

On-line Analysis of Cr_2O_3 Content of the Slag in Pilot Scale EAF by Measuring Optical Emission Spectrum of Electric Arc

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Control of slag Cr_2O_3 content is essential in stainless steelmaking electric arc furnace (EAF). Excessive Cr_2O_3 content of slag lead to high Cr_2O_3 content after the EAF tapping, since the solid precipitates forming in high Cr_2O_3 contents are not reduced significantly during the tapping procedure. In this work the slag Cr_2O_3 content during the EAF process was analysed by measuring the optical emission spectrum of the electric arc. The measurements were conducted in a pilot EAF situated in Aachen, Germany. Cr_2O_3 content of the slag was increased with periodical additions of Cr_2O_3 powder. The line ratios calculated from the optical emission spectra were compared to the results of the X-ray fluorescence (XRF) analysis of the slag samples taken from the furnace. The results indicate that best accuracy in a pilot scale can be obtained by using Ca I, Fe I or Mn I lines as reference for Cr I lines. By combining the most accurate line ratios of these three components, the Cr_2O_3 composition of the slag could be measured with an average absolute error of 0.62%-points and a standard deviation of 0.49%-points. The results suggest that Fe I and Mn I lines are the most promising reference lines for analysing Cr_2O_3 content of industrial EAF slag.

KEY WORDS: EAF; OES; chromium; on-line measurement; stainless steelmaking.

1. Introduction

Controlling the amount of chromium oxides in electric arc furnace (EAF) slag in stainless steelmaking is essential in ensuring high energy and resource efficiency of the EAF process, as well as ensuring low chromium leaching from EAF slag. All the oxidized chromium left in the slag after the EAF tapping can be considered lost as an alloying agent. The amount of oxidized chromium has to be replaced in later processing to ensure the composition limits of specific steel grade are reached.

CrO_x in EAF slag is reduced to some extent in the EAF heating period, but the most intense reduction occurs during EAF tapping. The intense mixing increases the contact between EAF slag and steel melt, and the silicon and carbon dissolved in steel reduce the chromium oxides. The chromium recovery can be ensured by having high silicon content in steel melt with ferrosilicon additions near the end of the heat.¹⁾ However, if the CrO_x content of the slag is high, larger fraction of chromium is in spinel precipitates, which are not thought to directly react with dissolved silicon, but have to first dissolve to slag.²⁾ The consequence is that the target of low CrO_x content of the ladle slag is not reached when the CrO_x content of the slag before tapping is too high.

If the amount of chromium containing solid precipitates is high, the most effective means to promote chromium recovery is to enhance the kinetic conditions of dissolution of precipitates by increase in stirring or by employing different tapping procedures.²⁾

The challenge in reducing the chromium from slag with carbon or silicon additions is in the calculation of the optimum amount of additions. If too much silicon containing material is introduced to the furnace, the silicon level of the melt will rise to an undesirably high level. This is an issue in the converter process since silicon is oxidized along with carbon. Excessive oxidation of silicon causes the melt temperature to increase, which must be compensated with cooling scrap. In addition, the increased SiO_2 content of the slag has to be compensated with additions of CaO to keep slag basicity at acceptable levels, which increases the amount of slag.¹⁾ To charge the correct amount of reducing material to EAF or to employ the intensified stirring for dissolution of chromium containing precipitates, information about the chromium content of the slag is required.

The EAF slag composition has been conventionally measured by taking samples from the EAF slag and analysing the samples in the laboratory. The challenge in conventional sampling is the delay between obtaining the sample and the result of the analysis. The slag sample represents the slag composition only in the late stage of EAF processing when all of the scrap has molten. This heating stage can be quite

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short and it is not usually possible to wait for the analysis result to arrive. In addition, taking a representative sample from stainless steel EAF slag is not an easy task as it is very inhomogeneous due to high viscosity.

Recently, new methods to produce on-line data on the slag composition have been proposed. Some of these methods measure slag composition directly by electrochemical sensor^{3,4)} or by laser-induced breakdown spectroscopy (LIBS),^{5–7)} while others measure the slag composition indirectly by monitoring off-gas composition⁸⁾ or electrical parameters.⁹⁾ Both of these types have their advantages and limitations. Direct measurements usually suffer from having to place delicate equipment into hazardous furnace conditions. On the other hand, with indirect measurements, it is sometimes hard to distinguish the influence of other process parameters besides slag composition from the measured property.

In order to get around these challenges, a new method to analyse the slag composition by measuring the optical emission spectrum of the electric arc has been proposed.^{10,11)} It combines the remote data analysis with the possibility to measure the arc phenomena directly. The feasibility of analysing slag compositions from arc plasma with on-line optical emission spectrometry (OES) has been previously studied at the laboratory scale¹⁰⁾ and the feasibility of measuring optical emission spectrum from industrial EAF has been demonstrated.^{11,12)} During these measurements, it was found that the arc emission spectrum of EAF is dominated by the atoms originating from the slag components. The connection between arc emission spectrum and slag components suggest that the arc emission spectrum can be used to analyse the composition of the slag.

In this work the changes in arc plasma are mitigated using internal reference. Another possibility would be to use calibration free method by utilizing plasma diagnostics to define and correct the characteristics of the emitting arc plasma. However, this can be challenging due to non LTE conditions in transient AC arc plasma and constant movement of arc. The purpose of this study is to define the accuracy of measuring the chromium content of the EAF slag from arc

emission spectrum, propose a method to combine multiple reference components to measured relative Cr_2O_3 content of the slag and provide guidelines for selecting reference components for the application of the method in industrial EAF.

