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Article

Effects of Basicity and Mesh on Cr Leaching of EAF Carbon Steel Slag

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Abstract: The slag's chromium leaching is one of the most pressing concerns in Electric Arc Furnace (EAF) carbon and stainless steels production. In recent years, many studies have aimed at understanding which properties (basicity, cooling speed) and phases (spinel, wustite, silicates) determine the Cr leaching, defining different indices (sp-factor, cs-factor) in order to forecast the slag's behavior compared to the leaching of this toxic metal. The literature suggests that spinel formation is usually a good way to fix Cr and prevent its leaching. However, in some conditions (high basicity, low amount of spinel-forming species) soluble Cr-bearing phases can be formed, i.e., Ca-chromite or unstable spinel. In these conditions, Cr can be leached easily, even if it is bound in a spinel structure. In this paper, the effects of basicity and impurities (Ca, Si) on the instability of Cr-spinel was investigated, with respect to slag mesh. The influence of basicity was also studied on Mg-wustite stability, which might contribute to the leaching of Cr. Different samples of carbon steel slag, suspected of forming unstable spinels, belonging to different steel grade production, were also investigated. Both granulated (4 mm) and milled (<100 µm) slag were analyzed. Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS) analyses were carried out to measure the local chemical composition of Cr-bearing phases. This data was correlated with slag basicity (by X-Ray Fluorescence: XRF), spinel fraction (by X-Ray Diffraction: XRD), and Cr leaching (by Inductively Coupled Plasma Mass Spectrometry: ICP-MS). The main results indicate that the increase of the slag basicity implies an increase of the impurity content (Ca, Si) in the spinel, also over-saturated by Cr. This aspect, coupled with spinel geometrical features, seems to justify the unexpected Cr leaching of some slag samples. Basicity does not influence the chemistry of wustite, thus excluding it as an additional Cr leaching source.

Keywords: Electric Arc Furnace slag; Cr leaching; basicity; Cr-spinel; Ca-chromite; Mg-wustite; geometrical features

1. Introduction

Of the numerous toxic elements that can be leached from waste, chromium appears to be of greatest concern when it comes to human health. The hexavalent oxidation state of Cr is toxic, and several of the chromates are classified as carcinogenic by the WHO (World Health Organization) [1]. The main risk associated with Cr leaching is the contamination of ground water, generally used as public water supplies. For this reason, Cr concentration in drinkable water is restricted to very low limits, i.e., 0.1 mg/L in the US [2] or 50 µg/L in the European Union [3]. Specific studies on

the leaching behavior of Cr in slag started in the US over 30 years ago. The role of slag binary basicity (BI_2 : CaO/SiO_2), MgO concentration and slag processing after slagging were investigated by Kilau and Shah [4]. When BI_2 is above 2.0, Cr is present as calcium chromite ($CaO \cdot Cr_2O_3$), regardless of the MgO content, and the slag are prone to high Cr leachability. Leaching can be minimized if basicity is well below 2, with enough MgO to form insoluble picrochromite ($MgO \cdot Cr_2O_3$), the hypothetical Mg-Cr end-member of the spinel series. These results were confirmed about 20 years later by Arredondo-Torres et al. [5] and Cabrera-Real et al. [6] who studied the thermodynamics of the SiO_2 - CaO - MgO - Cr_2O_3 system. Both studies confirmed the role played by BI_2 in the formation of Ca-chromite, especially in a low-MgO-slag system. In our opinion, the use of a simply binary basicity index (BI_2) could not address the leaching behavior of Cr-spinels when formed in low Al_2O_3 -MgO slag [7,8]. For instance, in slag with low concentration of the above-mentioned chemical species, the spinels risk being over saturated in Cr, with potential risk of Cr leaching [8]. For this reason, in the present paper, BI_4 was used, thus also taking Al_2O_3 and MgO into account. Other basicity indexes are available, i.e., optical basicity (Λ) [9]. Λ is a good index because it considers the whole chemical composition of a slag but its computation requires a long time and its interpretation is not practical; since it is always below 1, it is difficult to understand if a slag is acidic or alkaline [10]. In addition, for certain oxides more optical basicity values are available in literature [11–14] and this results in a different interpretation of the behavior of an oxide with respect its capacity to donate or receive an oxygen anion. A strong contribution to defining the positive effects of spinel formation was given by Kuhn et al. [15], who delineated a simple but reliable index with which to forecast the Cr leachability in stainless steel EAF slag: The so-called sp-factor. However, the effectiveness of this parameter has been recently disproved in terms of predicting the leaching of Cr in carbon steel slag [7]. Recent investigations have focused on the dissolution of silicates and aluminates, since in high basicity slag, Cr tends to remain in solution in silicates complex instead of forming spinels [16,17]. In this regard, Geißler et al. [18] defined a new index, called cs-factor, which accounts for the Cr bound in calcium silicates, more solvable in water than spinels. Currently, a recently published paper explained a method to favor the migration of Cr from an unstable silicate-matrix to spinels: The key is the solidification pattern from liquid to solid that allows Cr to migrate from silicates to enrich spinels [19].

