

Cr(VI) Generation During Flaring of CO-Rich Off-Gas from Closed Ferrochromium Submerged Arc Furnaces

S.P. DU PREEZ, J.P. BEUKES, and P.G. VAN ZYL

Ferrochromium (FeCr) is the only source of new Cr units used in stainless steel production, which is a vital modern day alloy, making FeCr equally important. Small amounts of Cr(VI) are unintentionally formed during several FeCr production steps. One such production step is the flaring of CO-rich off-gas from closed submerged arc furnaces (SAF), for which Cr(VI) formation is currently not quantified. In this study, the influence of flaring temperature, size of the particles passing through the flare, and retention time within the flame were investigated by simulating the process on laboratory scale with a vertical tube furnace. Multiple linear regression (MLR) analysis was conducted on the overall dataset obtained, which indicated that retention time had the greatest impact on pct Cr(VI) conversion, followed by particle size and temperature. The MLR analysis also yielded an optimum mathematical solution, which could be used to determine the overall impact of these parameters on pct Cr(VI) conversion. This equation was used to determine realistic and unrealistic worst-case scenario pct Cr(VI) conversions for actual FeCr SAFs, which yielded 2.7×10^{-2} and 3.5×10^{-1} pct, respectively. These values are significantly lower than the current unsubstantiated pct Cr(VI) conversion used in environmental impact assessments for FeCr smelters, *i.e.*, 0.8 to 1 pct.

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I. INTRODUCTION

ALTHOUGH chemical oxidation states for chromium (Cr) range from -4 to $+6$,^[1] only Cr(III) and Cr(VI) are stable in the ambient environment.^[2-4] Cr(III) is considered an essential micro-nutrient that is essential for protein, carbohydrate, and lipid metabolism in animals and humans,^[5] while Cr(VI) is generally considered to be carcinogenic, mutagenic, and teratogenic.^[6,7]

Cr(VI) can be generated and/or released into the environment through various anthropogenic activities, *e.g.*, chromate chemical manufacturing,^[8,9] electroplating,^[10] leather tanning,^[11] cement manufacturing,^[12] paint industries,^[13] stainless steel welding,^[14] and stainless steel production.^[15] Of relevance in this paper is the generation of Cr(VI) during ferrochrome (FeCr) production. FeCr is produced from chromite ore and is a relatively crude alloy that consists mainly of Cr and iron (Fe). FeCr is the only source of new Cr units used during stainless steel production for which 80 to 90 pct of all produced FeCr is used.^[16] Stainless steel is a vital alloy in the modern society, making FeCr equally important.

Ma characterized off-gas dust from a FeCr smelter in South Africa, but did not specifically consider all the production steps that could lead to Cr(VI) formation.^[17] Beukes *et al.*^[18] reviewed the generation of Cr(VI)

during FeCr production. According to this paper and references therein, several ferrochrome production steps can lead to Cr(VI) formation. This review^[18] also highlighted uncertainties with regard to certain production steps that need to be further investigated in order to enhance the current understanding of Cr(VI) generation during FeCr production. One such process is the flaring of CO-rich off-gas from closed submerged arc furnaces (SAF). In Figure 1, an example of a typical off-gas flare from a closed FeCr SAF burning on a stack is presented.

Off-gas from a closed FeCr SAF is usually cleaned with wet venturi scrubbing, which removes 99.9 pct of particulate matter in the off-gas, reducing particulate matter from 35 to 45 g/Nm³ to 50 to 100 mg/Nm³.^[19] In certain first-world countries, the remaining particulate matter is further removed with sintered filters leaving less than 1 mg/Nm³ particulate matter in the cleaned furnace off-gas.^[19] However, in most developing countries, this last step, *i.e.*, sintered filtering after wet venturi cleaning, has not been implemented. This implies that some Cr-containing particulate matter will pass through the CO-rich off-gas stack flare, which could lead to the possible formation of Cr(VI). This release of Cr(VI) is of great concern, since Cr(VI) is considered to be carcinogenic, particularly for the respiratory track. Currently, almost no data exist in the peer-reviewed public domain to quantify the conversion of Cr(III), *i.e.*, the oxidation state of Cr in the chromite ore, to Cr(VI) during the flaring process. As far as the authors could assess, only a personal communication has been cited in an environmental impact assessment (EIA),^[20] which indicated that approximately 0.8 to 1 pct of Cr(III) is converted to Cr(VI) during flaring. This conversion factor has since been used in various EIAs, although it is largely

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Fig. 1—A typical CO-rich off-gas flare on top a closed FeCr SAF stack.

unverified since no supporting data were supplied in the afore-mentioned personal communication.

In order to partially address the uncertainty relating to Cr(III) to Cr(VI) conversion during flaring of CO-rich off-gas from closed FeCr SAFs, the influence of flaring temperature, size of the particles passing through the flare, and retention time within the flame were investigated in this paper. Although the oxidation of Cr(III) to Cr(VI) depends on various factors,^[21,22] these three factors are likely to be important within this context. Multiple linear regression was also used to combine the effect of the three parameters investigated to estimate the overall impact.