2. Experimental and Methods

2.1. Furnace Description

The experiments were performed in an airtight pilot arc furnace, which approaches the operation conditions of industrial scaled arc furnaces. The water-cooled furnace consists of a fixed top reactor and a moveable crucible with a maximum capacity of about 200 kg of steel melt. It is possible to operate in AC-mode with two electrodes or in DC-mode with one top electrode and an anode in the bottom of the crucible. In AC-mode, the maximum active power is 600 kW and in DC-mode it is 300 kW. The experiments in this paper have been carried out using the AC-mode. The transformer has a rated power of 850 kVA and the secondary voltage is adjustable in 10 steps from 250 to 850 V. The maximum arc current is 2 kA. A photograph of the vessel of the pilot furnace used in the measurements is presented in Fig. 1.

2.2. Measurement System Description

The measurement system consists of a measurement head, optical fibre, spectrometer and analysis computer. The measurement head is a stainless steel pipe with an aperture for the optical fibre. The measurement head was installed to the injection tube in the furnace shell, which had direct vision to the electric arc. The position of the arc was verified with visual observations. The measurement head configuration yielded a measurement area with a diameter of 15 cm in the estimated position of the electric arc.

A Thorlabs 600 μm fibre of 10 meters length was used in the measurements. The spectrometer was Avantes Avaspec ULS3648 with 10 μm slit, 500 nm blaze and spectral range of 400 nm to 900 nm. The spectrometer configuration has an optical resolution of 0.3–0.36 nm. The integration time was 5 ms or 10 ms depending on the intensity of the light

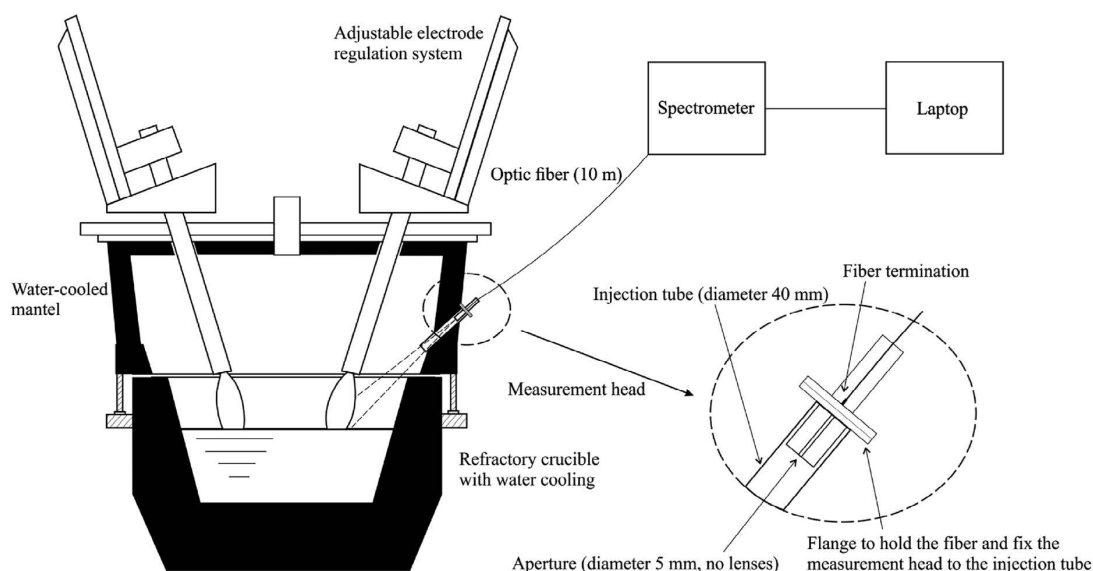


Fig. 1. Pilot EAF at RWTH Aachen University.

emission from the arc. CCD based averaging to 500 ms was used.

2.3. Test Period Description

Two heats with varying Cr_2O_3 content of the slag were measured. The furnace was first loaded with stainless steel, carbon steel scrap, anthracite and slag formers. After the first batch was molten partially, more stainless steel scrap was charged to the furnace along with more slag formers. After the second batch of scrap had molten, the actual measurements were started. Optical emission spectrum of the electric arc was continuously measured, while the Cr_2O_3 content of the slag was increased by subsequent additions of Cr_2O_3 powder. The additions were conducted by opening the furnace and mixing Cr_2O_3 powder to the slag with a shovel. Before each Cr_2O_3 addition, a slag sample was taken with a sampling cup. In between Cr_2O_3 additions the melt was heated for approximately seven minutes to supply the energy lost in opening of the furnace and to give time for the Cr_2O_3 powder to mix and dissolve into slag.

Same amount of slag formers was charged in both heats. The composition of slag according to the charged slag formers and X-ray fluorescence (XRF) analysed slag compositions after each Cr_2O_3 addition are presented in **Table 1**. The amounts of the charged slag formers were selected so that low viscosity slag with low melting point was obtained along with sufficiently high basicity. The slag formed in the beginning of heat was aimed to have liquidus temperature below 1500°C. It can be observed in Table 1 that the Cr_2O_3 content of the slag increases during the heats, as was the purpose of the Cr_2O_3 additions. All oxidation state of chromium were summed to Cr_2O_3 in XRF analysis. Therefore, throughout this study all chromium oxides in slag are referred with Cr_2O_3 . It is interesting to note that the FeO amount differs in both heats. This is likely caused by

differences in steel composition in both heats and varying amounts of anthracite additions.

2.4. Data Handling

Data was acquired by an in-house spectrum analysis software specifically created for the spectrum analysis. Spectral distortions were corrected according to the data provided by the manufacturers of the optical fibre and spectrometer. The software was used in off-line analysis of line intensities; the atomic emission lines were approximated by Gaussian functions.