Other than the formation of Ca-chromite, which releases Cr due to oxidation to $CaCrO_4$, one of the effects of high basicity seems to be the formation of unstable spinels, that feature a non-negligible content of impurities (Ca, Si) and irregular shape [8,20,21]. As stated by Albertson et al. the spinel phase found at higher levels of basicity and oxygen partial pressure has the stoichiometric composition of the Mg-spinel, but has an irregular structure, referring to both its crystal structure and shape or morphology. This is due to the presence of Cr^{6+} ions. Cr-spinels are thus not thermodynamically stable. This phenomenon has been well described in earlier studies by the same authors [20–23]. Unstable spinels are suspected to induce Cr leaching, and thus, an in-depth investigation about this point is needed. Very recently, Strandkvist et al. [24] demonstrate on a laboratory scale that in certain conditions (high MgO/FeO ratio) wustite, a common mineral always present in EAF slag, can also induce additional Cr leaching. Thus, a double check of Cr-spinels and wustite is mandatory in order to understand which phase is actually responsible for Cr leaching.

The present study originates from an unexpected relationship observed between the same slag tested in different size conditions, i.e., granulated (4 mm) and milled (<100 μm).

For instance, certain slag samples that can be considered safe compared to Cr leaching, released unexpected amounts of such an element. In detail, a hyperbolic relation was identified between the results of standard testing and in powder leaching tests (Figure 1). This behavior already pointed out by Mombelli et al. [8] was unexpected, since increasing the surface-to-volume ratio (S/V) of a particle, its dissolution rate rises [25]. This behavior may depend on different factors, which have been investigated in the present paper.

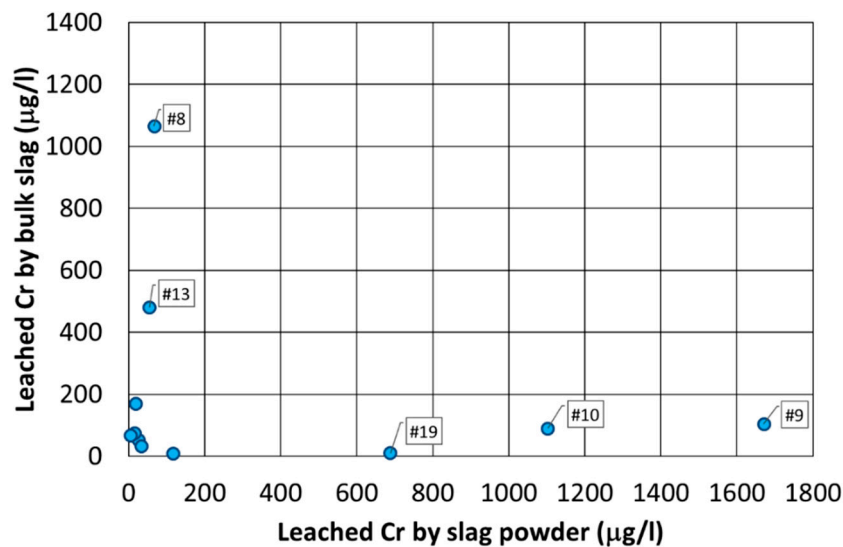


Figure 1. Relation between Cr leached by bulk slag (standard conditions) and by slag powder (marked samples represent remarkable behavior slag).

For this reason, the effect of slag basicity on the content of impurities (Ca, Si) and Cr-bearing phases (Cr-spinel, wustite, et al.) instability were investigated. Different samples of carbon steel slag suspected of forming unstable spinels, belonging to different steel grade production (reinforcing bar steel, high-alloyed steel and quality steel), were investigated, both in the form of granules (4 mm) and powder (<100 µm).

2. Materials and Methods

Nineteen (19) different samples provided by different Italian and European electric steelworks were analyzed. Chemical composition and mineralogical characterization were performed by means of ED-XRF and XRD, respectively. The results were reported in previous papers [7,8,26].

Standard leaching tests were performed according to EN 12457-2 (24 h in 10 l/kg deionized water stirred by a rotatory mixer at 10 rpm) both on granulated slag of 4 mm and on slag powder (obtained by ring-mill grinding). The leached concentration of Cr was measured by ICP-MS (Induced Coupled Plasma-Mass Spectroscopy, detection limit 10 µg/L). Chemical composition, basicity index ($BI_4 = \frac{CaO+MgO}{SiO_2+Al_2O_3}$), phase fraction, and Cr leached concentration are reported in Table 1. In all the investigated samples, Cr was mainly bound in spinels, and in three samples (8, 13 and 18) also in Ca-Cr compounds. In a few samples, Cr was also detected in brownmillerite [8,26,27], which is suspected of contributing to Cr leaching, but in this work its effects were not taken into consideration. Brownmillerite was excluded because the samples featured by this phase belong to the same group, thus making a non-significant comparison.

