

Aqueous solubility of Cr(VI) compounds in ferrochrome bag filter dust and the implications thereof

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ABSTRACT

The production of ferrochrome (FeCr) is a reducing process. However, it is impossible to completely exclude oxygen from all of the high-temperature production process steps, which may lead to unintentional formation of small amounts of Cr(VI). The majority of Cr(VI) is associated with particles found in the off-gas of the high-temperature processes, which are cleaned by means of venturi scrubbers or bag filter dust (BFD) systems. BFD contains the highest concentration of Cr(VI) of all FeCr wastes. In this study, the solubility of Cr(VI) present in BFD was determined by evaluating four different BFD samples. The results indicate that the currently applied Cr(VI) treatment strategies of the FeCr producer (with process water pH ≤ 9) only effectively extract and treat the water-soluble Cr(VI) compounds, which merely represented approximately 31% of the total Cr(VI) present in the BFD samples evaluated. Extended extraction time, within the afore-mentioned pH range, proved futile in extracting sparingly-soluble and water-insoluble Cr(VI) species, which represented approximately 34% and 35% of the total Cr(VI), respectively. Due to the deficiencies of the current treatment strategies, it is highly likely that sparingly water-soluble Cr(VI) compounds will leach from waste storage facilities (e.g. slimes dams) over time. Therefore, it is critical that improved Cr(VI) treatment strategies be formulated, which should be an important future perspective for FeCr producers and researchers alike.

Keywords: hexavalent chromium, Cr(VI), ferrochromium, ferrochrome, bag filter dust, smelter waste

INTRODUCTION

Since its discovery in 1798, chromite has remained the only commercially viable source of new chromium (Cr) units (Murthy et al. 2011; Riekkola-Vanhanen, 1999). Approximately 90% to 95% of mined chromite is used in the metallurgical industry for the production of various grades of FeCr, which is produced through the carbo-thermic reduction of chromite ore (Riekkola-Vanhanen, 1999). About 80% to 90% of ferrochrome (FeCr) is consumed by the stainless-steel industry, primarily as high-carbon or charge-grade FeCr (Murthy et al. 2011). Stainless steel is a vital alloy in various applications (Gasik, 2013), with the Cr content of stainless steel increasing its corrosion resistance. South Africa holds the largest chromite deposits and is the second-largest FeCr producing country (ICDA, 2012), with 14 FeCr smelters (Beukes et al., 2012).

Cr is present as Cr(III) in chromite ore, while Cr(0) occurs in the produced FeCr. Although completely unintended, small amounts of Cr(VI) are formed during FeCr production, which may be present in waste materials (Beukes et al., 2010). Cr(VI) is generally regarded as carcinogenic (IARC, 2012), with specifically airborne exposure to Cr(VI) being associated with cancer of the respiratory system (Proctor et al., 2002). In contrast to Cr(VI), Cr(III) and Cr(0) are not classified as carcinogenic. Cr(III) is in fact used a dietary supplement for certain human health abnormalities (Hininger et al., 2007).

The main types of waste generated during FeCr production are slag, sludge from wet venturi scrubbers and bag filter dust (BFD) (Van Staden et al., 2014). Slag-to-FeCr generation ratios of 1.1:1 up to 1.9:1 are common in this industry, with ratios varying according to different production technologies employed (Beukes et al., 2010; Niemelä and Kauppi, 2007). Although the volumes of slag generated are large, the Cr(VI) content of the slag is usually very low (Beukes et al., 2010; Niemelä and Kauppi, 2007). Additionally, FeCr slag can be used in various commercial applications (Niemelä and Kauppi, 2007; Zelić, 2005; Lind et al., 2001; Riekkola-Vanhanen, 1999). Sludge, which is generated during the wet venturi scrubbing of closed furnace off-gas (Beukes et al., 2010; Niemelä et al., 2004) does not usually contain significant Cr(VI) concentrations (Gericke, 1998). However, in contrast to slag and sludge, BFD generated during the cleaning of off-gas from open/semi-closed FeCr furnaces contains significant levels of Cr(VI) (Beukes et al., 2012; Maine et al., 2005; Gericke, 1998), which cannot be disposed without proper Cr(VI) treatment (Beukes et al., 2012). After the BFD is treated to reduce Cr(VI), it is usually disposed in fit-for-purpose waste facilities such as slimes dams.