II. MATERIALS AND METHODS

A. Materials

Two case study chromite ores were used, *i.e.*, a metallurgical grade chromite ore and an upgraded upper group 2 (UG2) ore that originated from platinum group metal (PGM) processing. Both these ores were obtained from a large FeCr producer in South Africa that used these ores as feedstock for the production of FeCr. A detailed characterization of these two ore samples was recently presented by Glastonbury *et al.*^[23] Of importance for this study is the Cr₂O₃ contents of these ores, which were 44.19 and 41.82 pct for the metallurgical grade and UG2 ores, respectively. These values were used to determine the conversion of Cr(III) to Cr(VI).

All chemicals used in this study were of analytical grade. Calibration of the Cr(VI) analytical instrument was performed using a chromate reference standard (Spectroscan) with a certified concentration of $1009 \pm 5 \mu\text{g/mL CrO}_4^{2-}$. Ammonium sulfate (Merck) and a 25 pct ammonia solution (Ace) were used to prepare the eluent utilized for Cr(VI) analysis. Post-column reagent was prepared using 1,5-diphenylcarbazide (Fluka Analytical), 98 pct sulfuric acid (Rochelle Chemicals), and HPLC grade methanol (Ace). Sodium hydroxide (Promark chemicals) and sodium carbonate (Minema) were used to prepare a Na₂CO₃-NaOH buffer to extract Cr(VI) from samples. Deionized water (resistivity 18.2 MΩ/cm) produced by a Milli-Q water purification system was used in all procedures that required dilution, as well as to clean glassware. Self-indicating silica gel (Labchem) was placed in desiccators used in procedures where samples had to be dried. 99.999 pct pure nitrogen (N₂) (AFROX) was used to purge all Cr(VI) extraction solutions and the headspace of extraction containers during leaching procedures.

B. Milling and Partitioning of Ore into Size Fractions

Since Cr(III) occurs in the spinel mineral structure in chromite, it is unlikely that any Cr(VI)/Cr(III) inter-conversions will take place in chromite ore samples in the ambient environment. However, Mandiwana *et al.*^[24] indicated that small amounts of Cr(VI) might occur in South African chromite ore, although this was questioned by Glastonbury *et al.*^[25] Fine chromite ores, such as metallurgical grade and UG2, are commonly upgraded in wet gravity separation methods (*e.g.*, spiral). Atmospheric SO₂ can dissolve in moisture, which can result in Cr(VI) reduction.^[26,27] Therefore, as a precautionary measure, the received ore samples were dried in desiccators prior to further use.

Since particle size was one of the parameters considered in this study, it was decided to separate ore particles into several size fractions, *i.e.*, >250, 125 to 250, 75 to 125, 63 to 75, 45 to 63, and <45 μm. For the >250, 125 to 250, and 75 to 125 μm size fractions, the as-received dried metallurgical grade and UG2 chromite ores were screened into these fractions with a Haver EML Digital Plus shaker and Haver & Boecker sieves. Since only a small weight percentage of both the case study ores contained particles <75 μm,^[23] the ores were milled to generate finer particles. A Siebtechnik pulverizer was used for this purpose. Milling time was kept to approximately 4 minutes to minimize Cr(VI) formation during milling.^[25] All parts of the pulverizer that made contact with the ore were made of tungsten carbide, preventing possible iron contamination. Five 100 g batches of both ores were milled. The mill was thoroughly cleaned after milling each batch in order to prevent contamination of the different ore types with each another. Thereafter, each milled 100 g ore batch was sieved for 30 minutes in the previously described shaker with the appropriate screen sizes to yield size fractions of 63 to 75, 45 to 63, and <45 μm. All the size-fractionated ore samples were collected, sealed in individual plastic containers, and stored in a desiccator for future use.

C. Particle Size Analysis

Particle size distribution analyses were performed on the size-fractionated chromite ores samples with laser diffraction particle sizing using a Malvern Mastersizer 2000. In order to prevent the use of chemical dispersant, samples were ultra-sonicated prior to the particle size measurements. Mechanical stirring was set to 2000 rpm and laser obscuration was kept between 10 and 15 pct.

D. Experimental Setup for Cr(VI) Generation

In order to investigate the rapid heat exposure associated with FeCr SAF off-gas flaring, a tube furnace was placed vertically, allowing ore fines to be exposed to heat as they were dropped through the tube. A 18kW Lenton Elite tube furnace with a Schunk AluSIK type C610 "A" impervious mullite ceramic tube (75 mm × 65 mm × 1500 mm) with a chemical composition of 60 pct Al₂O₃ and 40 pct SiO₂ was used. This experimental setup had a maximum operational temperature of 1774.15 K (1500 °C). During each experiment, 5 g of a specific sample, *i.e.*, a specific ore type and particle size fraction, was dropped through the furnace that was set at a predetermined temperature and collected at the bottom. The top end of the tube was closed off with a piece of flat ceramic material and only briefly opened to drop the sample down the tube, where after it was again closed off immediately to prevent ultra-fine particles being dragged upward due to the chimney effect. Samples were then allowed to cool down to room temperature. Cooled samples were then placed in sample containers that were sealed and stored in a desiccator until future use.

In order to evaluate the effect of retention time of particulate matter within the FeCr SAF off-gas flare on the formation of Cr(VI), specific samples were dropped multiple times through the furnace tube. However, only 950 mm of the 1500 mm furnace tube is insulated within the furnace housing of which only approximately the middle third of the isolated tube is accurately heated to the desired temperature. This implies that particulate matter dropped through the tube furnace was only exposed to the targeted temperature for 320 mm, which correlated to approximately 0.148 seconds. Samples that were dropped multiple times through the tube were not allowed to cool down between drops.

