed in slags with FeS_2. The slags with high basicity ($CaO/SiO_2 = 2$) and $FeSO_4$ contained $CaCr_2O_4$, $FeCr_2O_4$ and $Ca_5(SiO_4)_2SO_4$. The slags with FeS_2 and high basicity produced $FeS·Cr_2S_3$, $FeCr_2O_4$ and $Ca_3Cr_2Si_3O_{12}$. The results showed that the lowest chromium concentration levels in the leaching liquors corresponded to slags with $CaO/SiO_2 = 1$ and high FeS_2 contents, owing to the stable binding of chromium in the compounds $FeCr_2O_4$, Cr_3S_4 and $Ca_3Cr_2Si_3O_{12}$.

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1 Introduction

There is an increasing interest in finding ecological solutions for the safe disposal of industrial by-products that can cause environmental risks due to the mobility of the toxic elements therein. In particular, environmental concerns are on the rise due to the heavy metal content in stainless steel and ferrochrome slags, especially Cr [1, 2].

The stone-like properties of metallurgical oxide slags make them attractive in the civil engineering field as construction material; therefore, to prevent the leaching of heavy metals such as chromium, it is desirable to treat them prior to its application or even landfilling. Chemical 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. It has been proposed to fix the chromium into stable mineral phases by adding some materials to the liquid slag in the transfer ladle [1]. For instance, blast furnace slags can be used to stabilize Cr(III) and Cr(VI) in contaminated soils to decrease their leachability to safe levels [3, 4]; blast furnace slags have also been used for both physical and chemical immobilization of chromium in Portland and blended cements [3].

The influence of several slag forming agents over the leaching behavior of Cr has been analyzed. For instance,

adding MgO reduces the refractory wear down and modifies the slag composition, lowering the Cr-contents in the leachate [5] which can also be attained by adding spinel forming materials such as bauxite [6, 7]. In either case, the environment-friendly behavior of the slags is improved.

In a previous work [8] the authors studied the effect of slag basicity (CaO/SiO_2) and MgO and Al_2O_3 contents on the stability of the mineralogical species and the leachability of slags. It was found that $CaCr_2O_4$ and $CaCrO_4$ were present in slags prepared with neither MgO nor Al_2O_3. The Al_2O_3-based slags mainly produced $Ca_2Al_2SiO_7$ and the Cr(VI)-containing oxide complex $Ca_4Al_6CrO_{16}$, whilst MgO-based slags produced $MgCr_2O_4$ as main mineralogical species.

In this work, synthetic slags containing chromium have been prepared and the effects of slag basicity and $FeSO_4$ and FeS_2 contents on the stability of the mineralogical species formed have been evaluated. The morphology and composition of the slags have been analyzed by X-ray powder diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDS). The chemical stability of Cr has been evaluated by analyzing the leaching levels of chromium according to the Mexican Waste Norms [9].

2 Materials and Experimental Procedure

The slags were prepared from laboratory reagent-grade compounds (CaO, $FeSO_4 \cdot 7H_2O$, FeS_2, CaF_2, SiO_2 and Cr_2O_3) which were previously ground into fine powder whose particle size was between 45 and 74 μm. Two synthetic slag systems were prepared:

Slags A : $CaO, CaF_2, SiO_2, Cr_2O_3 + FeSO_4$

Slags B : $CaO, CaF_2, SiO_2, Cr_2O_3 + FeS_2$

The $FeSO_4$ and FeS_2 content in each type of slag ranged from 0 to 9 mass %, Cr_2O_3 and CaF_2 were 10 % and the slag basicity, defined as the ratio of CaO content to the SiO_2 content (mass %), was 1 or 2. The Cr_2O_3 content tested in these slags was higher than those actually found in ferrochrome or stainless steel production. Still this high Cr_2O_3 concentration was used in order to observe clearly the effect of chromium on the leaching behavior of the slags. Table 1 shows the mixture compositions for slags A. The experimental compositions for slags B were similar to those shown in Table 1, but FeS_2 was used instead of $FeSO_4$.

100 g of each slag system were prepared as follows. The powders were homogeneously mixed and placed in an Al_2O_3 crucible which was placed in a graphite protecting crucible inside an open induction furnace. Each mixture

was heated for 30 min at a temperature 50 °C above its melting point, to ensure complete homogenization. It was worth to note that it was difficult to estimate theoretically the melting temperature of these slags; then, the slags were heated between 1450 and 1550 °C, depending on the composition, and the melting temperature was checked mechanically using a stainless steel bar which was introduced in the melt. The furnace temperature was controlled within ± 5 K with an R-type thermocouple (Pt–Pt, 13 %Rh).

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. The morphology, shape and compositions of the solid crystallized phases were investigated: the presence of crystals with homogeneous composition and well-developed facets, was taken as an 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 these materials was evaluated by the following leaching technique, according to the Mexican environmental regulations [9]: 25 g of each slag was crushed below 74 μm and contacted with 500 cm^3 of an aqueous acetic acid solution at pH = 2.88 ± 0.05 in a rotary system during 20 h at 30 ± 2 rpm and 23 ± 2 °C. The solid residues were filtered through ashless filter paper (Whatman 542) and the chromium present in the leachate was determined by atomic absorption spectrophotometry. It was worth noting that this chemical analysis gave the total chromium in the leachate, including Cr^{3+}, Cr^{5+} and Cr^{6+}.

