



Effect of cooling conditions on the leachability of chromium in Cr_2O_3 -containing steelmaking slag

by Y. Yu*, D. Wang*, J. Li*†, M. Li‡, and Z. Xue*

Synopsis

The effects of temperature and atmosphere during cooling on the leachability of chromium from stainless steel slag were investigated. Experiments were performed under an oxidizing atmosphere in a muffle furnace and in a reducing atmosphere in an induction furnace. The slags were subjected to leaching tests using the standard procedure prEN12457-2. Results indicated that an oxidizing atmosphere enhances the leachability of chromium and that the extent of leaching increases with temperature. A reducing atmosphere tends to suppress the leaching of chromium. Differences between the chromium leached from the samples cooled under different atmospheres revealed that it is difficult for CO to completely reduce chromium Cr^{6+} to Cr^{3+} once hexavalent chromium has been generated. Therefore, it is necessary to utilize a neutral or reducing atmosphere for cooling the slag so as to prevent the formation of hexavalent chromium.

Keywords

atmosphere, oxidation, hexavalent chromium, stainless steel slag, chromium leaching.

Introduction

Stainless steel slags are generated in electric arc furnace (EAF), argon oxygen decarburization (AOD) furnace, and vacuum oxygen decarburization furnace operations. The transition metal chromium (Cr), which is an essential alloying element in stainless steel, is prone to oxidation because of its high reactivity during melting (Li *et al.*, 2013), and chromium oxides float in the molten slag phase. Trivalent and hexavalent chromium are the most common oxidation states in chromium compounds. Trivalent chromium is the most stable state under normal atmospheric conditions, whereas hexavalent chromium is toxic because of its strong oxidative property (Zhong *et al.*, 2015). The leaching of chromium from stainless steel slags can lead to economic and ecological issues (Loock-Hattingh *et al.*, 2015). Therefore, it is imperative to examine the mechanism involved in the leaching of chromium and design some effective treatments to stabilize chromium in slags.

Several studies have reported the leaching and stabilization of chromium (Engstrom, 2010; Durinck *et al.*, 2008; Albertsson, 2011; Tae and Morita, 2017; Gelfi, Cornacchia, and Roberti, 2010; Song and Garbers-Craig, 2016; Du Preez *et al.*, 2017). Engstrom (2010) and

Albertsson (2011) reported that the leachability of chromium depends mainly on the distribution of chromium in the slag. Stainless steel slag comprises various minerals. Some of these minerals, such as merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$), larnite (Ca_2SiO_4), akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), are slightly soluble in water. In contrast, other minerals, such as wüstite, and spinel, are resistant to dissolution and oxidation. The MgCr_2O_4 spinel phase, *i.e.*, magnesiochromite, in the slag is known to be important for controlling the leaching properties of chromium from the slag (Pillay, Von, and Petersen, 2003). Garcia-Ramos *et al.*, (2008) investigated the immobilization of chromium in $\text{CaO-SiO}_2\text{-Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-MgO}$ synthetic slags by MgO. Their results indicated that MgO-based slag exhibits the lowest chromium leachability, owing to the immobilization of chromium in MgO-spinel. Engström *et al.*, (2010) and Peter *et al.*, (2010) developed a new method for treating EAF slag obtained from stainless steelmaking. The agents that enhance the formation of the spinel solid solution are added into a transfer ladle during tapping of the steel and slag. The effect of the additions on spinel formation can be described as follows:

$$\text{factor } sp_{opt.} = 0.2 * \text{MgO} + 1.0 * \text{Al}_2\text{O}_3 + x_{opt.} \text{FeO}_n - 0.5 * \text{Cr}_2\text{O}_3 \text{ [%wt.]}$$

where $x_{opt.}$ depends on the oxidation state of the EAF slag.

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Effect of cooling conditions on the leachability of chromium in Cr₂O₃-containing steelmaking slag

For EAF slags with high values of $sp_{opt.}$, the leachable chromium content is almost negligible. These studies focused on the suppression of chromium leaching by adjusting the composition. Few studies have been reported regarding the effect of atmosphere on the leaching of chromium during cooling of stainless steelmaking slag. Considering the production of ferrochrome alloys from chromite ores, Beukes, Dawson, and Zyl (2010) reported that the generation of Cr(VI) is related to the presence of oxygen at a high temperature.

In this study, to increase understanding of the mechanism involved in the leaching of chromium from stainless steel slags, the effects of atmosphere and temperature on the leachability of chromium during the cooling of liquid slag were investigated by experiments performed in muffle and induction furnaces.