The local chemical composition of Cr-bearing phases and wustite was measured by SEM-EDS on slag molded in araldite-based resin, before being ground and polished. Ten (10) measurements for each phase were performed on each sample. This data was correlated with slag basicity, spinel fraction and leached Cr.

Table 1. Chemical and mineralogical characterization and leaching test results for the investigated samples.

Sample ID	Group	Chemical Composition (wt.%)		Phase Fraction (wt.%)			Cr Leaching ($\mu\text{g/L}$)	
		Cr_2O_3	BI_4	Wustite	Ca-Cr Compounds	Cr-Spinel	Bulk	Powder
1	A	4.28	0.829	29.7	-	19.6	n.d.	168
2	A	2.87	0.614	21.4	-	16.2	n.d.	10
3	A	2.84	1.103	31.6	-	12.6	n.d.	169
4	A	3.48	0.597	25.2	-	6.3	n.d.	30
5	A	4.30	0.751	43.1	-	14	10	117
6	A	2.04	0.862	10.2	-	-	n.d.	79
7	A	2.76	0.601	22.4	-	4.2	n.d.	81
8	B	29.52	4.378	1.37	33.7	14.4	1065	67
9	B	22.03	0.915	7.3	-	34.6	104	1671
10	B	25.00	0.915	7.3	-	40.0	90	1102
11	C	1.59	1.139	7.7	-	7.6	n.d.	114
12	C	1.44	1.125	15.6	-	7.2	n.d.	113
13	C	2.49	2.730	11.8	25.2	-	480	54
14	C	3.12	1.431	21.2	-	2.4	52.3	25
15	C	2.00	1.343	-	-	2.1	75	16
16	C	2.93	1.268	-	-	2.1	33	33
17	C	3.18	1.257	-	-	2.0	68	5
18	C	2.64	2.278	6.5	7.2	6.4	170	19
19	B	21.82	1.228	20.5	-	53.9	10.8	688

A: Reinforcing bar steel slag, B: High-alloyed steel slag, C: Quality steel slag. "n.d.": Not detected.

3. Results

3.1. Description of the Slag Samples

In Figure 2, an example of the most representative microstructure of the analyzed slag is reported. This picture, showing only six slag samples, is suitable to compare the phases' morphology as well as their arrangement as a function of the slag group. For instance, the slag belonging to group A (re-bar steel), are characterized by relative low basicity, high fraction of wustite and low fraction of Cr-spinel. This is due to the operative conditions of the furnace, i.e., low quality and strong scraps oxidation. The production of high quality and high-alloyed steels (group B and C) requires a better control of the scrap quality together with a low oxygen consumption in order to maximize the steel yield. This implies high basicity and a very low amount of wustite. A high basicity, augmented primarily by the copious addition of lime, induces the formation of high CaO-bearing phases, like $3\text{CaO}\cdot\text{SiO}_2$ (H in Figure 2), brownmillerite (B in Figure 2) or Ca-chromite (CaCr in Figure 2). Nonetheless, for the samples belonging to group B, due to the use of high-alloyed steel scraps, the average amount of CrO_x in the slag is significantly more than for the other two categories.

Increasing the chromium oxide (Cr_2O_3) concentration in the slag, the weight fraction of Cr-bearing phases increases (Figure 3a). From Figure 3a it can be noted that most of the samples are grouped in a limited range of Cr_2O_3 concentration (0–5 wt.%). Those slag are related both to re-bar and quality steels. Usually, the scraps used for this kind of productions are poor in alloying elements such as Cr and, for this reason, the amount of oxidized Cr migrating to the slag is relatively low. Nevertheless, re-bar steel slag presents a higher concentration of Cr_2O_3 compared to the quality steel slag since the former requires strong oxidation to remove the impurities within the scraps. Generally, these slag are characterized by small and dispersed Cr-spinels (max 20 μm), as can be seen in Figure 2. On the contrary, only a few samples (8, 9, 10, 19) feature very high (>20% wt.%) concentration of Cr oxide and all of them belong to the B-group, i.e., highly alloyed steel production. These slag are generally characterized by very coarse spinels (>50–100 μm) and, if the basicity is high, by needle-like Ca-chromite as well. An increase in Cr concentration in a slag also induces an enrichment of Cr in its

bearing phases (Figure 3b). This aspect must be taken into consideration since an excess of Cr needs other elements, i.e., Al, Mg, Fe, to form stable and safe phases. This condition is not always respected, and thus, in particular situations, the risk of leaching a high concentration of Cr can be relevant, even if Cr is fixed in apparently safe phases.