3. Results and Discussion

3.1. Overview of Arc Emission Spectra

Optical emission spectra of the electric arc contained numerous atomic and ionic emission lines, as was to be expected from the previous measurements. The overall form of optical emission spectrum is very similar to optical emission from industrial EAF, as can be observed in **Fig. 2**.

3.2. Slag Composition Analysis

The chromium content of the slag was analysed by calculating the spectral line ratios of chromium and other components. The line ratios were calibrated to the results of XRF analysis. The optical emission spectra during the last minute of heating before the furnace was shut down for slag sampling were used in composition analysis. The slag composition during this period can be assumed to correspond well to the slag composition analysed with slag samples because the added Cr_2O_3 powder had time to mix to the slag and the energy lost in the slag sampling has been supplied back.

Many of the observed spectral lines were related to the transitions of Cr I, Mn I, Mg I, Ca I, Fe I. Lines were compared to NIST database of atomic emission lines¹³⁾ to ensure there was no overlapping of major slag components. After the comparison, the suitable peak candidates were taken for further analysis. It can be observed in **Table 2** presenting the selected peak candidates that the lines selected for the further analysis were of Mn I, Cr I, Fe I, Ca I and Mg I transitions.

3.2.1. Cr I Lines and Slag Chromium Composition

All but the Cr I 735.589 of the Cr I lines selected to

Table 1. Starting slag composition according to charged slag formers and evolution of slag composition according to XRF analysis (wt-%, all oxidation states are summed to nominal oxides).

	MgO	Al ₂ O ₃	SiO ₂	CaO	Cr ₂ O ₃	MnO	FeO
Slag composition according to charged slag formers	10	19	29	42	0	0	0
Heat 1 - Sample 1	8.50	15.00	30.88	35.70	3.44	2.65	1.79
Heat 1 - Sample 2	8.54	15.03	30.76	35.29	4.37	2.73	1.75
Heat 1 - Sample 3	8.61	14.93	30.67	35.10	5.10	2.76	1.56
Heat 1 - Sample 4	8.44	14.69	30.62	34.39	6.62	2.78	1.66
Heat 1 - Sample 5	8.37	14.46	29.94	33.49	8.59	2.79	1.95
Heat 2 - Sample 1	8.97	15.10	29.18	33.88	7.03	2.31	2.51
Heat 2 - Sample 2	9.10	14.62	29.22	33.43	7.69	2.37	2.71
Heat 2 - Sample 3	8.91	14.42	29.02	33.32	8.29	2.36	2.77
Heat 2 - Sample 4	9.02	14.21	28.65	32.75	9.23	2.33	2.92
Heat 2 - Sample 5	8.71	13.96	28.89	33.08	9.25	2.29	2.95
Heat 2 - Sample 6	9.11	13.75	27.92	31.91	11.3	2.27	3.03

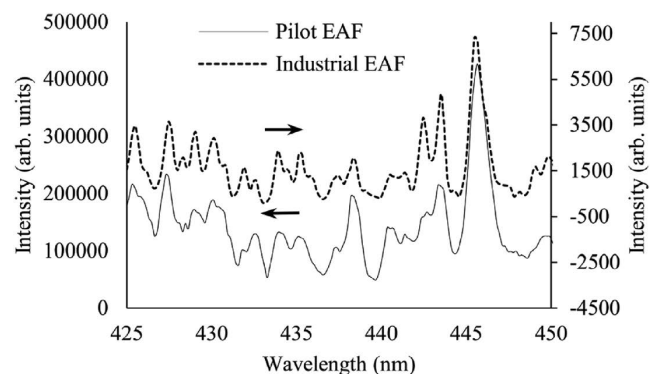


Fig. 2. Optical emission spectrum of pilot and industrial EAF.

slag Cr_2O_3 composition analysis were strong or persistent according to NIST categorization. The advantage of using intense lines is that their shape is easy to approximate and they are more robust against spectral interferences. The disadvantage is that intense lines are more prone to self-absorption than weaker lines.¹⁴⁾

The simplest method to analyse slag Cr_2O_3 composition is to approximate it with only intensities of Cr I lines. The accuracy of this type of analysis is intrinsically low, because the line intensities depend also on other phenomena besides the density of chromium atoms in plasma. Nevertheless, it provides a starting point for analysing the accuracy and added value of internal reference method.

It can be observed in **Table 3** that the linear regression between Cr I lines and slag Cr_2O_3 content is between 0.49 and 0.62. The accuracy of approximating slag Cr_2O_3 content with Cr I lines only is not sufficient, as can be observed in **Fig. 3** presenting the relation between slag Cr_2O_3 content and the line intensity with the highest linear R^2 to XRF analysed slag Cr_2O_3 content. The deviation from the expected behaviour is very high for some points, which means that the other phenomena besides the Cr_2O_3 content affect the Cr

I line intensities considerably. The main cause for low linear regressions is the changing overall level of the spectrum, which is likely attributed to the changing arc visibility conditions. The intensity of a single Cr I line has much higher correlation to the intensity of other Cr I lines than slag Cr_2O_3 content. The variation of the linear regression coefficients between different Cr I lines is caused by varying overlap of other atomic emission lines and varying intensity levels of Cr I lines. With low Cr_2O_3 content of the slag, some Cr I lines can be hard to differentiate from background noise. On the other hand, no self-absorption was observed for the selected Cr I lines.

3.2.2. Selection of Reference Lines

The effect of varying line intensity on spectrum analysis can be mitigated by comparing the intensity of Cr I lines to intensity of excitations lines of reference component. The selection of a reference line in EAF arc plasma has to be made meticulously, because it depends on the availability of suitable reference lines as well as information of the amount of reference component in arc plasma.