Since Cr(III) oxidation is dependent on temperature, the temperature range relevant to closed FeCr SAF off-gas flaring had to be established. According to Niemelä *et al.*, the minimum ignition temperature of CO in air is 904.15 K (630 °C) and the theoretical burning temperature of pure CO in air is 2524.15 K (2250 °C). This range, *i.e.*, 904.15 K to 2524.15 K (630 °C to 2250 °C), can therefore be used as an estimate of the relevant temperature range that had to be investigated experimentally. In addition to this literature-based information, the temperature range was also calculated using the thermodynamics software program HSC.^[28] Off-gas burns at a range of temperatures, depending on the composition of the gas. Typical gas compositions for a closed FeCr SAF have been reported to be CO 60 to 90 pct, CO₂ 10 to 40 pct, N₂ 2 to 7 pct, and H₂ 2 to 10 pct.^[19] The adiabatic flame

temperatures of various gas mixtures within the range of these gas compositions were subsequently calculated with HSC. Results indicated that a maximum temperature of 2525.35 K (2251.2 °C) was calculated for a gas composition of 100 pct CO, which correlated almost perfectly with the theoretical burning temperature reported by Niemelä *et al.* Considering the literature-based and thermodynamically calculated flaring temperatures of FeCr SAF off-gas, it was decided to expose particulate matter to temperatures ranging from 874.15 K to 1674.15 K (600 °C to 1400 °C). Higher temperatures could not be investigated due to instrumental limitations of the tube furnace utilized.

E. Cr(VI) Extraction from Heat-Treated Ores Fines

Total Cr(VI) had to be extracted from a solid matrix into an aqueous phase without causing any inter-conversions between Cr(VI) and Cr(III). Cr(VI) compounds can be classified as water soluble and water insoluble.^[29] Therefore, to accurately determine the total Cr(VI) concentrations, both water soluble and water insoluble compounds had to be extracted. This was achieved by conducting hotplate digestion extraction with a sodium carbonate and sodium hydroxide buffer solution, as suggested by Ashley *et al.* This buffer was prepared by dissolving 60 g sodium carbonate and 40 g sodium hydroxide in a 2 L volumetric flask. A hot alkaline extraction solution saturated with air could lead to *in situ* formation of Cr(VI) in the presence of Cr(III).^[29] Therefore, in order to prevent the unwanted oxidation of Cr(III), extraction solutions and the headspace of the extraction container were purged with N₂ prior to, during, and after Cr(VI) extraction. After extraction, the solutions were purged until the solution cooled down to room temperature. 0.5 g of each sample was leached in 50 mL buffer solution for 60 minutes during hotplate extraction. Thereafter, the aqueous solution was filtered using a 0.45 μm Whatman filter. The filtrate was then placed in an airtight glass container and stored until Cr(VI) analysis was conducted.

F. Cr(VI) Analysis

The analytical method utilized in this study was adapted from DIONEX Application updates 144 and 179,^[30,31] and Thomas *et al.*,^[32] as described by Looek *et al.*^[33] The Cr(VI) content of extracted solutions was determined using an ion chromatograph (IC) with a post-column 1,5-diphenylcarbazide (DPC) colorant delivery system (AXP pump) coupled to a UV-visible absorbance detector. The Thermo Scientific DIONEX ICS-3000 ion chromatograph system consists of a Dionex IonPac AG7 4 × 50 mm guard column, Dionex IonPac AS7 4 × 250 mm analytic column, a 1000 μL injection coil, and two 375 μL reaction coils fitted in series. An isocratic pump was used to transport injected samples with the eluent through the system. Flow rates utilized for DPC and eluent were 0.5 and 1.0 mL/min, respectively. Additional polyetherketone tubing was installed between the AXP pump and the back pressure tubing to reduce the pulse caused by the AXP pump,

which minimized the baseline noise of the chromatograms. This produced a smoother baseline and ensured more accurate analyses, especially for lower Cr(VI) concentrations. A six-point calibration line (between 5 and 75 $\mu\text{g/L}$) was used, which had a relative standard deviation ≤ 1.8 pct and a correlation coefficient ≥ 99.96 pct. The detection limit for this analytical setup was 1 $\mu\text{g/L}$.^[30] In addition to the excellent detection limit, the analytical procedure utilized also prevented false positive Cr(VI) values, which is common with the direct DPC UV-visible method.^[29]

The IC eluent was prepared by dissolving 66 g ammonium sulfate and 15.08 g ammonium hydroxide in 2 L deionized water. The DPC colorant was prepared by adding 28 mL 98 pct sulfuric acid to approximately 100 mL deionized water in a 1 L volumetric flask. The solution was then cooled down to room temperature. 0.5 g DPC was placed in a 100 mL volumetric flask with approximately 80 mL methanol. After most of the DPC had dissolved, the solution was diluted to 100 mL with methanol. Thereafter, the DPC methanol solution was steadily added to the sulfuric acid solution, which was then left to cool down to room temperature. Before the DPC solution was used for analysis, it was filtered with a 0.45 μm milli-pore filter to ensure that no solid particles were present that could block the fine tubes of the IC.