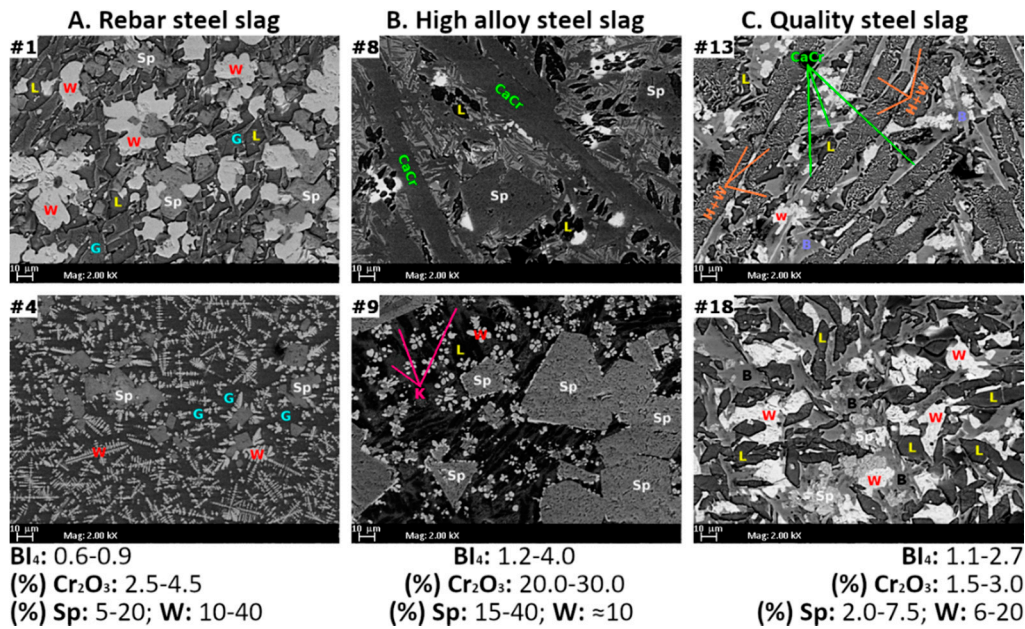


Figure 2. Example of SEM-BSE pictures of analyzed slag (samples 1, 4, 8, 9, 13, 18). B: brownmillerite; CaCr: Ca-chromite; G: gehlenite; H: hatrurite; K: kirschsteinite; L: larnite; Sp: spinel; W: wustite.

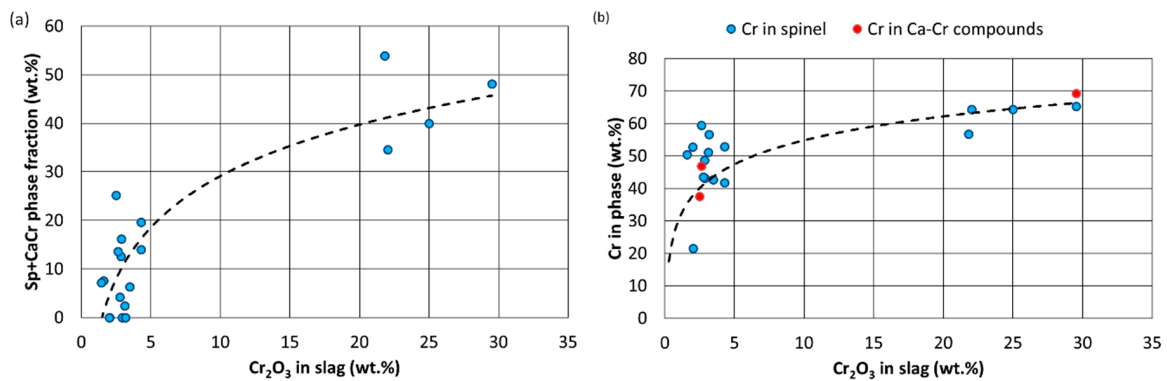


Figure 3. Cr-bearing phases fraction (a) and Cr concentration in Cr-bearing phases (b) as a function of Cr₂O₃ concentration in the slag.

3.2. Effect of Basicity on Phase Chemistry

One factor which determines Cr leaching behavior is slag basicity. As can be seen in Figure 4, increasing the basicity (BI₄), the Cr leached during standard testing increases as well. This result agrees with previous studies, since at high basicity other phases than spinels tend to form [5–7,23,26]. On the other hand, on milled slag, the more basic slag resulted in less leaching. This means that other factors contribute to determining the leaching behavior of milled slag.