Experimental

Raw material

Table 1 summarizes the chemical composition of the slags obtained from the stainless-steelmaking process. Samples S1 and S2, which were generated in an AOD furnace, had an extremely high calcium oxide content, 61.54 wt% and 54.46 wt%, respectively, whereas the chromium oxide content in both slags was quite low, only 0.19 wt% and 0.51 wt%, respectively. Sample S3, the EAF slag, had the lowest basicity (CaO/SiO₂), albeit with a fairly high Cr₂O₃ content (5.78 wt%).

Experimental set-up and procedure

The experimental set-up included the muffle and induction furnaces (Figure 1). The maximum temperature of the muffle furnace was 1200°C. A graphite crucible was used as the heating element for the induction furnace, with a maximum power of 60 kW and frequency of 3 kHz. Figure 2 shows the experimental procedure. First, 270 g of each of the slag samples was crushed to less than 4 mm. Then, 90 g of particles was used for the leaching test, which was conducted according to the European standard leaching procedure prEN12457-2. The remaining 180 g was charged in an Al₂O₃ crucible and heated in the muffle furnace at 600°C and 1000°C for 180 minutes under air. Then, 90 g of the oxidized slag obtained from the muffle furnace in the previous step was used in the leaching test, and the remaining 90 g was heated in the induction furnace at the same temperature as in the muffle furnace for 180 minutes. Finally, the reduced slags were subjected to the leaching test. The leachates obtained from the tests were analysed using inductively coupled plasma emission spectrometry (ICP-OES, IRIS Advantage ER/S), and HSC Chemistry 5.1 was employed to perform

thermodynamic calculations for some reactions.

The standard procedure is in compliance with the leaching of granular waste materials and sludge, and a one-stage batch test is conducted at a liquid-to-solid ratio of 10 L/kg for materials with a particle size of less than 4 mm. The complete leaching procedure included the following steps:

- (i) Add 90 g of slag into a 1 L polypropylene bottle
- (ii) Add 900 mL of deionized water to the bottle
- (iii) Place the capped bottle in a rotary agitator (GGC-D, Guohuan Institute of High-tech Automation)
- (iv) Agitate for 24 ± 0.5 hours at a rate of 10 r/min
- (v) Filter the mixture using a vacuum filtration device (TTGM, 2000 mL, Lianlink).

Atmosphere in an induction furnace

Notably, a graphite crucible is used as the heating element in the induction furnace; thus, the interactions between O₂, CO₂, and CO occur at a high temperature (Huang, 2006).

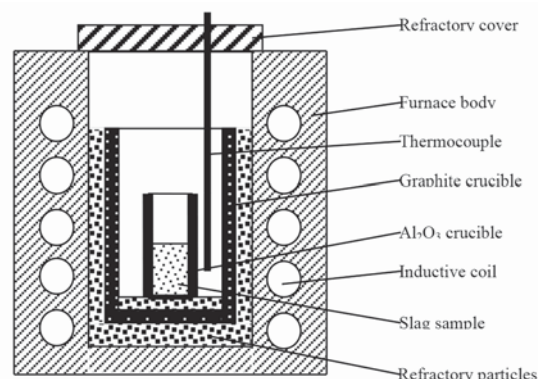


Figure 1 – Experimental set-up of the induction furnace

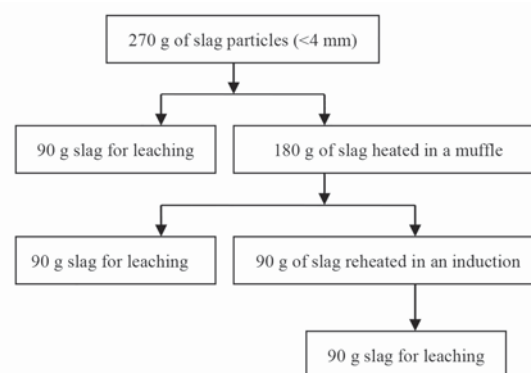


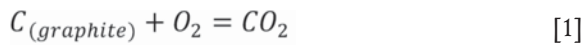
Figure 2 – Flow chart of the procedure for the treatment of stainless steel slag under different atmospheres

Table 1

Composition of the stainless steel slags, wt%

No.	CaO	SiO ₂	MgO	Al ₂ O ₃	Cr ₂ O ₃	MnO	TiO ₂	FeO	CaO/SiO ₂
S1	61.54	30.27	6.65	1.31	0.19	0.55	0.45	0.31	2.03
S2	54.46	29.57	7.90	5.39	0.51	0.42	0.53	0.29	1.84
S3	34.14	26.23	9.71	6.64	5.78	2.50	6.95	0.96	1.30