G. Expressing Cr(VI) Conversion

Since the percentage of Cr(VI) converted from Cr(III) during FeCr SAF off-gas flaring is currently utilized in EIAs for FeCr smelters,^[20] all results were expressed as percentage Cr(VI) conversion, *i.e.*, pct Cr(VI) conversion. As explained later, expressing the results in this format enables the calculation of actual Cr(VI) emissions from individual FeCr smelters, which makes the results both scientifically significant and practically usable. All results reported are mean values calculated from triplicate repetition of particular experimental conditions and subsequent Cr(VI) analysis. Since it is well known that Cr(VI) can be generated during the milling of chromite,^[25,34] the Cr(VI) contents of the size-fractionated ores samples were determined to establish a baseline. These baseline values were subtracted from the Cr(VI) contents determined after exposure to heat, to reflect the real Cr(VI) conversion.

H. Multiple Linear Regression Analysis

Linear regression is denoted by constants or known parameters (c), an independent variable (x) and a dependent variable (y). Multiple linear regression (MLR) is characterized by more than one independent variable (x). In MLR, the relationship between the dependent variable (y) and independent variables (x) is denoted by the equation:

$$y = c_0 + c_1x_1 + c_2x_2 + c_3x_3 + \dots c_zx_z \quad [1]$$

In this study, MLR was used to determine an equation for the dependent variable, *i.e.*, pct Cr(VI)

conversion (y in Eq. [1]), expressed in terms of the independent variables, *i.e.*, flaring temperature, particle size, and retention time (x in Eq. [1]). This was achieved by utilizing a fit-for-purpose Matlab program.

III. RESULTS AND DISCUSSION

A. Particle Size Analysis of Size-Fractionated Samples

Various size-fractionated particle samples were generated from both case study ores, *i.e.*, >250, 125 to 250, 75 to 125, 63 to 75, 45 to 63, and <45 μm . D_{90} (defined as the equivalent particle size of which 90 pct of the particles are finer), d_{50} , and d_{10} values for both ores, as a function of all size fractions, were determined and are presented in Table I. In the rest of the paper, d_{90} will mostly be used as a reference for particle size for the various size fractions.

B. Influence of Temperature on Pct Cr(VI) Conversion

The effects of temperature on the pct Cr(VI) conversion observed for metallurgical grade and UG2 chromite ore fines are presented in Figures 2(a) and (b), respectively. The retention time of the particles in the hot zone of the tube furnace was kept constant at 0.148 seconds, *i.e.*, a single pass. Minimum, maximum, and/or standard deviation values are not indicated for the experimental results presented in these and subsequent figures, in order to prevent cluttering of the graphs. However, the maximum standard deviation observed in all experiments was approximately two orders of magnitude lower than the actual pct Cr(VI) conversion values, indicating very good repeatability of the results.

As is evident from the results presented in Figure 2(a), metallurgical grade chromite ore fines exposed to the lowest experimentally investigated temperature (874.15 K, 600 °C) had the lowest pct Cr(VI) conversion with conversion percentages ranging from 7.1×10^{-4} pct for the size fraction with the largest particles (d_{90} of 910 μm) to 1.97×10^{-3} pct for the size fraction with the smallest particles (d_{90} of 45 μm). The pct Cr(VI) conversion thereafter increased with an increase in temperature for all size fractions. At the maximum experimentally investigated temperature, *i.e.*, 1674.15 K (1400 °C), pct Cr(VI) conversion reached the highest levels. The size fraction with the largest particles had a pct Cr(VI) conversion of 1.37×10^{-3} pct, whereas the size fraction with the smallest particles had a conversion of 3.69×10^{-3} pct.

Results obtained for UG2 ore fines (Figure 2(b)) exposed to the different temperatures were very similar to that obtained for the metallurgical grade ore fines (Figure 2(a)). At 874.15 K (600 °C), the size fraction with the largest particles (d_{90} of 985 μm) had a pct Cr(VI) conversion of 7.6×10^{-4} pct, while the size fraction with the smallest particles (d_{90} of 45 μm) had a conversion of 1.83×10^{-3} pct. Percent Cr(VI) conversions reached 1.48×10^{-3} pct for the size fraction with the largest particles and 3.81×10^{-3} pct for the size fraction with the smallest particles at 1674.15 K

Table I. d_{90} , d_{50} , d_{10} Values of Metallurgical Grade Chromite and UG2 Ores as a Function of Sieved Size Fractions

	Sieve Sizes (μm)					
	>250	125 to 250	75 to 125	63 to 75	45 to 63	<45
Metallurgical Grade						
d_{90}	910.5	310.9	173.9	87.8	79.7	45.6
d_{50}	582.3	220.4	122.6	19.7	28.4	18.5
d_{10}	363.4	156.1	86.2	1.6	2.3	1.6
UG2						
d_{90}	985.4	310.3	161.8	87.1	60.4	45.3
d_{50}	587.8	219.5	113.6	17.8	18.3	22.1
d_{10}	337.5	155.4	79.7	0.9	1.1	2.1