The accuracy of analysing slag Cr_2O_3 ratios with atomic

Table 2. Peaks selected for the composition analysis (“S” refers to structures consisting of multiple merged lines of the same atomic species).¹³⁾

Mn I		Cr I		Fe I		Ca I		Mg I	
Wavelength (nm)	Upper level energy (eV)	Wavelength (nm)	Upper level energy (eV)	Wavelength (nm)	Upper level energy (eV)	Wavelength (nm)	Upper level energy (eV)	Wavelength (nm)	Upper level energy (eV)
403.0 S	3.073–3.075	427.481	2.900	437.593	2.833	422.673	2.933	516.732	5.108
404.136	5.181	437.128	3.839	438.5 S	4.312–6.427	558.876	4.744	517.268	5.108
404.876	5.225	492.226	5.623	440.475	4.371	559.012	4.739	518.360	5.108
405.893	5.232	520.6 S	3.322–3.323	495.7 S	5.308–5.352	560.129	4.739		
406.353	5.214	524.756	3.323	536.747	6.725	610.272	3.910		
407.924	5.225	540.979	3.321	536.996	6.680	612.222	3.910		
408.3 S	5.199–5.214	578.792	5.464	537.0 S	3.266–6.780	616.217	3.910		
417.660	5.199	735.589	4.574	538.337	6.615	616.9 S	4.531–4.535		
417.660	7.200	740.018	4.574	539.713	3.211	643.907	4.451		
425.766	5.864			544.692	3.266	644.981	4.443		
449.008	5.714			545.561	3.283	646.257	4.441		
449.890	5.696					671.769	4.554		
470.972	5.520					714.815	–		
472.748	5.542					732.615	–		
476.5 S	5.542–5.520								
478.342	4.889								
482.352	4.889								
542.036	4.429								
543.255	2.282								

Table 3. Linear regression between Cr I lines and XRF analysed slag Cr_2O_3 content.

Wavelength (nm)	427.481	437.128	492.222	520.6 S	524.756	540.979	578.792	735.590	740.018
Linear regression R^2	0.49	0.51	0.54	0.50	0.56	0.47	0.62	0.61	0.60

emission lines of different components can be approximated by calculating the linear regression between line ratios and slag compositions ratio. **Table 4** presents the number of high correlations with different reference components and their magnitude. It can be observed that the use of reference components significantly increases the accuracy due to the lower effect of changing overall level of the spectrum. More accurate regression can be obtained by the use of higher order polynomial regression function. However, with only eleven samples it is hard to differentiate between actual non-linear behaviour and random scatter in the plot.

The scatter of the intensity ratios can be expressed with median absolute deviation from median (MAD). MAD was

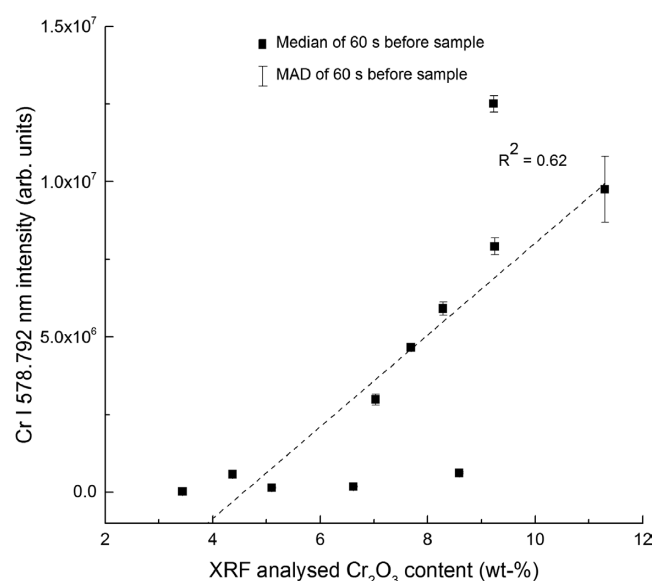


Fig. 3. Slag Cr_2O_3 content and the intensity of the Cr I line with the highest correlation to slag Cr_2O_3 content.

Table 4. Linear regression between the line ratios and the respective slag composition ratios.

Line ratio	The highest R^2	Average of five highest R^2	Count of over 0.75 R^2
Cr I	0.62	0.60	0
Cr I/Mg I	0.74	0.74	0
Cr I/Ca I	0.85	0.83	8
Cr I/Fe I	0.84	0.78	3
Cr I/Mn I	0.86	0.83	8

used as a measure of variability because the data contained outliers. The MAD values of different samples are presented in **Table 5** for each line ratio with the highest linear regression R^2 to XRF analysed slag composition.

3.2.3. Mg I Lines as Reference

Mg I lines measured from pilot EAF arc emission spectrum are highly broadened. Using Mg I as a reference is difficult since broadening causes the lines to overlap with other nearby lines and reduces the intensities. Strong Mg I lines at 552.840 and 571.109 nm, which were good reference lines in laboratory scale analysis,¹⁰⁾ are broadened to an extent that they are impossible to be distinguished from other nearby lines. The only suitable Mg I lines were at 516.732, 517.268 and 518.360 nm. 518.360 nm is not ideal for composition analysis since it is overlapping with nearby Ca I line.

The correlation between analysed XRF composition and Cr I/Mg I line ratios was the poorest of the tested reference components, as can be observed in Table 4. It is interesting to note that the Cr I/Mg I line ratios have better correlations to slag Cr_2O_3 content than the actual slag $\text{Cr}_2\text{O}_3/\text{MgO}$ ratio.