Effect of cooling conditions on the leachability of chromium in Cr₂O₃-containing steelmaking slag



$$\Delta G_1^\theta = -395350 - 0.54T \text{ J} \cdot \text{mol}^{-1} \quad [2]$$



$$\Delta G_3^\theta = -228800 - 171.54T \text{ J} \cdot \text{mol}^{-1} \quad [4]$$



$$\Delta G_5^\theta = 166550 - 171T \text{ J} \cdot \text{mol}^{-1} \quad [6]$$



$$\Delta G_7^\theta = -5619000 - 170.46T \text{ J} \cdot \text{mol}^{-1} \quad [8]$$

The partial pressures of O₂, CO, and C₂ are calculated at 600°C and 1000°C at the equilibrium state of the C–O system. A non-oxidizing atmosphere is present at high temperatures (Table II). CO was used for the reduction of slag. Niemelä, Krogerus, Oikarinen, (2004) and Kleynhans *et al.* (2016) have revealed that CO does not reduce Cr₂O₃. The possibility of the reduction of chromium from the hexavalent to the trivalent state by CO is discussed in the following sections.

Experimental results

The slag samples were heated at 600°C and 1000°C in the muffle furnace for 180 minutes and then leached according to the standard leaching procedure prEN12457-2. Higher chromium concentrations were observed in the leachates of the oxidized slags compared with those in the original slag samples. The chromium concentration increases with temperature (Figure 3). After sample S1 had been subjected to oxidation at 600°C and 1000°C, the concentrations of chromium in the leachates were 466% and 2197% greater than those of the original slag, respectively. The corresponding values for sample S2 increased to 4.82 mg/L and 56.90 mg/L. These values are considerably greater than that of the original slag (1.80 mg/L). Moreover, the concentrations of chromium in the leachates of sample S3 increased by 333% and 3270% compared with the original slag.

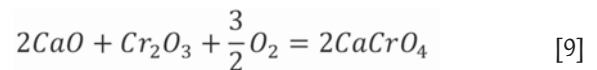
After reduction of the slag in the induction furnace, the content of chromium in the leachate decreases in comparison with that in the original slag (Figure 4). The three slag samples exhibited the same tendency: the highest chromium content in the leachate is observed for the original slag, whereas the lowest concentration chromium is observed for the slag reduced at 600°C. When S1 was oxidized at 600°C in

the muffle furnace and then reduced at 600°C in the induction furnace, the leachate chromium content decreased from 2.15 to 0.15 mg/L. When the sample was processed at 1000°C following the same procedure, the concentration of chromium in the leachate fell from 8.73 to 0.37 mg/L. The concentrations of leached chromium for the reduced samples of S2 and S3 were dramatically less than those observed for the corresponding oxidized samples. The decrease is greater for reduction at 1000°C than at 600°C. For example, the concentrations of chromium in the leachate from the reduced samples of slag S3 were 0.61% and 0.15% of those of the samples oxidized at 600°C and 1000°C, respectively. Furthermore, the concentrations of chromium in the leachates collected from the samples reduced at 1000°C were always greater than those at 600°C.

Discussion

Effect of atmosphere on chromium leaching

Thermodynamically, the amount of chromium dissolving into water from the stainless steel slag depends on the CaCrO₄ content (Lee and Nassaralla, 1997), which is expressed by the following reactions:



$$\Delta G^\theta = -RT \ln \frac{a_{CaCrO_4}^2}{a_{CaO}^2 \cdot a_{Cr_2O_3} \cdot p_{O_2}^{3/2}} \quad [10]$$

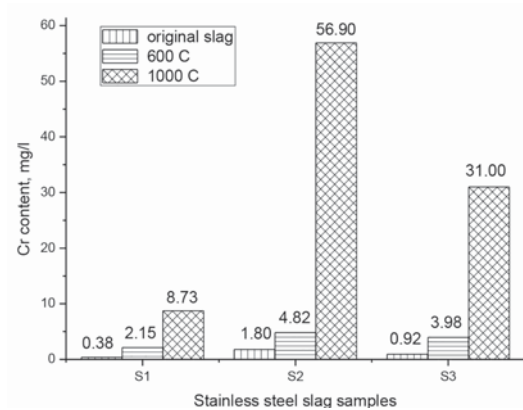


Figure 3—Effect of temperature on the leaching of chromium under an oxidizing atmosphere