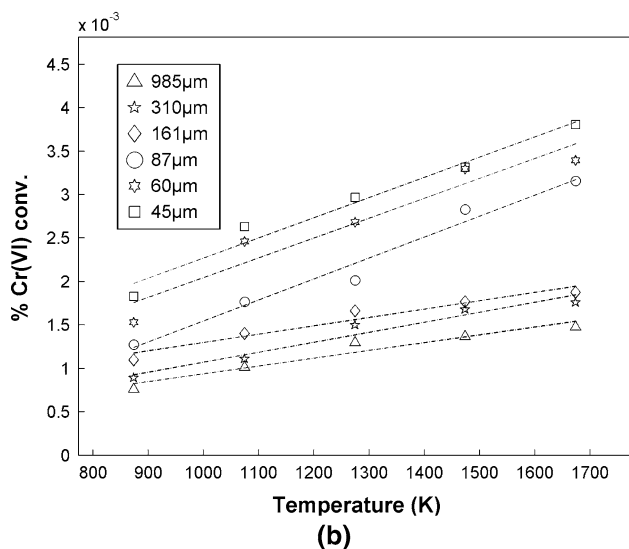
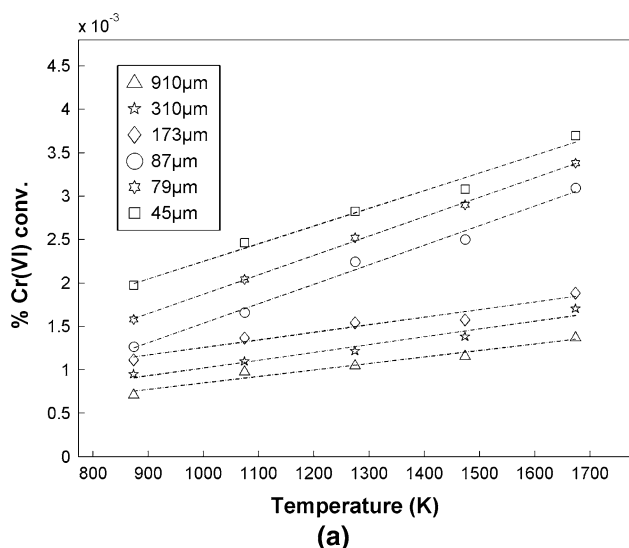


Fig. 2—The influence of temperature on pct Cr(VI) conversion for all particle size fractions (indicated with d_{90} values) of (a) metallurgical grade chromite and (b) UG2 ore fines. The retention time of the particles in the hot zone of the tube furnace was kept constant at 0.148 s, *i.e.*, a single pass.

(1400 °C). From Figure 2, it is also clear that the pct Cr(VI) conversion increased linearly with an increase in exposure temperature for the metallurgical grade and the UG2 ores.

As is evident from the results presented in both Figures 2(a) and (b), the slope, *i.e.*, pct Cr(VI) conversion increase per temperature unit, was different for the as-received, sieved size fractions (>250, 125 to 250, 75 to 125 μm), if compared to the slope for the milled size fractions (63 to 75, 45 to 63, and <45 μm). Milling could have resulted in some chromite crystalline damage, which might make these particles more susceptible to oxidation. However, more research needs to be conducted to postulate a reasonable explanation.

C. Influence of Particle Size on Pct Cr(VI) Conversion

For a constant amount of particulate matter, the surface area will increase as the particle size decreases. For smaller particles, this implies a larger surface area that can be oxidized within the off-gas flare. The effects of d_{90} particle size on pct Cr(VI) conversion for metallurgical grade chromite and UG2 ore fines are presented in Figures 3(a) and (b), respectively.

As is evident from the results (Figure 3(a)), metallurgical grade ore fines with a d_{90} of 910 μm had the lowest pct Cr(VI) conversion at each of the temperatures investigated, with pct Cr(VI) conversions ranging from 7.1×10^{-4} pct for samples exposed to 874.15 K (600 °C) to 1.37×10^{-4} pct for samples exposed to 1674.15 K (1400 °C). Thereafter, pct Cr(VI) conversion increased almost in an exponential manner as the d_{90} particle size decreased. The smallest particles (size fraction with d_{90} of 45 μm) had the highest Cr(VI) conversions of 1.97×10^{-3} pct for samples exposed to 874.15 K (600 °C) and 3.69×10^{-3} pct for samples exposed to 1674.15 K (1400 °C). Results obtained for all size fractions of UG2 ore fines (Figure 3(b)) showed a similar trend when compared to metallurgical grade chromite fines (Figure 3(a)). Fitting of the aforementioned results indicated that the relationship between pct Cr(VI) conversion and particle size had a power factor dependence with the general format of $d_{90}^{0.3203}$.

D. Influences of Retention Time on Pct Cr(VI) Conversion

To investigate the influence of retention time on pct Cr(VI) conversion, the two size fractions with the largest particles (d_{90} of 910 and 310 μm for metallurgical grade and d_{90} of 985 and 310 μm for UG2) were exposed to