3 Results and Discussion

### 3.1 Result of Slags A ($FeSO_4$)

Figure 1 shows the XRD patterns of the slag A without $FeSO_4$ with different basicity ratios. Cuspidine ($Ca_4Si_2O_7F_2$), calcium chromate ($Ca_3(CrO_4)_2$), calcium chromite ($CaCr_2O_4$) and free Cr_2O_3 are present in both cases, despite the difference in basicity. The valence of chromium in the compounds $CaCr_2O_4$ and $Ca_3(CrO_4)_2$ are 3+ and 5+, respectively. Figure 2 shows the SEM micrographs and the EDS semi-quantitative analysis for some chemical species found in this slag ($CaSiO_3$, Cr_2O_3 and $CaCr_2O_4$).

The XRD patterns for slags A with 9 % $FeSO_4$ are shown in Fig. 3. $FeCr_2O_4$, $CaCr_2O_4$ and the complex compound $Ca_5(SiO_4)_2SO_4$ are obtained for both the slag

Table 1 Mixture compositions of slags A used for experiments in mass pct

Slag number	CaO/SiO₂	FeSO₄	CaO	SiO₂
A-1	1	0	40.0	40.0
A-2	1	3	38.5	38.5
A-3	1	6	37.0	37.0
A-4	1	9	35.5	35.5
A-5	2	0	53.3	26.7
A-6	2	3	51.4	25.7
A-7	2	6	49.4	24.7
A-8	2	9	47.4	23.7

% Cr_2O_3 = 10, % CaF_2 = 10
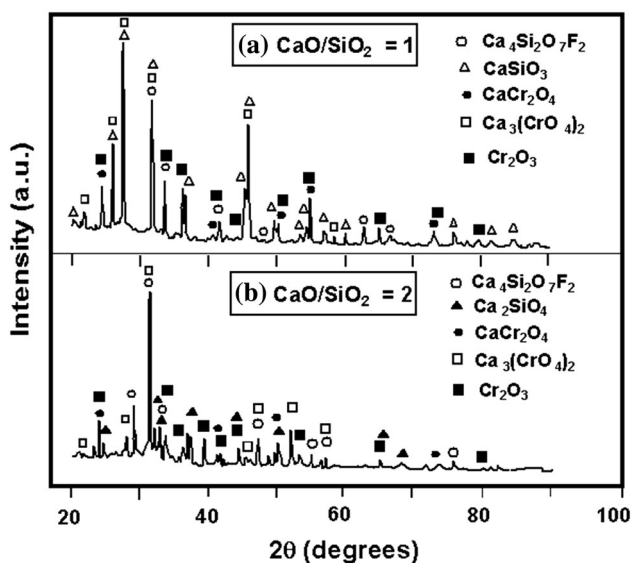
Fig. 1 XRD patterns of slags A with 0 % $FeSO_4$ and **a** CaO/SiO_2 = 1; **b** CaO/SiO_2 = 2

basicities. However, calcium silicates of the garnet group, andradite ($Ca_3Fe_2Si_3O_{12}$) and uvarovite ($Ca_3Cr_2Si_3O_{12}$), are present in slags with CaO/SiO_2 = 1. The $Ca_5Cr_2SiO_{12}$ with valence Cr^{5+}, is observed in slags with CaO/SiO_2 = 2. The garnet group comprise of several minerals with related chemical formulas. The generic formula for the common garnets is: $X_3^{2+}Y_2^{3+}Si_3O_{12}$, where X represents Ca, Fe^{2+}, Mn or Mg, and Y represents Al, Cr or Fe^{3+}. The species $Ca_5Cr_2SiO_{12}$, a pentavalent Cr^{5+} compound, is formed in the slags with high basicity. Cr^{5+} and Cr^{6+} form stable anions in aqueous solution [10] and it is expected that the leachability of chromium by acid solutions may be high in these slags.

The SEM–EDS semi-quantitative analysis confirm the XRD results, as can be observed in the micrographs shown in Fig. 4, corresponding to the slag with 9 % $FeSO_4$ and CaO/SiO_2 = 1. The trapezohedral crystal (labeled A)

contains calcium, chromium, silicon and oxygen. So it is believed that it corresponds to uvarovite ($Ca_3Cr_2Si_3O_{12}$). High contents of chromium, iron and oxygen are found in the octahedron crystals (labeled B). It has been reported [11] that chromite ($FeCr_2O_4$) crystallizes in cubes or octahedrons, such as those observed in this sample; thus, it is believed that chromite ($FeCr_2O_4$) is formed in this slag. The crystal labeled C, contains mainly calcium, silicon, sulfur and oxygen, and they probably correspond to $Ca_5(SiO_4)_2SO_4$, identified by XRD in Fig. 3.