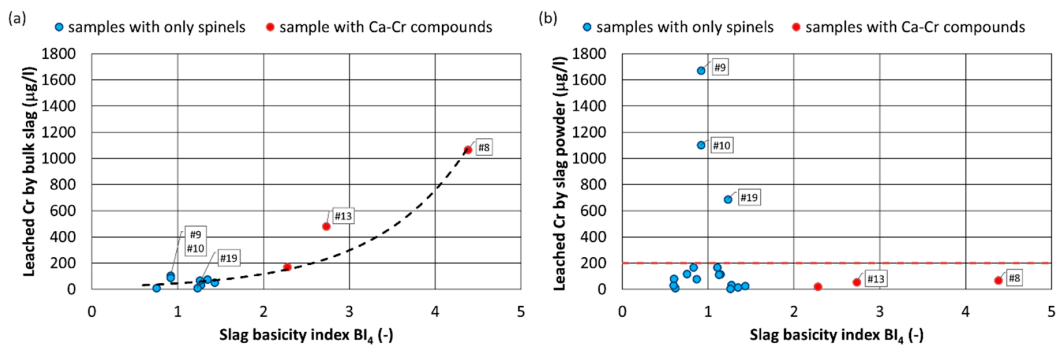


Figure 4. Effect of slag basicity on Cr leaching for (a) bulk slag and (b) slag powder. Marked samples represent remarkable behavior slag.

Basicity plays a key role in the characteristics of slag, especially in spinel formation and evolution. For instance, increasing the slag basicity, the concentration of non-spinel-forming elements (Ca, Si) increases in the slag spinel; as is also worthy of note is the fact that the higher the basicity, the higher the Cr concentration in the spinel is (Figure 5a). When Cr concentration in a spinel increases, the probability to form unstable spinel also increases, since more Cr requires more spinel-forming elements (Al, Mg, Fe) (Figure 5a) [8]. However, by increasing the basicity, the opposite occurs. In fact, the spinels are enriched by destabilizing species (Ca and Si) as reported in Figure 5c. In addition, a cut-off value can be identified ($Bl_4 > 2$), which leads to the formation of calcium-chromium compounds. When basicity is in the range of 2–3, one can identify the coexistence of Cr-spinel and Ca-chromate ($CaCrO_4$) (Figure 5b). If basicity is increased to over 4, Ca-chromate evolves in Ca-chromite ($CaCr_2O_4$). This is due to a decrease of Ca in Ca-Cr compounds and a collateral enrichment in Cr. These results are in line with previous researches [5,6,15,28]. The Cr enrichment in Ca-Cr compounds also corresponds with a dilution of other elements, i.e., Fe, Si, Mg, which can be considered as impurities of the above-mentioned phases (Figure 5d).

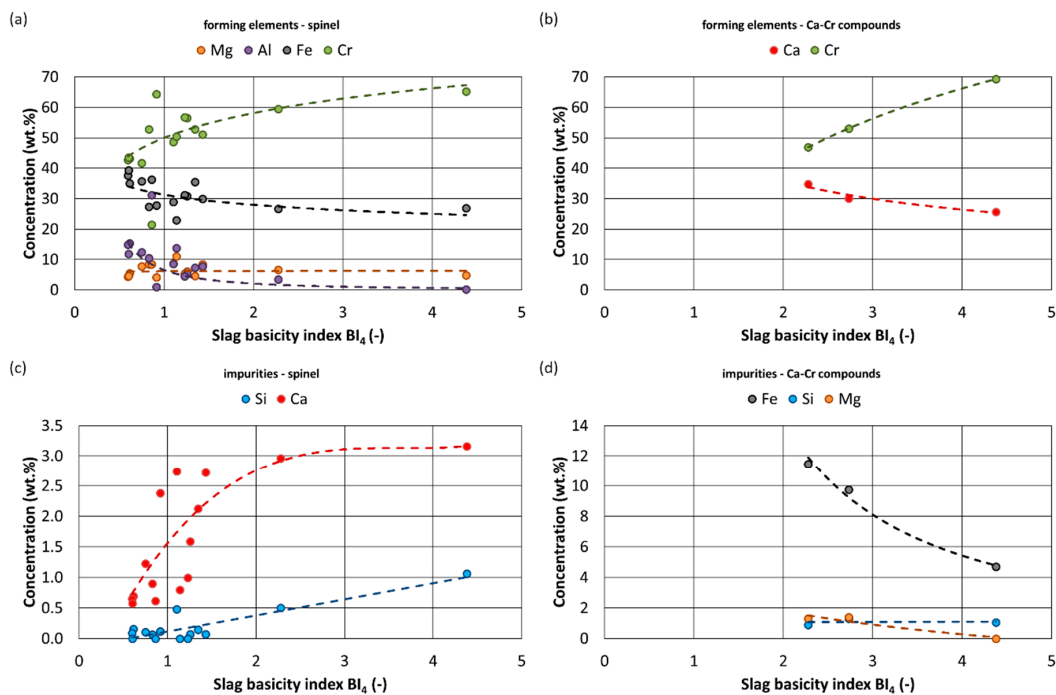


Figure 5. Elements distribution within the Cr-bearing phases: forming-elements in (a) spinel and (b) Ca-Cr compounds; impurities in (c) spinel and (d) Ca-Cr compounds.