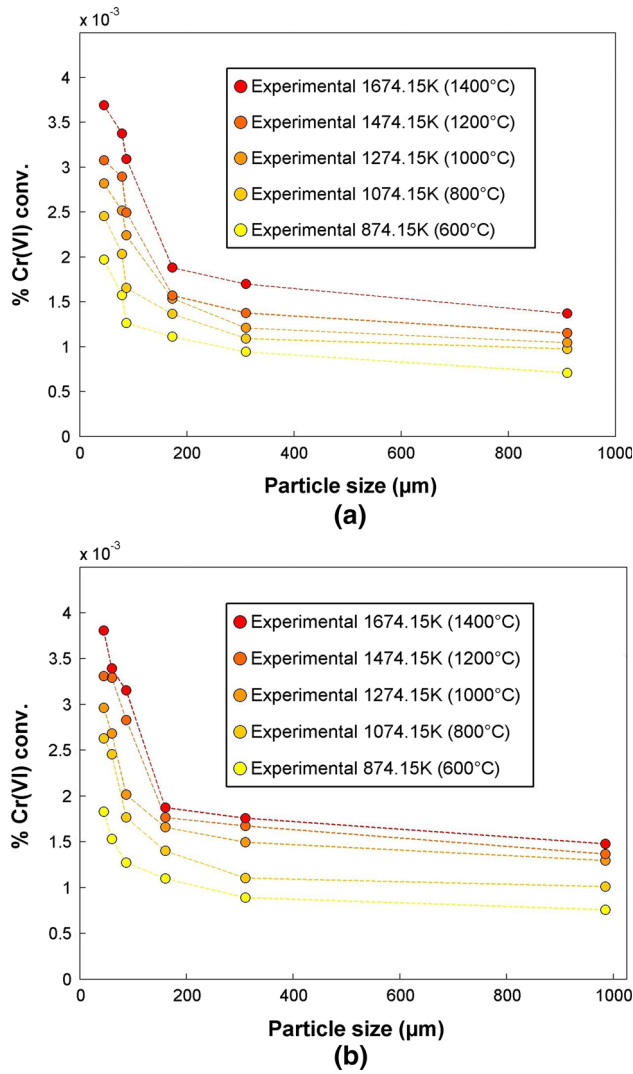


Fig. 3—The influence of particle size (indicated with d_{90} values) on pct Cr(VI) conversion for all temperature ranges of (a) metallurgical grade chromite and (b) UG2 ore fines. The retention time of the particles in the hot zone of the tube furnace was kept constant at 0.148 s, *i.e.*, a single pass.

the highest temperature 1674.15 K (1400 °C) in consecutive multiple drop experiments through the tube furnace. These larger particles were less prone to the chimney effect, making consecutive multiple drop experiments feasible. The effects of retention time on pct Cr(VI) conversion for the metallurgical grade chromite and UG2 ore fines are shown in Figure 4.

It is evident from these results (Figure 4) that increased retention times led to higher pct Cr(VI) conversions. Cr(VI) conversions ranged from 1.34×10^{-3} to 1.74×10^{-3} pct at the shortest evaluated retention time, *i.e.*, 0.148 seconds, for both ore types and the two sized fractions. At the longest evaluated retention time, *i.e.*, 0.594 seconds, the pct Cr conversions ranged from 4.185×10^{-3} to 6.53×10^{-3} pct. Fitting of the afore-mentioned results indicated that the relationship between pct Cr(VI) conversion and retention time had an exponential dependence with the general format of $0.001075e^{(2.75754)(\text{Retention time})}$.

E. Multiple Linear Regression to Calculate Overall Pct Cr(VI) Conversion

In Figure 5, the relationship between the number of independent variables included in the optimum MLR analysis solution (x -axis) and the root mean square error (RMSE) (y -axis) difference between the calculated and experimental pct Cr(VI) conversions is presented. In this statistical analysis, all possible independent variable combinations of temperature, particle size after being converted to $d_{90}^{-0.3203}$ and retention time after being converted to $0.001075e^{(2.75754)(\text{Retention time})}$, were considered to calculate the dependent variable, *i.e.*, pct Cr(VI) conversions. The data for both case study ore types were combined in the MLR analysis, since the intention was to determine a single MLR equation that could be applied to any Cr-containing off-gas particulate material and not only specific ores.

According to the MLR analysis conducted, statistically, retention time was the independent variable that had the most significant impact on minimizing the difference between the experimental pct Cr(VI) conversion and MLR calculated value. This is graphically illustrated in Figure 5, which shows that an MLR equation containing only the retention time had an RMSE difference between the calculated and experimental pct Cr(VI) conversion of approximately 7.9×10^{-4} . Addition of particle size, *i.e.*, d_{90} , which was found to be the second most significant independent variable, to the optimum MLR solution decreased the RMSE further. When all three investigated independent variables were included in the MLR solution, the RMSE decreased to approximately 2.83×10^{-4} .

From the above-mentioned MLR analysis, the optimal equation, containing all three the investigated independent variables, was determined as follows:

$$\begin{aligned} \text{Pct Cr(VI) conversion} = & -3.78 \times 10^{-3} \\ & + (1.51 \times 10^{-6} \times \text{Temp}) + (1.07 \times 10^{-2} \times d_{90}^{-0.3203}) \\ & + \left(0.94 \times 1.08 \times 10^{-3} e^{(2.75754)(\text{Retention time})}\right), \end{aligned} \quad [2]$$

where Temp is the exposure temperature (K), d_{90} the d_{90} particle size (μm) of the particulate matter passing through the tube furnace, and Retention time the retention time (seconds) of particles within the hot zone of the furnace.