Spinel-type compounds, such as $FeCr_2O_4$, are very resistant to oxidation and dissolution in acid environment; therefore low chromium levels of leaching are expected. It can be seen that the presence of $FeSO_4$ leads to the formation of chromite $FeCr_2O_4$ instead of $Ca_3(CrO_4)_2$ in these slags, diminishing the formation of leachable chromium compounds.
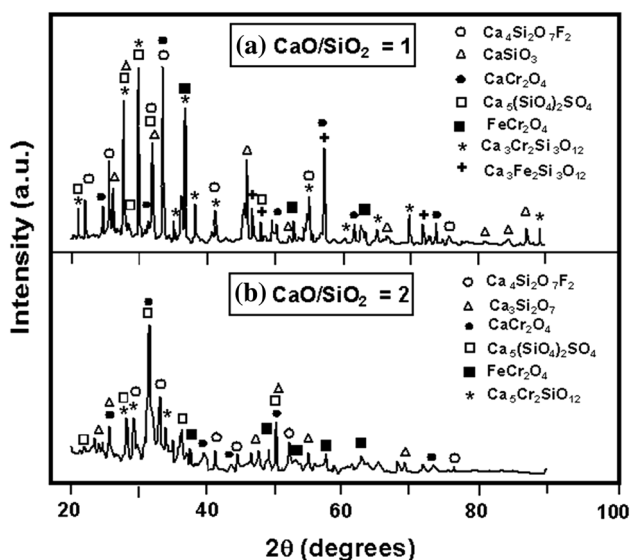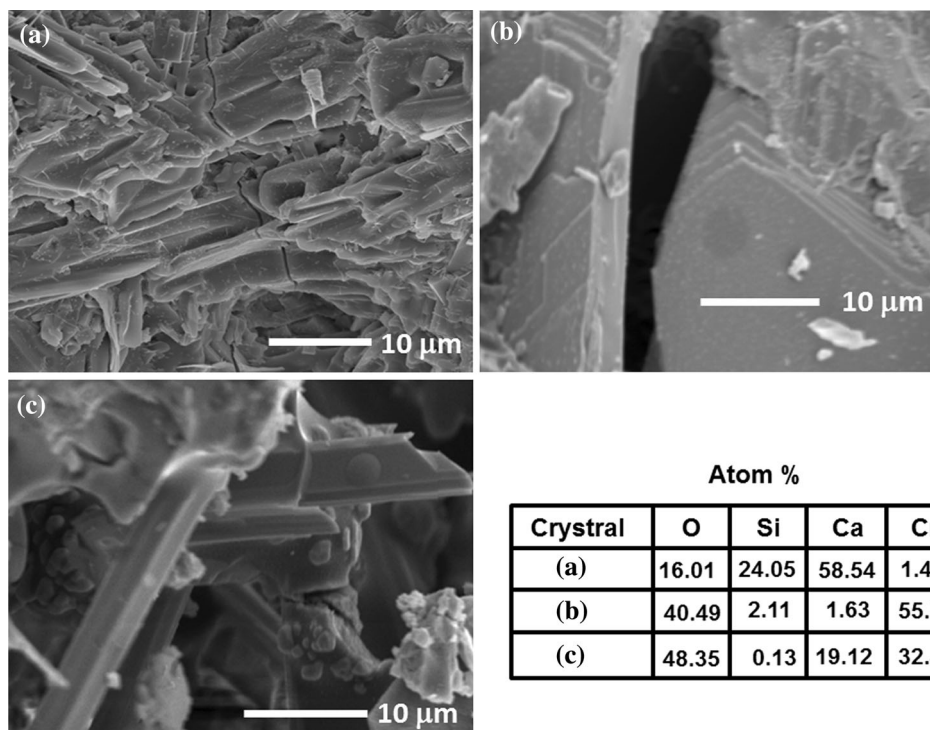
3.2 Result of Slags B (FeS_2)

Figure 5 shows the X-ray diffraction patterns for slags B with 3 % FeS_2 and CaO/SiO_2 = 1 and 2. As has been observed in slags A with $FeSO_4$, the slags with FeS_2 contain cuspidine ($Ca_4Si_2O_7F_2$) and calcium silicates. The Cr-based compounds for the slags with CaO/SiO_2 = 1 are $Ca_3Cr_2Si_3O_{12}$ and Cr_3S_4. The last compound (Cr_3S_4), named brezinaite, is a complex compound formed by CrS and Cr_2S_3, which has been reported to form at very reducing conditions. Figure 5b shows that increasing the slag basicity, the Cr-based compounds are $Ca_3Cr_2Si_3O_{12}$, $CaCrSi_4O_{10}$ and $CaCr_2O_4$. Brezinaite (Cr_3S_4) is also observed in the FeS_2-based slags with high basicity.

Figure 6 shows the SEM micrographs and the EDS results for the crystalline phases of the slag with 3 % FeS_2 and CaO/SiO_2 = 1. Crystal labeled A shows a trapezohedral structure with calcium, chromium, silicon and oxygen, probably corresponding to uvarovite ($Ca_3Cr_2Si_3O_{12}$). Crystal labeled B contains mainly chromium and sulfur and it is believed that it corresponds to brezinaite (Cr_3S_4), identified by XRD in Fig. 5. The triclinic crystal observed in this slag corresponds to wollastonite ($CaSiO_3$), according to the EDS results.

Figure 7 shows the X-ray diffraction patterns for slag B with 9 % FeS_2 and CaO/SiO_2 = 1 and 2. The X-ray results show that the mineralogical species obtained in this slag are basically the same as those obtained with 3 % FeS_2. It is worth noting that the main difference regarding the Cr-based compounds is that, with low basicity, brezinaite is obtained, whilst at high slag basicity, calcium chromite ($CaCr_2O_4$) and FeS·Cr_2S_3 are formed. Magnetite (Fe_3O_4) is also detected in the slags with FeS_2.