Treatment of BFD (and indeed any Cr(VI) containing FeCr waste) usually involve the aqueous reduction of Cr(VI) with an appropriate inorganic reducing agent such as Fe(II) (Beukes et al., 2012; Seaman et al., 1999; Buerge and Hug, 1997) and S(IV) (Beukes et al., 2001 and 1999), or bacterial reduction (Dhal et al., 2013; Molokwane et al., 2008). Although Cr(VI) can also be reduced with numerous organic compounds (Kassem, 2010; March, 1992), this is usually avoided due to the potential solubilisation of Cr(III) (Beukes et al., 2012; Apte et al., 2006). In this paper, the leaching potential of Cr(VI) from BFD is investigated and it is proven that this can be a major limitation in the effectiveness of the conventional Cr(VI) treatment used by industry.

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MATERIALS AND METHODS

Materials

Numerous factors can influence the composition of BFD, including the production technology employed (e.g. open or semi-closed furnace technology, type of filters used in the bag filter plant), physical separation in the bag filter plant itself (e.g. some compartments containing finer material than others), metallurgical operating conditions (e.g. basic or acid slag operating conditions) and composition of feed materials (e.g. chemical and physical differences of ores). Therefore, four different BFD samples were obtained from FeCr producers in South Africa. These producers preferred to remain anonymous and therefore the samples are merely referred to as BFD samples A, B, C and D.

All chemicals used were analytical grade reagents. Standard Cr(VI) solutions were prepared from a $1\,009 \pm 5 \text{ mg}\cdot\text{mL}^{-1}$ aqueous chromate (CrO_4^{2-}) analytical solution (Spectrascan, distributed by Teknolab AB, Sweden), which were used for calibration and verification of the analytical technique employed. The post-column reagent that was used during Cr(VI) analysis was prepared using 1,5-diphenylcarbazide (DPC) (FLUKA), 98% sulfuric acid (Rochelle Chemicals) and HPLC grade methanol (Ace). Solutions of sodium hydroxide (Merck) and perchloric acid (Merck) were used to adjust the pH of aqueous solutions/mixtures. According to solubility data, Cr(VI) chemicals can be classified as water soluble, sparingly water soluble and water insoluble (IARC, 2012; Ashley et al., 2003). Ammonium sulphate with 99% purity (Merck SA) and 25% ammonia solution (Associated chemical enterprises) were used to prepare a $0.05 \text{ M } (\text{NH}_4)_2\text{SO}_4 - 0.05 \text{ M } \text{NH}_4\text{OH}$ extraction buffer that is capable of leaching all water-soluble and sparingly water-soluble Cr(VI) compounds (Ashley et al., 2003). Sodium hydroxide (Promark chemicals) and anhydrous sodium carbonate (Merck SA) were used to prepare a 3 wt% $\text{Na}_2\text{CO}_3 - 2 \text{ wt\% NaOH}$ extraction buffer, to quantitatively extract all Cr(VI) in the BFD samples, including the water-insoluble fraction (Ashley et al., 2003). Ultra-pure deionized water (resistivity, $18.2 \text{ M}\Omega\text{cm}^{-1}$), produced by a Milli-Q water purification system, was used for all dilutions and aqueous extractions. 99.999% pure nitrogen gas (N_2) (AFROX) was used to provide an inert environment during leaching. Hydrophilic PVDF $0.45 \mu\text{m}$ filters (Millipore Millex, USA) were used for the filtration of solutions.

BFD sample characterisation

A Malvern Mastersizer 2000 was used to determine the particle size distribution of the BFD samples. A diluted suspension of material was ultra-sonicated for 1 min prior to the particle size measurement, in order to disperse the individual particles and to prevent the use of a chemical dispersant. Laser obscuration was kept at 10% to 15%, while mechanical stirring was set to $2\,000 \text{ r}\cdot\text{min}^{-1}$. Ten measurements were made for each sample and the average taken.

Scanning electron microscopy with energy dispersive x-ray detectors (SEM-EDS) was used to perform morphological and chemical characterisation of the BFD particles. FEI Quanta 250 FEG ESEM incorporating Oxford Inca X-Max 20 EDS system with a 15 kV electron beam at a 10 mm working distance was used. BFD samples were prepared with two different procedures for SEM analysis. Firstly, samples were mounted onto a specimen stub with carbon-coated tape and subsequently gold coated in order to determine the general BFD particle characteristics, e.g., size and shape. In order to determine the

chemical compositions of the BFD samples by SEM-EDS, the samples were set in resin and polished before being analysed. The SEM-EDS analysis was performed by scanning a wide rectangular area of the sample surface in a raster-like pattern for 60 s. Spot analyses were also performed to determine the composition of individual particles present in the BFD.