In Table 4 it can be observed that using Mg I as a reference yields better results than the use of only Cr I lines, but it is still only suitable for the analysis of large changes in $\text{Cr}_2\text{O}_3/\text{MgO}$ ratio of slag. The scatter does not explain the lack of accuracy since MAD in Table 5 is low. The deviation between line ratios and XRF analysed $\text{Cr}_2\text{O}_3/\text{MgO}$ ratio can be explained by the broadening of Mg I lines, which causes the intensity of the Mg I lines to reflect broadening conditions rather than amount of Mg I lines in the arc plasma.

3.2.4. Fe I Lines as Reference

Fe I lines observed in the spectrum are of very low intensity, which makes them susceptible to spectral interferences. On the other hand, Fe I lines in optical emission spectrum are very numerous and their intensity being low means that they are not affected by self-absorption. In Table 4 it can be observed that using Fe I lines as a reference yields high linear regression, but the amount of reference lines with high regression is lower than for Ca I and Mn I as reference. In addition, the temporal variance of Cr I/Fe I line ratios is high, as can be observed from the high MAD in Table 5. MAD is higher in the spectra measured from heat 1, which is likely caused by lower intensity of Fe I lines due to lower amount of FeO in the heat 1.

Table 5. Mean absolute deviations (MAD) for each line ratio with the highest linear regression R^2 to XRF analysis.

Line ratio with the highest R^2 for each reference component	MAD for different samples (heat: sample number)										
	1:1	1:2	1:3	1:4	1:5	2:1	2:2	2:3	2:4	2:5	2:6
Cr I 740.018 nm/Mg I 518.360 nm	0.000	0.013	0.039	0.037	0.069	0.039	0.020	0.029	0.147	0.027	0.200
Cr I 740.018 nm/Ca I 616.217 nm	0.000	0.013	0.043	0.038	0.030	0.061	0.042	0.049	0.057	0.098	0.114
Cr I 492.226 nm/Fe I 440.475 nm	0.345	0.262	0.652	1.105	0.411	0.212	0.151	0.096	0.119	0.087	0.095
Cr I 578.792 nm/Mn I 482.352 nm	0.068	0.041	0.093	0.148	0.078	0.091	0.047	0.091	0.086	0.078	0.120

3.2.5. Ca I Lines as Reference

Line ratios of Cr I/Ca I have surprisingly high linear fit R^2 considering that the Ca I lines are prone to absorption due to the high CaO content of the slag. It can be observed in Table 4 that the accuracy of measuring slag $\text{Cr}_2\text{O}_3/\text{CaO}$ ratio is approximately the same as for measuring $\text{Cr}_2\text{O}_3/\text{FeO}$ and $\text{Cr}_2\text{O}_3/\text{MnO}$. Many high intensity Ca I lines are observed, which make them easy to fit and free from spectral interferences.

3.2.6. Mn I as Reference

Manganese as a reference behaves in a similar way as calcium, as can be observed in Tables 4 and 5. On the other hand, using Mn I lines as a reference yielded the highest linear regression R^2 of all composition ratios (Fig. 4). Mn I lines have relatively high intensity, which makes the approximating their intensity easier. Many distinct Mn I lines are observed in the spectrum, which is reflected in the high amount of possible reference lines with a high correlation to slag $\text{Cr}_2\text{O}_3/\text{MnO}$ ratio. Some spectral overlapping was observed, Mn I lines between 404 and 408 nm tended to merge into a wide structure, from which it was hard to distinguish individual lines. Temporal fluctuations of Cr I/Mn I line ratios are also lower than Cr I/Fe I ratios due to the higher intensity of Mn I lines, which can be observed as very low MAD.

3.3. Combining Multiple Line Ratios to Measure the Change in Slag Cr_2O_3 Content

Using internal reference method has a disadvantage of the measured line ratio being related to the amount of both analysed and reference component. If the amount of reference component fluctuates, the measured line ratio cannot be directly related to the amount of analysed component in the slag. The fluctuation of a single reference component can be mitigated by using multiple reference components. Since the amount of major components in the slag is linked through the sum of component fractions in slag being 1,

the fluctuations of different slag components compensate each other. For example, high amount of CaO in the slag increases $\text{Cr}_2\text{O}_3/\text{CaO}$ ratio, but decreases other ratios. By measuring the relative amount of Cr_2O_3 to other slag components, it is possible to determine if the Cr_2O_3 content of the slag is high. This kind of indicator is a mostly qualitative description of the amount of chromium in slag.

One method to combine information from multiple reference components is to normalize the fluctuation of the line ratios by using their relative form. The relative change of line ratios will fluctuate between 0 and 1 when the momentary values are divided with the maximum line ratio over a selected measurement history. Information about the amount of reference component in slag is not required when relative fluctuations of line ratios are studied. The data about temporal variation of line ratios is still required to acquire the maximum of line ratios.

Ideally, Cr I lines should be compared to all other slag components to obtain the most accurate description of relative amount of Cr_2O_3 in slag. However, with current measurement set-up only composition ratios of $\text{Cr}_2\text{O}_3/\text{FeO}$, $\text{Cr}_2\text{O}_3/\text{CaO}$ and $\text{Cr}_2\text{O}_3/\text{MnO}$ can be measured with relatively high accuracy. The high scatter of Cr I/Fe I line ratio does not decrease the accuracy when temporal filters, e.g. average or median, is utilized. The formula for calculating the relative content of Cr_2O_3 in slag ($x_{\text{Cr}_2\text{O}_3}$) by combining line ratios obtained with multiple reference components is presented in Eq. (1):

$$x_{\text{Cr}_2\text{O}_3} = \sum_{i=1}^n \left(\frac{I_{\text{Cr}/\text{ref}_i}}{\max(I_{\text{Cr}/\text{ref}_i})} \right) = \frac{1}{3} \left(\frac{I_{\text{Cr}/\text{Fe}}}{\max(I_{\text{Cr}/\text{Fe}})} + \frac{I_{\text{Cr}/\text{Ca}}}{\max(I_{\text{Cr}/\text{Ca}})} + \frac{I_{\text{Cr}/\text{Mn}}}{\max(I_{\text{Cr}/\text{Mn}})} \right) \dots (1)$$

where I is the line intensity ratio. The relative content of Cr_2O_3 in slag can be modified to describe the absolute amount of Cr_2O_3 in slag by fixing the outlier of relative content to known values. In case of these measurements, the outliers of relative slag Cr_2O_3 content can be fixed to the outlier of XRF analysed slag composition.