Figure 8 shows micrographs of the crystalline structures obtained in slags B with 9 % FeS_2 and CaO/SiO_2 = 2. The

Fig. 2 SEM micrographs of the crystalline phases of the slags A with 0 % $FeSO_4$ and $CaO/SiO_2 = 1$. **a** $CaSiO_3$; **b** Cr_2O_3; **c** $CaCr_2O_4$

Crystral	O	Si	Ca	Cr
(a)	16.01	24.05	58.54	1.40
(b)	40.49	2.11	1.63	55.77
(c)	48.35	0.13	19.12	32.40

Atom %

Fig. 3 XRD patterns of slags A with 9 % $FeSO_4$ and **a** $CaO/SiO_2 = 1$; **b** $CaO/SiO_2 = 2$

octahedron crystals (labeled A), which contain mainly iron, chromium and oxygen, probably correspond to chromite ($FeCr_2O_4$), as identified by XRD (see Fig. 7). The crystals labeled B contain mainly chromium, iron and sulfur, and it is possible that they correspond to the complex compound $FeS\cdot Cr_2S_3$, observed in the XRD results. Elongated crystals (labeled C) correspond to calcium chromite ($CaCr_2O_4$). Hashimoto et al. [12] also obtained needle-like $CaCr_2O_4$

crystals by heating a powdered mixture of $CaCO_3$ and Cr_2O_3, which are very similar to the crystals shown in Fig. 8.
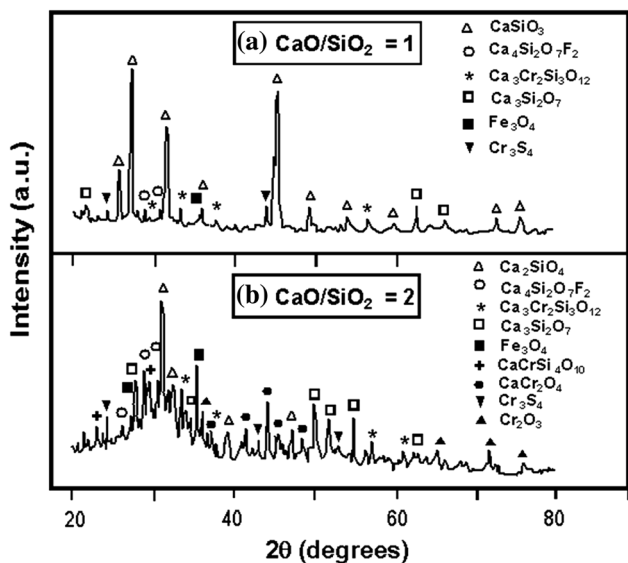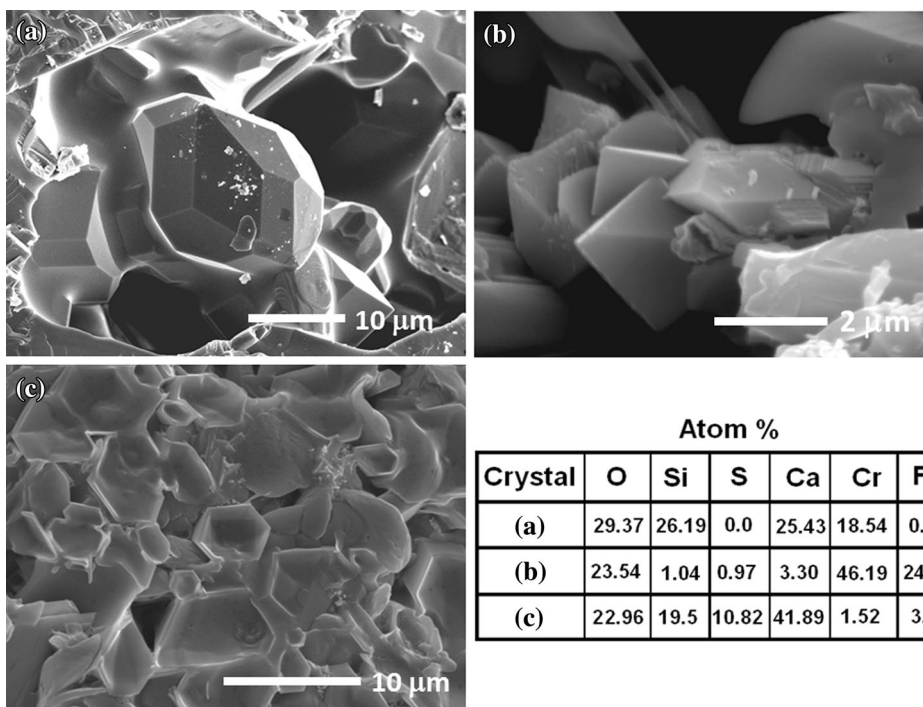
3.3 Leaching Trials Results

Figure 9 shows the effect of $FeSO_4$ and the CaO/SiO_2 ratio in the slags on the leaching behavior of chromium. As can be seen, the maximum chromium extractions of 8.8 and 34.3 mg/l Cr are reached when $FeSO_4$ is not added to the slag and the basicities are 1 and 2, respectively; whilst 4.8 and 27.1 mg/l Cr are leached for slags with 9 % $FeSO_4$ and CaO/SiO_2 equals 1 and 2, respectively. These results show that the lowest chromium concentration levels in the leaching liquors correspond to $FeSO_4$-based slags and low slag basicity ($CaO/SiO_2 = 1$) owing to the stable binding of chromium in the spinel ($FeCr_2O_4$) and the garnet compound uvarovite ($Ca_3Cr_2Si_3O_{12}$).