As reported by Albertsson et al. [20] and Arredondo-Torres et al. [5], a slag with high basicity is interested by a (Mg,Ca)Cr₂O₃ solid solution precipitation from the liquid slag with a high amount of impurities and irregular lattice structure and morphology. This seems attributable to the presence of Cr⁶⁺ which induces spinel instability. Cr⁶⁺ formation is favored in high basicity slag, since it should have a high fraction of non-combined CaO that could react with Cr to yield Cr⁶⁺ [29]. Despite an increase in basicity leading to a higher concentration of impurities, these do not seem to have a marked influence on the release of chromium. The balance of the constituent elements of a spinel itself seems to be the parameter controlling Cr leaching, in line with the study carried out by Liao et al. [30]. Among these elements, the most influential with regards to Cr elution seems the Cr itself, as can be seen from the graph in Figure 6a. An increase in Cr concentration seems to favor its leaching. Nevertheless, most studies assessed that if Cr is fixed in spinels, the leaching does not depend on the Cr₂O₃ content in the slag. This aspect should be analyzed in relation to the stoichiometry of spinel composition. The general formula used to indicate the spinel group is XY₂O₄, where X is a divalent cation and Y is a trivalent cation. In the system under examination, the elements that can appear as trivalent cations are Fe, Cr and Al. Possible divalent elements are, instead, Mg and $\overline{\text{Fe}} = \text{Fe} + \text{Mn}$. For an ideal crystal the ratio between trivalent and divalent cations is 2:1. In Figure 6b the deviation from the ideality of this ratio (Δ) compared to the leachate Cr is reported. Δ was determined by Equation (1).

$$\Delta = 2 - \frac{\text{Mg} + \overline{\text{Fe}}}{\text{Al} + \text{Fe} + \text{Cr}} \text{ (at. \%)} \quad (1)$$

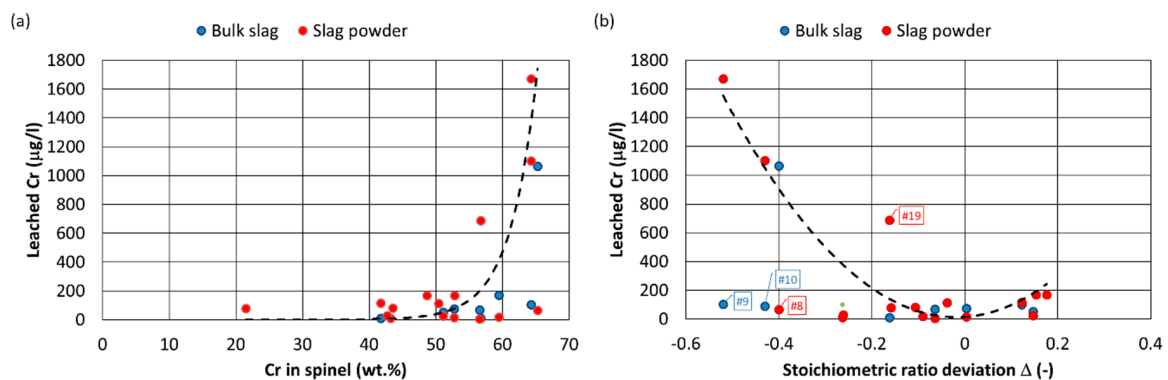


Figure 6. Effect of Cr (a) and stoichiometric ratio deviation (Δ) (b) on Cr leaching.

Figure 6b shows that non-stoichiometric spinel favors Cr leaching. The obtained parabolic trend allows one to demonstrate analytically that Cr leaching increases with the deviation from stoichiometric spinel composition. The samples in the left branch of the parabola show a negative Δ , i.e., they are over-saturated with trivalent cations such as Cr. This excess of Cr makes the spinel unstable and subject to leaching phenomena. In other words, the compounds formed with large difference from stoichiometric ratio result chemically active and, when in contact with a solution, are responsible for Cr leaching. As was shown before (Figure 5a,c), such spinels are those featuring a lower amount of other element-forming species and a high concentration of impurities, i.e., formed in high basicity slag. Also, positive deviations (Δ) (right branch of the parabola) lead to an increase of the leachate, although in a less obvious manner: These deviations are probably due to an increase in the Cr⁶⁺/Cr³⁺ ratio, due to an excess of divalent cations [20–23]. The identified parabolic relation fits the experimental results quite well except for in four points (samples 8,9,10,19, marked in Figure 6b). Such Cr concentrations in the leachate are related to samples featuring Ca-Cr compounds and/or very coarse spinels. In addition, these slags behave in different ways in relation to their size (granulated or milled). Based on the results discussed above, the leaching of chromium seems as if it is not a phenomenon determined by

purely chemical factors but rather one controlled by other factors, i.e., phase size and morphology, as is discussed in the next paragraph.