X-ray diffraction (XRD) analyses were performed on BFD samples ground to $< 45 \mu\text{m}$ using a Rigaku D/MAX 2500 rotating-anode powder diffractometer with Cu K α radiation at 50 kV, 260 mA, a step-scan of 0.02° , and a scan rate at 1 min^{-1} in 2θ from 5° to 70° . Phase identifications were made using JADE v.9.3 coupled with the ICSD and ICDD diffraction databases.

Trace metal analysis

Inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent 7500CE ICP-MS with Octopole Reaction System) was used to determine the total metal concentrations, irrespective of oxidation state, present in aqueous leach solutions. These solutions were obtained as described in the next section.

Cr(VI) extraction and analysis

For each BFD sample, 0.50 g was transferred into a 100 mL glass beaker, which contained 50 mL of deionized water. The initial pH of the deionized water had been adjusted to a predetermined value. Leaching solutions were purged with N_2 for 10 min prior to Cr(VI) extraction to remove dissolved oxygen from the solution, which may cause unwanted Cr(III) oxidation (Ashley et al., 2003). Each beaker and its contents were placed on a magnetic stirrer and agitated for a period of 2 h. A steady stream of N_2 was continually used to purge the suspension, ensuring an inert environment during leaching. After Cr(VI) extraction, the leaching solutions were filtered through hydrophilic Millipore $0.45 \mu\text{m}$ PVDF filters to remove particulate matter, followed by another pH measurement to ensure that no pH drift occurred. Thereafter the filtrates were transferred to 100 mL A-grade volumetric flasks and diluted to a final volume of 100 mL with pH-adjusted deionized water. 50 mL of each solution was used for aqueous trace metal analyses, while the remaining 50 mL was used for Cr(VI) analysis. All pH measurements were conducted with a HANNA - HI 991001 pH meter with a temperature probe.

In addition to Cr(VI) extraction at specific pH values, Cr(VI) extractions were also performed using hot plate digestion. A buffer of $0.05 \text{ M } (\text{NH}_4)_2\text{SO}_4$ and $0.05 \text{ M } \text{NH}_4\text{OH}$ was used to leach water-soluble and sparingly water-soluble Cr(VI) compounds, while a buffer of 3 wt% Na_2CO_3 and 2 wt% NaOH was used to leach total Cr(VI) (Ashley et al., 2003; NIOSH 7605, 2003). The afore-mentioned buffer ($\text{Na}_2\text{CO}_3 - \text{NaOH}$) enhances the dissolution of insoluble Cr(VI) compounds at higher pH levels by the addition of carbonate (CO_3^{2-}), as indicated in Eq. 1. In the presence of a large excess of CO_3^{2-} the equilibrium shifts quantitatively to the right of Eq. 1 and insoluble Cr(VI) becomes soluble (Ashley et al., 2003).



with M = cation associated with chromate

The Cr(VI) concentrations of aliquots were determined with a Thermo Scientific Dionex ICS 3000 ion chromatograph (IC) according to the procedure described by Looock et al. (2014) and Du Preez et al. (2015), which was derived from Dionex Application Update 179 (2011), Dionex Application Update 144 (2003), and Thomas et al. (2002). The IC system was equipped with a Dionex IonPac AG7 $4 \times 50 \text{ mm}$ guard column

and a Dionex IonPac AS7 4 x 250 mm analytical separation columns. A 1 000 μL injection coil and a 2 x 375 μL knitted reaction coil coupled to a UV-visible absorbance detector set at a wavelength of 530 nm were used. 250 mM ammonium sulphate was used as an eluent and an isocratic pump carried the eluent and the injected sample through the system. 2 mM DPC solution was used for post column coloration, which was delivered into the system by an AXP pump. The flow rates of the eluent and colorant were 1.0 $\text{mL}\cdot\text{min}^{-1}$ and 0.5 $\text{mL}\cdot\text{min}^{-1}$, respectively. A six-point calibration was performed for Cr(VI), ranging from 5 to 75 $\mu\text{g}\cdot\text{L}^{-1}$. The correlation coefficient of this linear calibration line was $> 99.96\%$. The detection limit of this method at a confidence level of 98.3%, which was calculated according to the method specified by Skoog et al. (2013), was experimentally determined as 0.9 $\mu\text{g}\cdot\text{L}^{-1}$ by Looock-Hattingh (2016). The accuracy of the specific analytical method (and the specific instrument used) was recently indicated (Venter et al., 2016) by analysis of a Community Bureau of Reference (former reference materials program of the European Commission) BCR N° 545 welding dust filter certified reference material (individual identification N° B7-36, purchased on 25 January 2013), for which a value of 39.7 $\text{mg}\cdot\text{g}^{-1}$ Cr(VI) was obtained, which was within the uncertainty of the reference material that was defined as the half width of the 95% confidence interval of the mean of 40.2 $\text{mg}\cdot\text{g}^{-1}$ Cr(VI).