An example of using the combination of three line ratios of $\text{Cr}_2\text{O}_3/\text{CaO}$, $\text{Cr}_2\text{O}_3/\text{FeO}$ and $\text{Cr}_2\text{O}_3/\text{MnO}$ with the highest linear regression R^2 to slag composition ratios is presented in Fig. 5. Outliers caused by fluctuating plasma conditions were removed by defining the 20th largest intensity ratio in the measurements as Max_I . The Cr_2O_3 content of the slag can be approximated with the linear regression presented in Fig. 5 with an average absolute error of 0.62%-points and a standard deviation of 0.49%-points.

Despite combining the effects of multiple line ratios, some temporal variation in average relative line ratios still exists. In Fig. 6 presenting the fluctuation of indicator formulated by combining the three line ratios, it can be observed that during heat 1 the line intensities varied considerably, although the overall level rises with increased Cr_2O_3 content of the slag. The variation is caused by the variation of Cr I/Fe I. If the aim of the measurement is to analyse the evolution of slag Cr_2O_3 content, temporal variation does not decrease accuracy when it can be removed with a median filter. In the heat 2 the temporal variations are not as high, but the median of the samples 7 and 9 somewhat differs

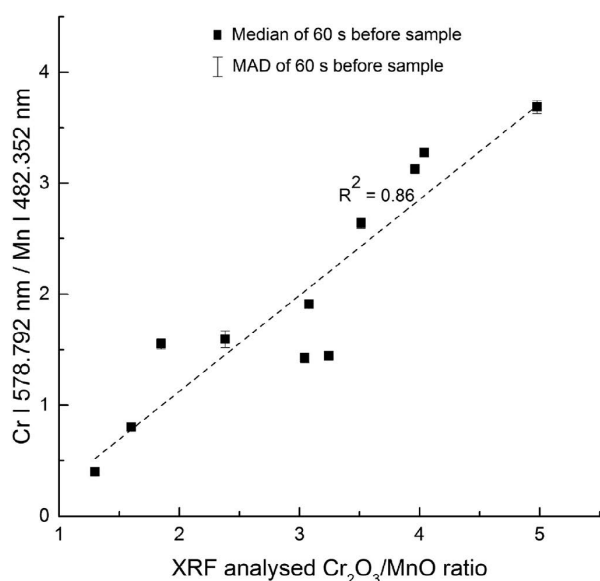


Fig. 4. Linear regression between the Cr I/Mn I line ratio and XRF analysed $\text{Cr}_2\text{O}_3/\text{MnO}$ with the highest R^2 .

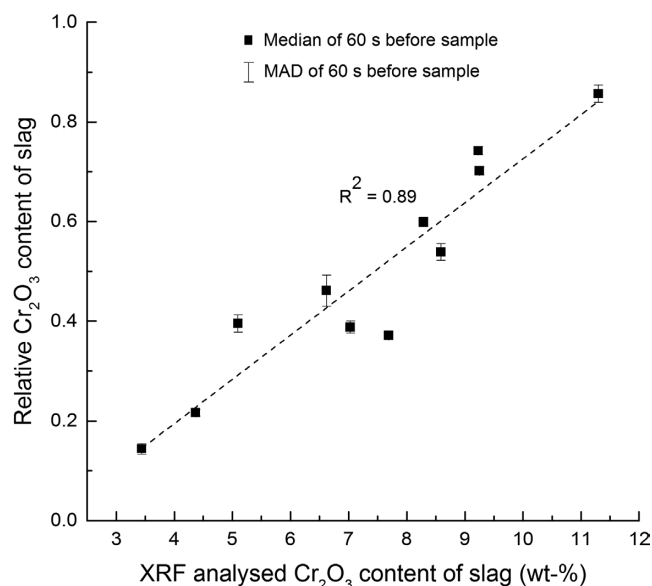


Fig. 5. Relative slag Cr_2O_3 content calculated from Cr I/Ca I, Cr I/Mn I and Cr I/Fe I line ratios and XRF analysed slag Cr_2O_3 content.