Figure 10 shows the leaching results for the slags with FeS_2. It is clear that FeS_2 is better than $FeSO_4$ in controlling the chromium leachability, which can be due to the stable binding of chromium in brezinaite (Cr_3S_4) and uvarovite ($Ca_3Cr_2Si_3O_{12}$).

3.4 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

Fig. 4 SEM micrographs of the crystalline phases of the slags A with 9 % FeSO$_4$ and CaO/SiO$_2$ = 1. **a** Ca$_3$Cr$_2$Si$_3$O$_{12}$; **b** FeCr$_2$O$_4$; **c** Ca$_5$(SiO$_4$)$_2$SO$_4$

Crystal	O	Si	S	Ca	Cr	Fe
(a)	29.37	26.19	0.0	25.43	18.54	0.47
(b)	23.54	1.04	0.97	3.30	46.19	24.96
(c)	22.96	19.5	10.82	41.89	1.52	3.31

Fig. 5 XRD patterns of slags B with 3 % FeS$_2$ and **a** CaO/SiO$_2$ = 1; **b** CaO/SiO$_2$ = 2
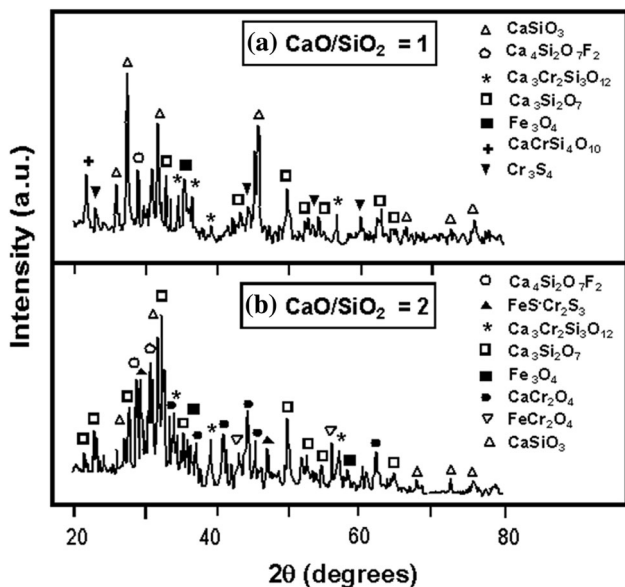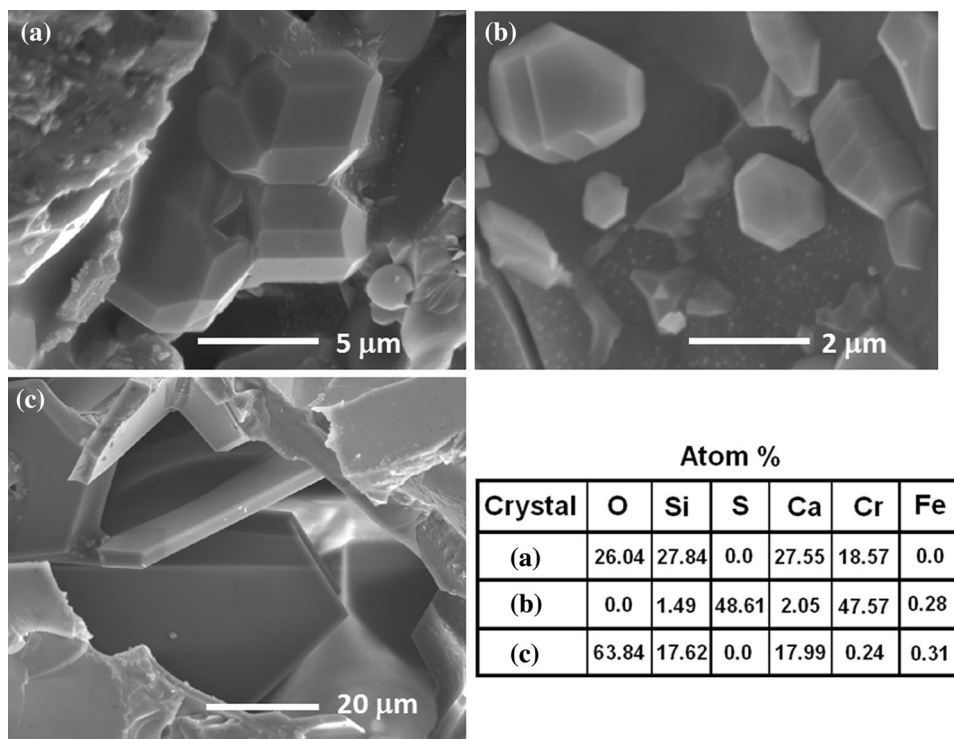
FACTSage computational thermodynamic package [13] and its database have been used to determine the potential-pH diagrams at 298.15 K (25 °C) for the Ca–Cr–H$_2$O, Ca–Cr–Si–H$_2$O and Fe–Cr–H$_2$O systems. The E-pH diagrams are shown in Figs. 11 and 12. Water is only stable in the region bounded by the dashed lines. The equilibrium conditions that can be utilized for the leaching of minerals or any solid compound in aqueous solutions at ambient temperature are constrained to those defined by the region of water stability.