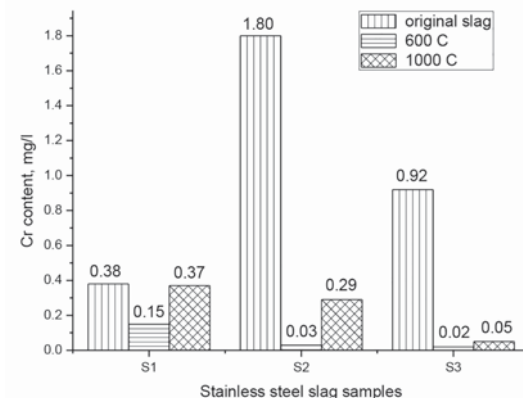
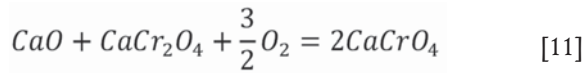


Figure 4—Effect of temperature on the leaching of chromium under a reducing atmosphere

	600°C	1000°C
p_{CO}	0.26	0.99
p_{CO}/p_{CO_2}	0.36	99
p_{O_2}	1.54×10^{-24}	4.42×10^{-19}

Effect of cooling conditions on the leachability of chromium in Cr₂O₃-containing steelmaking slag



$$\Delta G^\theta = -RT \ln \frac{a_{\text{CaCrO}_4}^2}{a_{\text{CaO}} \cdot a_{\text{CaCr}_2\text{O}_4} \cdot p_{\text{O}_2}^{3/2}} \quad [12]$$

where a is the activity and p is the partial pressure. When pure solid CaO, Cr₂O₃, CaCr₂O₄, and CaCrO₄ are chosen as the standard states of activities, the standard Gibbs energy of formation for solid CaCrO₄ is expressed as follows:

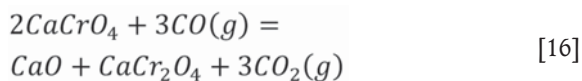
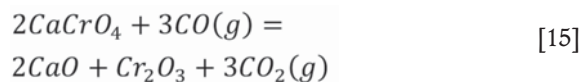
$$\Delta G^\theta = \frac{3}{2}RT \ln p_{\text{O}_2} \quad [13]$$

The slags were heated in the muffle furnace under air; thus, the partial pressure of oxygen was constant at 0.21. According to Equation [13], the standard Gibbs energy changes of reactions [9] and [11] can be expressed as a function of temperature, namely:

$$\Delta G^\theta = -19.46T \quad [14]$$

Hence, the treatment of slag in the muffle furnace enhances the formation of CaCrO₄, and a high temperature may also favour the reactions. The concentration of chromium in the leachate therefore increases as a result of heating in the muffle furnace, and it increases with temperature.

As stated in the section 'Atmosphere in an induction furnace', the atmosphere in the induction furnace maintains strong reducibility. The data shown in Table II revealed that the partial pressure of oxygen is less than 4.42×10^{-19} at a temperature of less than 1000°C, and it increases with temperature in the induction furnace. The soluble component, CaCrO₄, will decompose according to reactions [15] and [16]:



According to thermodynamic calculations performed using the FactSage 7.0 thermodynamic database, the standard Gibbs energy change of Equation [15] is expressed as follows:

$$\Delta G^\theta = -247.39 - 0.33T \quad (kJ) \quad [17]$$

Consequently, CaCrO₄ formed in the muffle furnace can be reduced by CO produced by the interaction between graphite and air in the induction furnace, and the chromium contained in the slags transforms from the soluble state (Cr⁶⁺) into the stable states (Cr₂O₃ and CaCr₂O₄), leading to a significant decrease in the amount of chromium leached.

Moreover, the difference between the amounts of chromium dissolved from the three slags can be interpreted in terms of kinetics. The oxidation and reduction of chromium are gas–solid reactions, for which the interface is known to be a key factor. Pillay, Von, and Petersen, (2003) reported that the oxidation of a mixture of CaO and Cr₂O₃ supposedly occurs at the boundaries between CaO and Cr₂O₃ via the diffusion of oxygen along the particle boundaries, whereas that of Cr³⁺ occurs across the boundaries, leading to the formation of CaCrO₄. In the furnace slags in which CaO and Cr₂O₃ would form a solid solution, oxidation possibly occurs at the exposed surface of particles containing this type of solid solution.