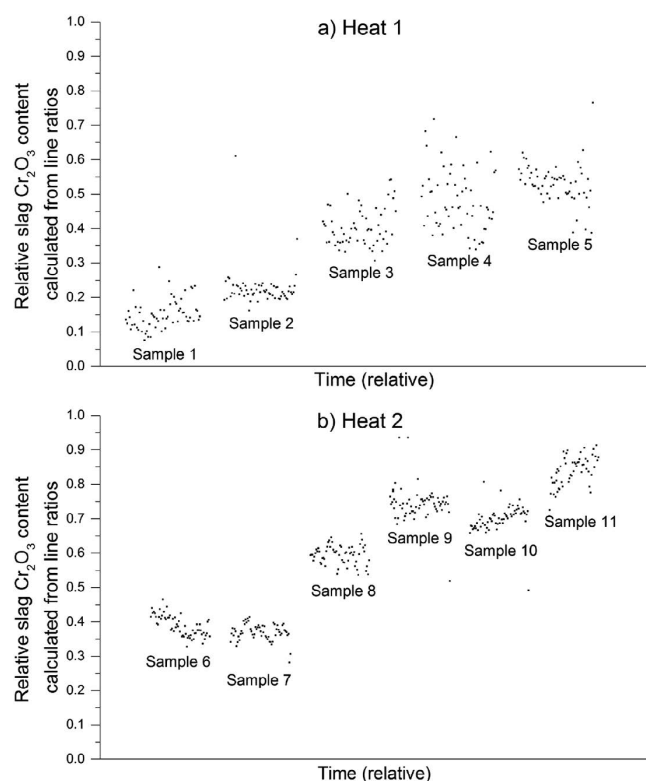


Fig. 6. Average of relative line ratios during 60 seconds before each sample (a) Heat 1 (b) Heat 2 (Outliers cut off from the figure).

from the trend of increasing Cr_2O_3 content. It is not certain if the remaining variation in heat 2 is related to the precision of the calculated indicator or slag inhomogeneity, the latter of which is difficult to correct.

3.4. Industrial Relevance of Slag Composition Ratios

A comparison of pilot scale AC arc furnace emission spectrum to slag composition indicate that the slag composition ratios of $\text{Cr}_2\text{O}_3/\text{CaO}$, $\text{Cr}_2\text{O}_3/\text{FeO}$ and $\text{Cr}_2\text{O}_3/\text{MnO}$ can be

measured with relatively high accuracy. Measuring the slag Cr_2O_3 content with an average absolute error of 0.62%-points would provide a reasonably accurate qualitative signal when to deviate from standard operational practice to ensure low ladle slag Cr_2O_3 content. The exact amount of Cr_2O_3 in the EAF slag is not important in minimizing chromium losses, assuming the amount of solid chromium containing precipitates is low and standard operational practice will reduce it to acceptable levels in the tapping. The main focus in analysing the measured emission spectra should be to define the relation between relative EAF slag Cr_2O_3 content and ladle slag Cr_2O_3 content. By obtaining this relation, it would be possible to define appropriate process practices for different levels of relative EAF slag Cr_2O_3 content.

The feasibility of using the method in industrial scale depends on how well the results from pilot EAF can be translated to industrial EAF. There are three types of situations which can decrease the accuracy of the on-line OES measurement: if the measured line ratios do not reflect the plasma composition, if the measured plasma composition does not reflect the slag composition or if the measured local slag composition does not reflect the overall slag composition. The accuracy of measuring plasma composition in industrial EAF is significantly affected by the selection of correct reference component. On the other hand, relative differences in vaporization and thermal stability of slag components can affect the correlation between plasma and slag composition. The most difficult situation is if the accurately measured slag composition only reflects the local slag composition, which can be irrelevant in process control due to inhomogeneity of slag.

3.4.1. Fluctuation in the Amount of Reference Components

Based on these measurements, the accurate measurement of $\text{Cr}_2\text{O}_3/\text{MgO}$, $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and Cr/SiO_2 is still not realized. Because the ratios of chromium to all major slag components could not be analysed accurately, variation of the selected reference component affects the accuracy of the Cr_2O_3 measurement.

The amount of CaO in industrial EAF slag depends on the amount of lime additions and volume of slag. The lime additions follow the predetermined process practice, which means that the amount of added CaO is known with certain accuracy. On the other hand, the amount of slag is difficult to define, as it depends on the amount of non-metallic material in the scrap charge and oxidation of metals during the EAF process. Therefore, the variation of CaO content of the slag depends on the amount and quality of the scrap melted in EAF. For example, the slag samples obtained for the earlier laboratory measurements had CaO between 37 and 53 mass percent.¹⁰⁾

Although the fluctuation of CaO content of the slag is high, the relative fluctuation is in the order of tens of percent. In this work, the slag Cr_2O_3 content fluctuated between 3.4 and 11.3 mass percent while the amount of CaO was relatively constant. Because of the relatively constant amount of CaO in the slag, $\text{Cr}_2\text{O}_3/\text{CaO}$ reflects the amount of Cr_2O_3 in the slag quite accurately. It is not certain how the line ratio of Cr I/Ca I of the slag is affected by the variation in the CaO content of the slag, which will be much higher

in industrial EAF.

Slag MgO fluctuates in a similar way as CaO in stainless steelmaking EAFs. MgO is introduced to the furnace by charging dolomite lime and from the dissolution of refractories. The amount of MgO in slag fluctuates according to the amount of slag in EAF. However, the dissolution of refractories lowers the fluctuation of MgO in slag since a low amount of MgO in slag will lead to the faster dissolution of refractories. Even if the MgO amount in EAF would be constant, the accuracy of measuring slag $\text{Cr}_2\text{O}_3/\text{MgO}$ ratio would be low with the current of spectrometer configuration. Increasing the accuracy of measuring slag $\text{Cr}_2\text{O}_3/\text{MgO}$ ratio requires a spectrometer with higher optical resolution to isolate the broadened Mg I lines better.

In industrial stainless steelmaking EAFs, the amount of Cr_2O_3 , FeO and MnO is linked. When comparing the heats of the same steel grades, their amount in EAF slag does not depend highly on the amount of slag, but the oxidation conditions in the furnace. The amount of these components in slag is significantly increased by oxygen blowing and decreased by reduction with carbon and silicon dissolved in steel.^{1,2)} This behaviour is advantageous in analysing slag Cr_2O_3 content with FeO and MnO as a reference since the variance of the composition ratios are induced by the changes in process conditions rather than the composition of the scrap charge. Therefore, the line ratios of Cr I/Fe I and Cr I/Mn I are promising for analysing slag Cr_2O_3 content.