From Eq. [2], it was possible to calculate pct Cr(VI) conversions for both case study ores and compare these mathematically calculated values to experimental values, which are presented in Figures 6(a) and (b) for metallurgical grade chromite and UG2 ore fines, respectively. In these figures, all experimentally investigated independent variable (exposure temperature, retention time and particle size) conditions are presented in one figure for each ore type. The first six columns indicate pct Cr(VI) conversions as a function of varying particle size (indicated in x -axis) and temperature (indicated with color) for a fixed retention time, *i.e.*, 0.148 seconds, while the last two columns indicate pct Cr(VI) conversions as a function of longer retention times, *i.e.*, from

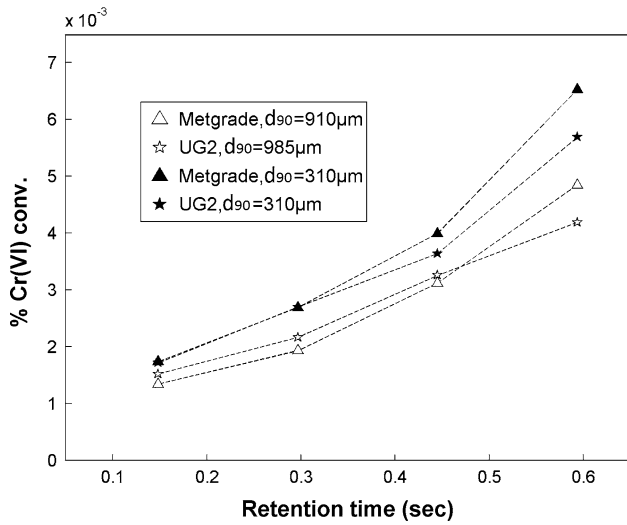


Fig. 4—The influence of retention time on pct Cr(VI) conversion for metallurgical grade chromite and UG2 ore fines at 1674.15 K (1400 °C).

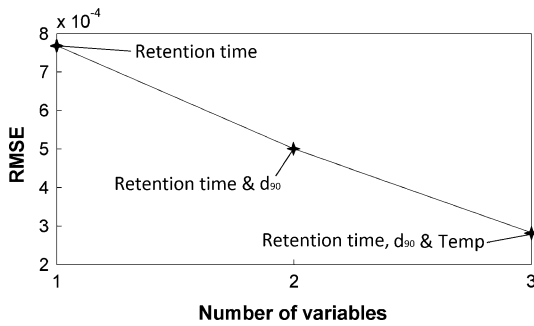


Fig. 5—RMSE difference between calculated pct Cr(VI) conversion for the combined dataset determined for metallurgical grade chromite and UG2 ore fines as a function of the independent variables included in the MLR solution.

0.148 to 0.593 seconds, at a constant temperature [1674.15 K (1400 °C)]. Although there are some differences between the experimentally determined pct Cr(VI) conversions and values calculated with the MLR Eq. [2], it is evident from Figures 6(a) and (b) that Eq. [2] can be used relatively effectively to determine pct Cr(VI) conversions.

F. Industrial Relevance and Practical Application

The optimum MLR Eq. [2], which was determined in Section II-E, can be used by specific FeCr smelters to estimate pct Cr(VI) conversion more accurately than the present estimations. Since three independent variables were included in the optimum MLR solution, *i.e.*, retention time, d_{90} , and temperature, these parameters have to be determined or estimated for such application.

Retention time will depend on the length of the flare and the exit velocity of the off-gas. The length of the flare will depend on the operating conditions of a particular SAF—an SAF running at full power input (MWh) will produce more off-gas than an SAF operating at reduced power input. In practice, the flare

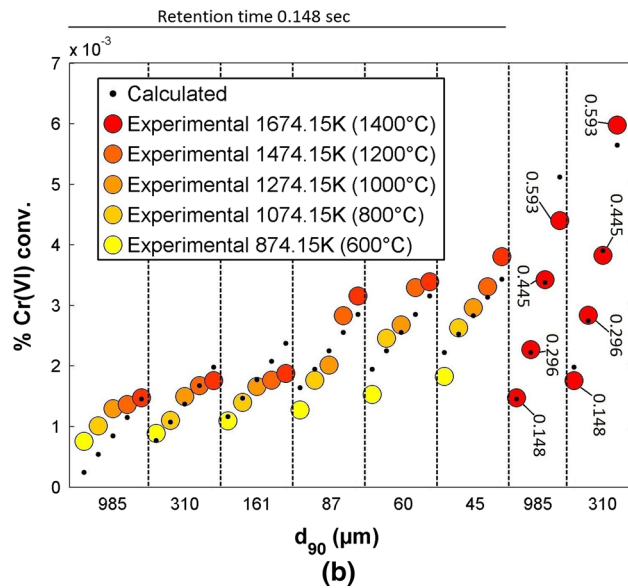
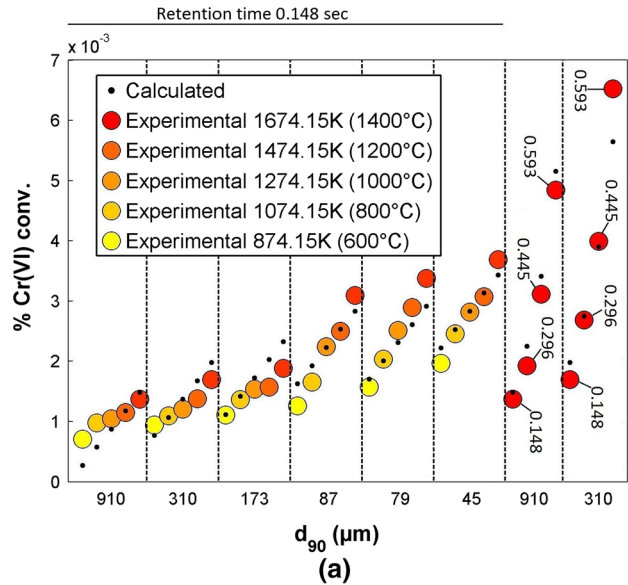