3.3. Effect of Basicity on Phase Geometry

The chemical aspects cannot fully explain the inverse proportional relation between the standard leaching test and the leaching test on powder. A strong relation between the phase geometry and the leaching is predictable. In particular, the higher the Cr_2O_3 concentration in slag, the higher the average size (equivalent diameter or area) of Cr-bearing phases becomes, both for spinels and Ca-Cr compounds. More in detail, in the slag with high Cr concentration large phases (>100 μm up to 1 mm) were detected, along with very small ones (~10 μm) (Figure 7).

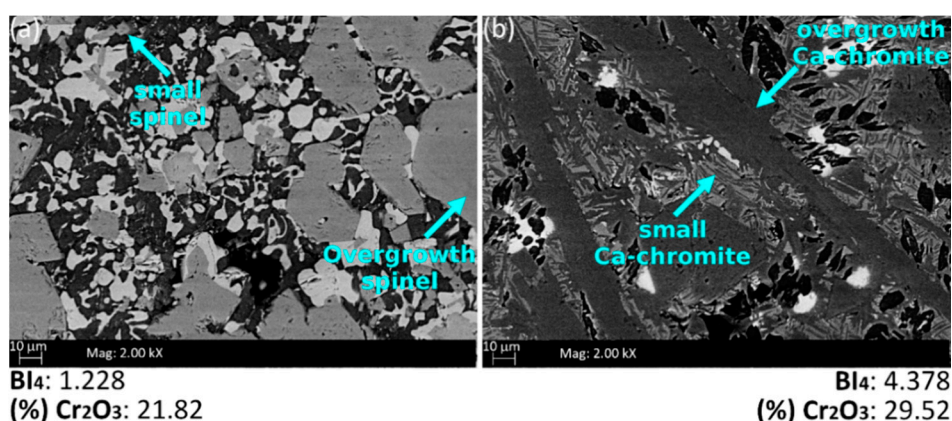


Figure 7. Examples of slag samples where overgrowth Cr-bearing phases coexist with small ones. (a) sample #19 (b) sample #8.

Even the basicity has the same effect on the phase size (Figure 8). Thus, the combination of high chromium concentration with high basicity induces uncontrolled growth of oversaturated Cr-bearing phases. Large phases are characterized by low S/V ratio, which should help to reduce the leaching, since the dissolution rate should be low. Actually, during the standard test, the samples characterized by very large spinel (9,10,19–Figure 7a), leached low amount of Cr (less than 100 $\mu\text{g}/\text{L}$). Probably, that leaching was only due to the small spinels that feature a high S/V ratio, and, in view of the consideration stressed above, are also unstable. Thus, that amount of leached Cr might be determined by the number of small and soluble spinels. This seems to be supported by the behavior of samples containing Ca-Cr compounds (8,13,18) as well. In fact, even sample 8 is characterized by large and long CaCr_2O_3 needles (Figure 7b), Cr concentration in the leachate was very high (>1 mg/L). This was determined by the small needles, which possess high solubility and high S/V ratio and are even in a larger amount than the overgrowth Ca-chromite crystals.

Cr leaching in milled slag demonstrates quite the opposite behavior. In fact, in the samples containing the overgrowth Cr-bearing phases, some of them are of a larger size than those reached by milled slag particles (Figure 9a). This means that during the milling, the overgrowth phases are smashed. This results in an augmented fraction of small, high S/V ratio, soluble phases, at least with the same size as a particle, that boost the Cr leaching (Figure 9b). This hypothesis seems to be confirmed by the results of low basicity-low Cr_2O_3 slag. In fact, in those samples, spinels are largely smaller than the final size of the milled particles and after grinding they appear practically unaltered, and for this reason the slag behaves in the same way during the two leaching tests (points close to 0 in Figure 1).

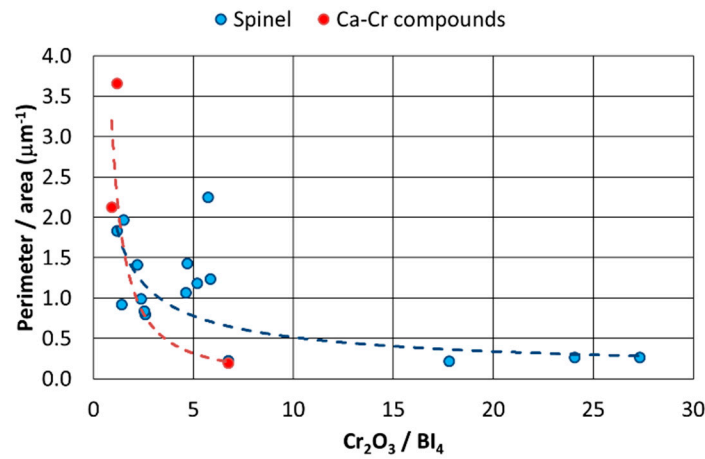


Figure 8. Combined effect of Cr_2O_3 concentration and slag basicity on Cr-bearing phases dimension (p/A).