The accuracy of analysing slag Cr_2O_3 content with multiple reference components would be increased if more reference components could be introduced. The major slag components not analysed in this study are SiO_2 and Al_2O_3 . Using Si I or Al I lines as a reference would require spectrometer configuration specifically modified to see the atomic emissions of these elements, because the strong lines of Si I and Al I are in wavelengths below the spectrometer range or highly overlapped with other lines.

3.4.2. Phenomena Affecting the Connection between Slag Composition, Plasma Composition and Optical Emissions from Plasma

The second factor affecting accuracy of slag composition analysis is the difference in the vaporization and thermal stability of slag components. Relative differences in vaporization and thermal stability of slag components can affect the amount of atomic elements in the arc plasma. These phenomena only affect the accuracy of on-line OES with internal reference if they cause relation between the slag composition and arc plasma composition to fluctuate. This can occur if the composition of the arc plasma significantly depends on the plasma temperature or the electron density of the plasma.

Even if the composition of the arc plasma is constant, the differences in plasma temperature can affect the connection between the slag composition and line ratios. The intensity of an atomic emission line depends on the amount of excited atoms in the upper level, which is influenced by the plasma temperature. When using internal reference, plasma temperature affects the line intensity ratios if the excitation energy of the analysed line differs from the reference line.¹⁵⁾

The effect of fluctuating plasma temperature can be assessed by comparing the correlations of the different line

ratios and XRF analysed slag composition ratio. The line ratios with the highest correlations to the XRF analysed slag composition do not have the closest possible upper level energies, which indicates that other phenomenon have greater effect on the accuracy of measuring slag composition ratios. For example, ratio Cr I 740.018 nm (upper level energy 4.574 eV)/Ca I 616.217 nm (3.910 eV) has higher correlation to the slag $\text{Cr}_2\text{O}_3/\text{CaO}$ amount than Cr I 740.018 nm (4.574 eV) ratios with Ca I 643.907 nm (4.451 eV), Ca I 644.981 nm (4.443 eV) or Ca I 646.257 nm (4.441 eV) as a reference. Similar line ratio candidates with the closer upper level energies and smaller correlations to the slag composition ratios can be observed for all reference components.

The differences in thermal stability and vaporization of slag components, as well as changing plasma temperature already affect the on-line OES measurement in pilot scale EAF. Cr_2O_3 content of the slag could be measured with a reasonable accuracy in these measurements, which suggests that the effects caused by the differences in plasma characteristics could be sufficiently mitigated by using internal reference and median filter.

The accuracy could be potentially somewhat increased if plasma diagnostics would be included in the linear regression model. One substantial difference between pilot and industrial EAF plasma is the larger diameter of the industrial EAF plasma. The large diameter arc plasma in industrial EAF is more prone to self-absorption, which has to be considered when selecting atomic or ionic emission lines used in the analysis.

3.4.3. Slag Inhomogeneity

The third factor causing the error in measuring the slag composition in industrial EAF is the slag inhomogeneity. There are two types of slag inhomogeneity in industrial EAF, local inhomogeneity and inhomogeneity between slag in the different parts of EAF. The local inhomogeneity of slag surface does not affect the measured relative Cr_2O_3 content of the slag, because data is obtained continuously and temporal filters can be utilized. Electric arc moves constantly on the slag surface, which means that the time average of line ratio represent the average of a certain slag area. This type of averaging is not possible with discrete slag composition data obtained with manual probes. In addition, the difference between surface and bulk slag composition affects the OES measurement less than LIBS measurement, because the arc plasma penetrates deeper to slag surface than the laser pulse in LIBS.

Slag inhomogeneity between different parts of the EAF is caused by the varying oxidation and mixing conditions. The intense mixing caused by the electric arc can make the slag at the centre of EAF relatively homogenous, but certain compositional difference between the centre and the less mixed furnace sides will exist. Oxygen or carbon injection can also locally reduce slag components or oxide alloying elements to the slag. It is likely that some of the variation in the slag Cr_2O_3 analysis in this work is induced by inhomogeneity of the slag, although the inhomogeneity can be expected to be higher in industrial EAF. The effect of large scale slag inhomogeneity on the accuracy of measuring slag Cr_2O_3 content can only be verified by testing the system in industrial conditions.

4. Conclusions

In this work the optical emission spectra of the electric arc from pilot EAF was used to analyse the Cr_2O_3 content of the slag. The optical emission spectrum resembles highly that of an industrial electric arc and multiple lines of Cr I, Mn I, Fe I, Ca I, Mg I were observed. The comparison of calculated line ratios to XRF analysed slag composition suggest that the best accuracy can be obtained in pilot EAF with the slag component ratios $\text{Cr}_2\text{O}_3/\text{CaO}$, $\text{Cr}_2\text{O}_3/\text{FeO}$ and $\text{Cr}_2\text{O}_3/\text{MnO}$. The use of other reference components require spectrometer configuration having a higher optical resolution or a narrower wavelength range.

By combining the line ratios with highest linear regressions to the slag composition, the slag Cr_2O_3 content could be approximated with an average absolute error of 0.62%-points and a standard deviation of 0.49%-points. This error would be acceptable considering there is no on-line information of EAF slag Cr_2O_3 content currently available.

The application of the method to industrial EAFs requires meticulous selection of reference components and lines in order to mitigate the fluctuation of reference components. In this regard, the most promising reference components are MnO and FeO since they are linked to slag Cr_2O_3 content due to oxidation and the reduction of these components in the industrial EAF. In order to validate the results, testing the measurement system in industrial conditions is required.

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