Figure 11 shows the pH values calculated specifically to compare the domains of Ca$_3$Cr$_2$Si$_3$O$_{12}$ and CaCr$_2$O$_4$ and in this way to establish which Ca–Cr compound makes the slag less vulnerable to leaching. The molality of all the aqueous species in these systems has been fixed to m = 1. Figure 11a shows that CaCr$_2$O$_4$ becomes unstable when the pH of the leaching solution is slightly acidic, about pH < 6, where Ca^{2+} and Cr(OH)$^{2+}$ ions are produced. The domain of Ca$_3$Cr$_2$Si$_3$O$_{12}$ is larger than that corresponding to CaCr$_2$O$_4$ and it is stable in solutions with pH > 3. This is in agreement with the results of the work by Tae and Morita [14] who reported that the mineralogical species in the immobilization process of hexavalent chromium in wastewater using a granulated BF slag and hydrothermal treatment is the uvarovite (Ca$_3$Cr$_2$Si$_3$O$_{12}$). It is worth noting that the thermodynamic information of Ca$_3$(CrO$_4$)$_2$, Ca$_5$Cr$_2$SiO$_{12}$ and CaCrSi$_4$O$_{10}$ are not available and these species have not been included in the E-pH diagrams.

Figure 12 shows the potential-pH diagrams at 298.15 K (25 °C) for the Fe–Cr–H$_2$O systems with two ranges of the Fe/(Fe + Cr) molar ratio. The main Cr–Fe compound in this system is the solid iron chromite (FeCr$_2$O$_4$). This figure shows that with low Fe/(Fe + Cr) ratio (between 0 and

Fig. 6 SEM micrographs of the crystalline phases of slag B with 3 % FeS_2 and $CaO/SiO_2 = 1$. **a** $FeCr_2O_4$; **b** $FeS \cdot Cr_2S_3$; **c** $CaCr_2O_4$

| Crystal	O	Si	S	Ca	Cr	Fe
(a)	26.04	27.84	0.0	27.55	18.57	0.0
(b)	0.0	1.49	48.61	2.05	47.57	0.28
(c)	63.84	17.62	0.0	17.99	0.24	0.31

Fig. 7 XRD patterns of slags B with 9 % FeS_2 and **a** $CaO/SiO_2 = 1$; **b** $CaO/SiO_2 = 2$

0.333) $FeCr_2O_4$ is stable in relatively high acid solution (about pH > 2.2); however, Cr^{3+} and $Cr(OH)^{2+}$ are dissolved in the liquid solution. The stable species for the systems with Fe/(Fe + Cr) > 0.333 are $FeCr_2O_4$ and Fe_2O_3, avoiding in this way the leaching of any Cr-ion species. In the slags of the present work, the value Fe/(Fe + Cr) > 0.333 is obtained for the systems with 9 mass % of $FeSO_4$ or FeS_2.

3.5 Effect of the Slag Basicity

Different chromium oxides exist in silicate melts. Turkdogan [15] reported that chromium is present in silicate melts, depending on the temperature and composition, in bi- tri- or hexavalent states. The ratio between the concentrations of Cr^{2+}, Cr^{3+} and Cr^{6+} is regulated by the reactions

$$2(Cr^{2+}) + 1/2O_2 = 2(Cr^{3+}) + (O^{2-}) \qquad (1)$$

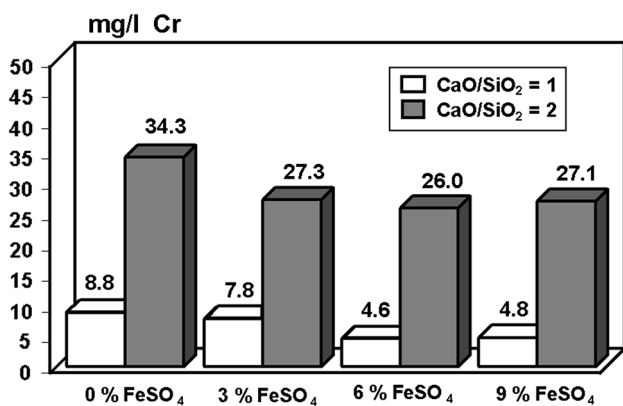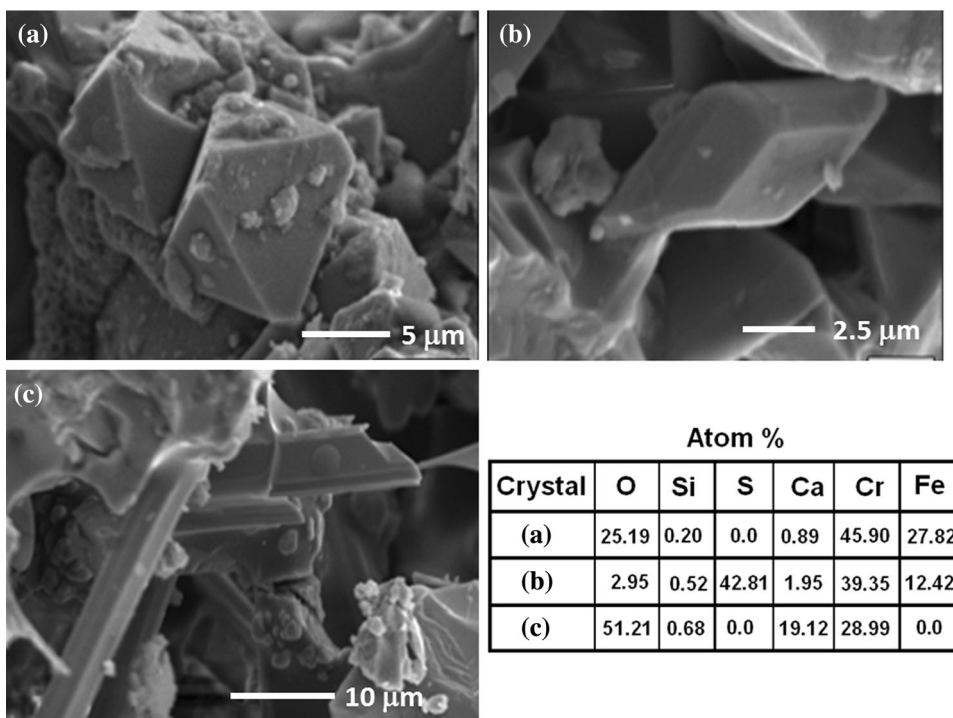$$(Cr^{3+}) + 5/2(O^{2-}) + 3/4O_2 = (CrO_4^{2-}) \qquad (2)$$
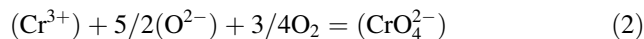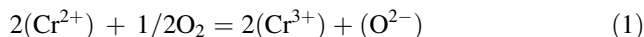
In oxidizing conditions, the anions of chromates are stable in basic melts, but decompose to form an ion of trivalent chromium in acid melts. In silicate slags silicon is present in the orthosilicate anion which is formed by the reaction:

$$SiO_2 + 2(O^{2-}) = SiO_4^{4-} \qquad (3)$$

Consequently, the solution of silica reduces the concentration of free anions of oxygen (O^{2-}). The addition of SiO_2 diminishes the slag basicity and the equilibrium of
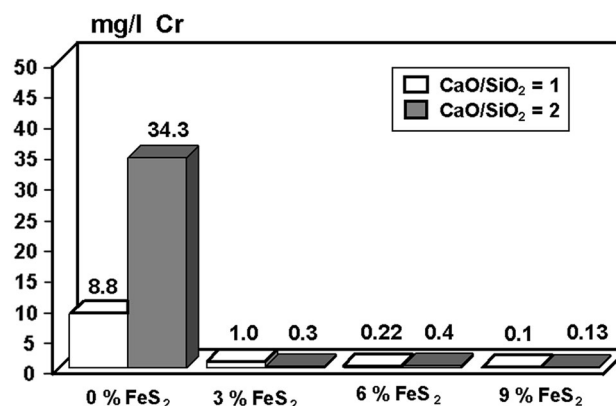
Fig. 8 SEM micrographs of the crystalline phases of slag B with 9 % FeS$_2$ and CaO/SiO$_2$ = 2. **a** FeCr$_2$O$_4$; **b** FeS·Cr$_2$S$_3$; **c** CaCr$_2$O$_4$

Crystal	O	Si	S	Ca	Cr	Fe
(a)	25.19	0.20	0.0	0.89	45.90	27.82
(b)	2.95	0.52	42.81	1.95	39.35	12.42
(c)	51.21	0.68	0.0	19.12	28.99	0.0

Atom %

Fig. 9 Effect of the CaO/SiO$_2$ ratio and FeSO$_4$ content on the leaching behavior of Cr

Fig. 10 Effect of the CaO/SiO$_2$ ratio and FeS$_2$ content on the leaching behavior of Cr

reaction (2) is shifted to the left and the hexavalent chromium is reduced to the trivalent state.

It is worth to note that the experiments in this work have been carried out in an open furnace with the oxygen partial pressure close to PO$_2$ = 0.21 atm. Even though the alumina crucible is placed in a graphite protecting crucible, the experimental setup is not exposed to a reducing atmosphere above the slag system. If air is used as an atmosphere, hexavalent chromium compounds appear in the high-lime region, whereas at high silica slag content, all the chromium is virtually in the +3 oxidation state as has been reported by Glasser and Osborn [16]. So, if air is used as atmosphere, the stable chromium compounds depend only on the CaO/SiO$_2$ ratio.