The chromium content dominates the distribution on the surface of the slag particles. Hence, S2 exhibits a higher amount of dissolved chromium compared with S1 because of the higher chromium content. However, S3 exhibits the highest chromium concentration, and the amount of dissolved chromium is less than that in S2 after treatment in a muffle furnace at 600°C and 1000°C (Figure 3). This discrepancy can be explained by the mode of occurrence of chromium in the furnace slags. Notably, chromium exists mainly as a solid solution, such as merwinite, akermanite, and matrix, which is related to the extremely low content in the AOD slag. However, for the EAF slag, the majority of the chromium would occur in spinel minerals, such as MgCr₂O₄ and FeCr₂O₄, which are thought to be resistant to oxidation and dissolution in water (Samada, Miki, and Hino, 2011).

Effect of temperature on chromium leaching

Notably, temperature has a considerable effect on the dissolution of chromium in the lixiviant (Figures 3 and 4). At a high temperature, a large amount of CaCrO₄ is formed in the muffle furnace, which is reduced by CO in the induction furnace. These reactions can be explained by Arrhenius's Law, as shown in Equation [18] (Hua, 2004), indicating that either the increase in temperature or decrease in the activation energy can increase the reaction rate.

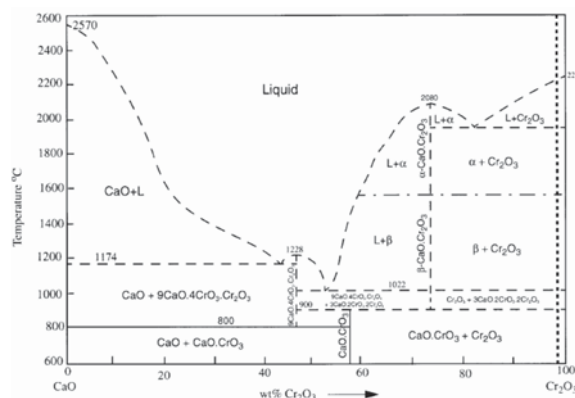


Figure 5—Phase diagram of the CaO–Cr₂O₃ system

Effect of cooling conditions on the leachability of chromium in Cr₂O₃-containing steelmaking slag

$$k = Ae^{-\frac{E}{RT}} \quad [18]$$

where k is the reaction rate, A is the pre-exponential factor, E is the activation energy, and R is the universal gas constant.

Nevertheless, the formation of CaCrO₄ is restricted by temperature. Lee and Nassaralla (1998) reported that the formation of hexavalent chromium (Cr⁶⁺) in a magnesite-chrome refractory is affected by the reaction temperature and chemical composition. According to the CaO–Cr₂O₃ phase diagram shown in Figure 5 (Lee and Nassaralla, 1997), the concentration of Cr⁶⁺ increases at a temperature below the critical point of 1022°C. Hexavalent chromium is thought not to exist in the liquid slag, indicating that Cr⁶⁺ is formed during cooling. Hence, the neutral or reducing atmosphere during cooling possibly suppresses the formation of Cr⁶⁺ and the subsequent leaching of chromium.

In addition, the difference in the chromium concentration in the leachates shown in Figure 4 indicated that once hexavalent chromium is formed, it is difficult to completely reduce Cr⁶⁺ to Cr³⁺, suggesting that it is necessary to utilize a protective atmosphere for the cooling of slag to inhibit the formation of Cr⁶⁺.

Conclusions

To further understand the mechanism involved in the leaching of chromium from stainless steel slags, the effects of atmosphere and temperature on the leaching of chromium from slags were investigated at temperatures of 600°C and 1000°C in a muffle furnace under an oxidizing atmosphere and an induction furnace under a reducing atmosphere, and an efficient method for suppressing the leachability of chromium was identified.

Chromium can be oxidized to the hexavalent state by oxygen, and a high amount of chromium can leach into water at a high temperature under an oxidizing atmosphere. After the oxidation of sample S1 at 600°C and 1000°C, the concentrations of chromium were respectively 466% and 2197% these values are greater than that of the original slag.

Under a reducing atmosphere, CaCrO₄ can be reduced to calcium oxide and chromium oxide by CO, leading to a decrease in the chromium concentration in the leachates. After sample S2 was first oxidized and then reduced at 1000°C, the concentration of leached chromium decreased from 56.90 to 0.29 mg/L. Once hexavalent chromium was formed, it was difficult to completely reduce to Cr³⁺. Thus, a neutral or reducing atmosphere can favour the suppression of chromium leaching.

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