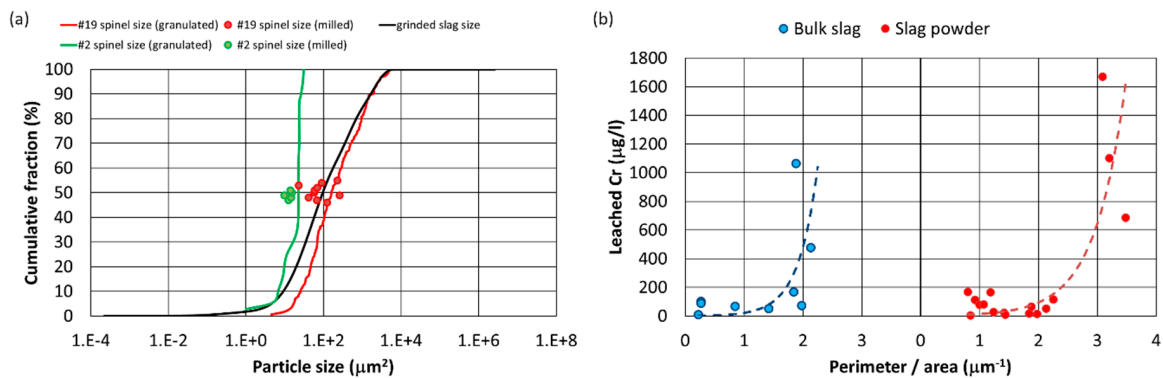


Figure 9. Comparison between milled particle size distribution and spinel size distribution (a) and role of phase dimension (p/A ratio) (b) on Cr leaching.

3.4. Role of Mg-Wustite

In a recent study [24], Mg-wustite was suspected to collaborate with calcium-silicates to drive Cr into the leachate. For this reason, its contribution is discussed in this section. In Figure 10 no evident correlation between the slag basicity and the chemical composition of wustite can be observed. In addition, no correlation exists between the concentration of Cr in Mg-wustite and the leached Cr, thus indicating the complete extraneousness of Mg-wustite in the Cr leaching process. On the other hand, increasing the Cr content in wustite would help to maintain the overall Cr concentration in the leachate at a low level, in those samples characterized by the presence of Ca-Cr compounds. In addition, all the investigated samples have a concentration of FeO in wustite greater than 60% by weight and as stated by Strandkvist et al. [24], wustite isn't responsible for Cr leaching.

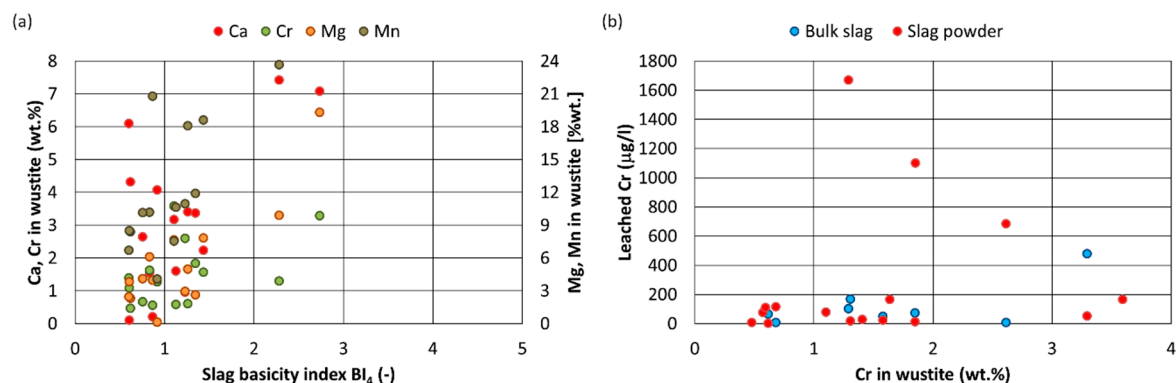


Figure 10. Cr, Ca, Mn and Mg distribution within Mg-wustite as a function of slag basicity (a) and effect of Cr concentration within Mg-wustite on Cr leaching (b).

4. Conclusions

In this work, the role of basicity to control the instability and the geometry of Cr-bearing phases (spinel, calcium chromite and wustite) was investigated both on granulated (4 mm) and milled (<100 μm) slag. Slag basicity determines the chemistry, stoichiometry and geometry of Cr-bearing phases and influences their leaching behavior:

- High basicity granulated slag are characterized by high Cr leaching. The same slag, but milled, show low chromium leaching;
- High basicity and high Cr_2O_3 concentration in the slag lead to overgrowth phases, oversaturated in Cr, coexisting with underdeveloped unstable phases;
- At high basicity, a high concentration of impurities (Ca and Si) occurs in the Cr-bearing phases, inducing instability and facilitating Cr mobility;
- It is confirmed that Mg-wustite does not contribute to Cr leaching. In addition, high Cr-wustite would help to reduce the overall leached Cr, especially in those samples characterized by the presence of Ca-Cr compounds.

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