4 Conclusions

Synthetic slag samples of the system CaO–CaF$_2$–SiO$_2$–Cr$_2$O$_3$–(FeSO$_4$ and FeS$_2$) were prepared in order to understand the effect of FeSO$_4$ and FeS$_2$ content and the slag basicity on the stability of the mineralogical species and the leachability of slags. The following results were obtained:
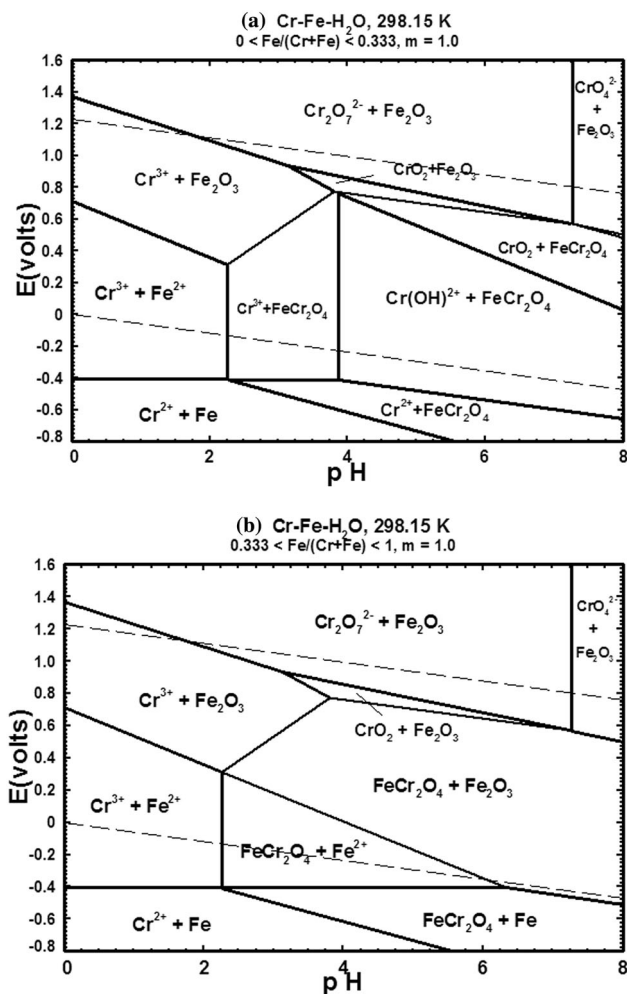
(a)　Slags without FeSO$_4$ and FeS$_2$ contained Ca$_3$(CrO$_4$)$_2$, a pentavalent chromium species (Cr^{5+}), and CaCr$_2$O$_4$. The FeSO$_4$–based slags produced the complex compound Ca$_5$(SiO$_4$)$_2$SO$_4$, together with garnet-type
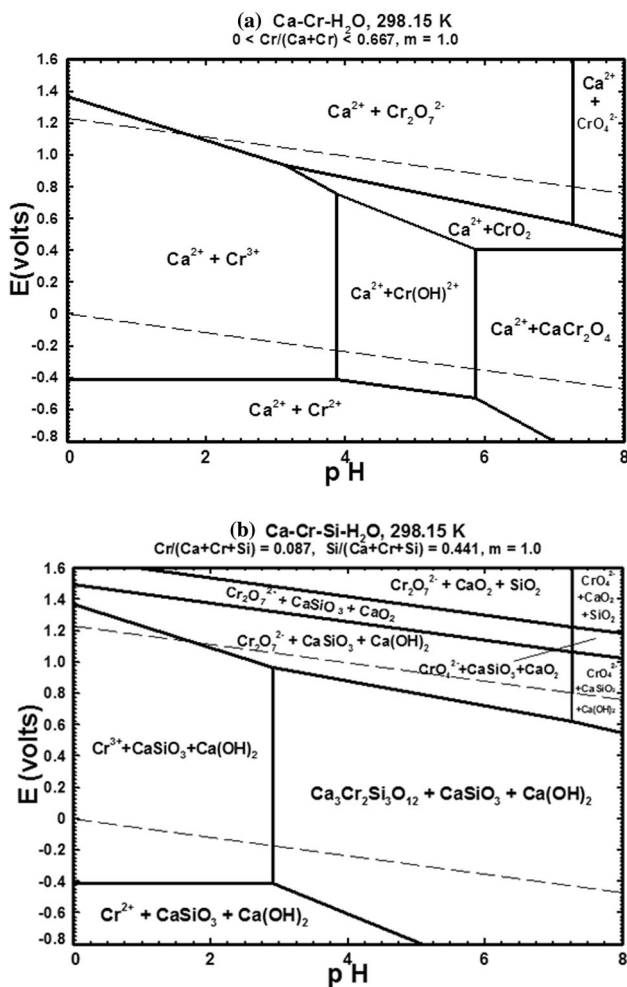
Fig. 11 Calculated Potential-pH diagrams for the **a** Ca–Cr–H$_2$O and **b** Ca–Cr–Si–H$_2$O systems at 298.15 K

Fig. 12 Calculated Potential-pH diagrams for the Fe–Cr–H$_2$O systems at 298.15 K

compounds (Ca$_3$Cr$_2$Si$_3$O$_{12}$ and Ca$_3$Fe$_2$Si$_3$O$_{12}$). The slags with FeS$_2$ formed Ca$_3$Cr$_2$Si$_3$O$_{12}$ and the sulfur-based compounds (Cr$_3$S$_4$ and FeS·Cr$_2$S$_3$).

(b) The results showed that the slags without FeSO$_4$ or FeS$_2$ produced the highest chromium extraction in the leachates. The presence of FeSO$_4$ in the slag led to the formation of chromite (FeCr$_2$O$_4$) and uvarovite (Ca$_3$Cr$_2$Si$_3$O$_{12}$), diminishing the formation of leachable chromium compounds; however, the CaO/SiO$_2$ ratio was to be maintained at a low level in order to avoid the formation of Ca$_5$Cr$_2$SiO$_{12}$, where Cr had a valence of 5+.

(c) The leaching results showed that FeS$_2$ was better than FeSO$_4$ in controlling the chromium leachability, which could be due to the stable binding of chromium in chromite (FeCr$_2$O$_4$), brezinaite (Cr$_3$S$_4$) and uvarovite (Ca$_3$Cr$_2$Si$_3$O$_{12}$).

(d) The potential-pH diagrams showed that the stability domain of Ca$_3$Cr$_2$Si$_3$O$_{12}$ and FeCr$_2$O$_4$ were larger than that corresponding to CaCr$_2$O$_4$; therefore, the formation of these compounds minimized the leachability of the slag.

References

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