Fig. 6—Calculated pct Cr(VI) conversion values using Eq. [2] compared to experimental values for (a) metallurgical grade chromite and (b) UG2 ore fines.

length can be determined using a photo of the stack flare (such as Figure 1), with the diameter of the furnace flare stack serving as the scale to calculate the flare length. For the flare indicated in Figure 1, for instance, the flare length was calculated to be approximately 6.05 m. The off-gas velocity of this particular stack was also known to the authors, *i.e.*, 6 m/s. From these two parameters, the retention time of particulate matter in the flare can be determined. For the flare shown in Figure 1, it was calculated to be 1.01 seconds.

The d_{90} particle size of actual particles can be determined by collecting and analyzing particles from piping/equipment after the wet venturi scrubber. It would not be advisable to collect such particles during operation, since CO gas is very poisonous and can also result in a CO gas explosion. However, some particles tend to collect/build up within the off-gas piping and/or

the blades of the venturi fan, which can be accessed during plant maintenance periods. The d_{90} size of these particles can be determined by performing laser diffraction particle size analysis, as discussed in Section II-C.

The off-gas flare temperature can be determined using an infrared thermometer or infrared camera to visually determine the temperature, or alternatively it can be calculated with thermodynamic software based on the actual off-gas composition, as was indicated in Section II-D.

As an example of the practical application, the pct Cr(VI) conversion for a typical closed SAF can be considered. In this example, the retention time of the particulate matter is 1.01 seconds (for 6 m flare and exit velocity of 6 m/s, derived from Figure 1). According to Niemelä *et al.*, it is theoretically difficult to remove particles smaller than 1 μm from the off-gas stream with a wet venturi scrubber; therefore, the d_{90} was assumed to be 1 μm . The flaring temperature was assumed to be 2274.15 K (2000 °C), which is less than the burning temperature of pure CO due to typical dilution from other gases present in the off-gas, *e.g.*, CO₂ and N₂. Replacing these values into Eq. [2] yielded a pct Cr(VI) conversion of 2.7×10^{-2} for this specific FeCr SAF.

For an unrealistic worst-case scenario, it can be assumed that the retention time is 2.02 seconds (which represents a 12 m flare with an exit velocity of 6 m/s), the d_{90} particle size is 0.005 μm (which is an unrealistic small d_{90} particle size), and the flaring temperature is the highest temperature obtained from literature/thermodynamic calculations for pure CO combustion, *i.e.*, 2525.35 K (2251.2 °C). Equation [2] yielded a pct Cr(VI) conversion of 3.5×10^{-1} for this scenario. These calculated values indicate that the realistic and unrealistic worst-case scenarios pct Cr(VI) conversions are significantly lower than the pct Cr(VI) conversion values currently used in EIAs to determine the Cr(VI) emissions from FeCr smelters.

If the pct Cr(VI) conversion for a specific closed FeCr SAF is calculated as indicated above with Eq. [2], the total amount of Cr(VI) released from it can also be calculated if the average Cr(III) content of the off-gas and total off-gas volume is known or estimated.

IV. CONCLUSIONS

As far as the authors could assess, this is the first investigation published in the peer-reviewed public domain on the formation of Cr(VI) during the flaring of off-gas from closed FeCr SAFs. Three parameters considered to be critical during flaring were experimentally investigated in a tube furnace, *i.e.*, retention time of the particles in the hot zone, size of particulate matter passing through the hot zone (d_{90}), and temperature of the hot zone. MLR analysis indicated that retention time had the greatest impact on pct Cr(VI) conversion, followed by particle size and temperature. From the MLR analysis, an optimal equation, *i.e.*, Eq. [2], containing all three the investigated independent variables was determined, which reflected the overall impact of these parameters on pct Cr(VI)

conversion. Equation [2] was subsequently used to calculate pct Cr(VI) conversions, which compared well to the experimentally determined values. Thereafter, this equation was used to determine pct Cr(VI) conversions for closed FeCr SAFs, which yielded 2.7×10^{-2} and 3.5×10^{-1} for realistic and unrealistic worst-case scenarios, respectively. In this practical application of Eq. [2], it was necessary to extrapolate to smaller particles sizes, higher temperatures, and longer retention times than the conditions that could be experimentally investigated. However, the overall pct Cr(VI) conversions obtained from Eq. [2] represent a much more reliable representation than the unsubstantiated pct Cr(VI) conversion currently being used in EIAs for FeCr smelters, *i.e.*, 0.8 to 1 pct. In future, the Cr(VI) conversion of a specific FeCr smelter can be calculated utilizing Eq. [2]. This conversion factor can then be included as an emission factor in an atmospheric dispersion model applied during an EIA to determine the Cr(VI) levels to which communities will be exposed. These exposure levels can then be related directly to possible health impact. Additionally, FeCr producers should be encouraged to flare less CO-rich off-gas, considering the international drive to reduce flaring,^[35] as well as the increasing pressure on FeCr producer to reduce their carbon footprint and electricity consumption.

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