X-ray absorption spectroscopy (XAS)

XAS experiments were carried out at PNC-CAT's bending magnet beam-line 20-BM of the Advanced Photon Source (APS), Argonne, IL, USA. Finely ground and homogenized BFD samples were placed as monolayers on tapes and loaded into Plexiglass sample holders. Experiments were carried out at room temperature both in transmission and fluorescence modes using ion chambers filled with nitrogen and helium gases, and a Canberra 13-element detector. A Cr foil was used for energy calibration. Between 4 and 6 scans were collected from each sample and the reference materials. Data reduction and analysis were performed with ATHENA (Ravel and Newville, 2005). The least squares fitting of the XANES spectra were made with LSFITXAFS (Paktunc, 2004). XAS, including both X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) regimes, was employed to determine the sources and quantitative speciation of Cr in the BFD samples and possible cation association of CrO_4^{2-} that could be leached and precipitated from the BFD samples. Precipitates were prepared by contacting 50 g of BFD with 1 L of deionized water for 4 consecutive 24 h contacting periods. After 24 h contact, the water was separated from the BFD by means of filtration, after which the BFD were re-contacted with fresh water and the procedure repeated. All four leachates were combined and then allowed to evaporate at room temperature in a fume cupboard circulated with filtered air to prevent contamination, producing a solid residue that was analysed with XAS spectroscopy techniques.

RESULTS AND DISCUSSION

Particle size analysis

The d_{90} , d_{50} and d_{10} of the particle size distribution of the different BFD samples are presented in Table 1. The d_{90} is defined as the equivalent particle size for which 90% of the particles are smaller,

with definitions of d_{50} and d_{10} derived similarly. The particle size analyses indicated that the d_{90} of all four BFD samples ranged between 32.8 and 152.2 μm , with the A and B samples being coarser than the C and D samples. The particle sizes reported here are similar to BFD particle sizes reported previously (Van Staden et al., 2014; Beukes et al., 2010).

TABLE 1 The average d_{90}, d_{50} and d_{10} values of BFDs			
BFD	Particle size (μm)		
	d_{90}	d_{50}	d_{10}
A	140.6	39.4	4.3
B	152.2	37.6	4.2
C	32.8	10.3	1.7
D	33.3	9.7	1.7

SEM observations

Figures 1(a), 1(b), 1(c) and 1(d) indicate SEM micrographs of BFD samples of A, B, C and D. Each of these figures present combined images, with the larger images indicating cross-sectional polished micrographs. The smaller images (in the bottom right-hand corners) represent micrographs of the BFDs pressed onto stubs with adhesive carbon tape. It is evident from these micrographs that the BFD samples consisted mainly of very small particulate matter (mostly $< 40 \mu\text{m}$), with some larger particles of up to approx. 200 μm . It was previously shown that the larger unevenly-shaped particles observed in BFD are unreacted or partially-reacted feed materials such as chromite, fluxes or reductants, while the very small spherical particles represent the actual off-gas particulates (Van Staden et al., 2014; Beukes et al., 2010; Beukes et al., 1999). However, to confirm that unreacted/partially-reacted chromite particles were present in the BFD samples, one of the unevenly-shaped grey particles, marked with a white box in Fig. 1(a) (BFD sample A), was analysed with SEM-EDS, which revealed Cr and Fe contents of 30.7 and 20.8 wt%, respectively. These correspond to a Cr/Fe ratio of 1.48 which is comparable to typical South African chromite ore (Cramer et al., 2004). The SEM micrographs also revealed that the BFD samples A and B (Figs. 1(a) and 1(b)) contained more unreacted/partially-reacted larger raw material particles when compared to C and D (Figs. 1(c) and 1(d)). The SEM observations confirmed the particle size analysis results (Table 1), which indicated that the A and B samples were coarser than C and D. As previously indicated, the presence of a greater number of larger raw material particles in the BFD could be ascribed to the differences in the technology applied or the feed materials used at different production facilities. For instance, some FeCr smelters utilize a cyclone to remove larger and denser particles before the off-gas is cleaned in the bag filter plant, while others merely use a drop-out box that is less effective.

SEM-EDS chemical analyses of the BFD samples are presented in Table 2. These results should be considered as semi-quantitative, with O content determined by difference. Carbon (C) was not analysed, since a carbon-based resin was used to set the BFD samples prior to polishing. Cr content of the samples varied between 3.28% (Sample C) and 7.62% (Sample B). As expected, the elements with lower elemental mass that

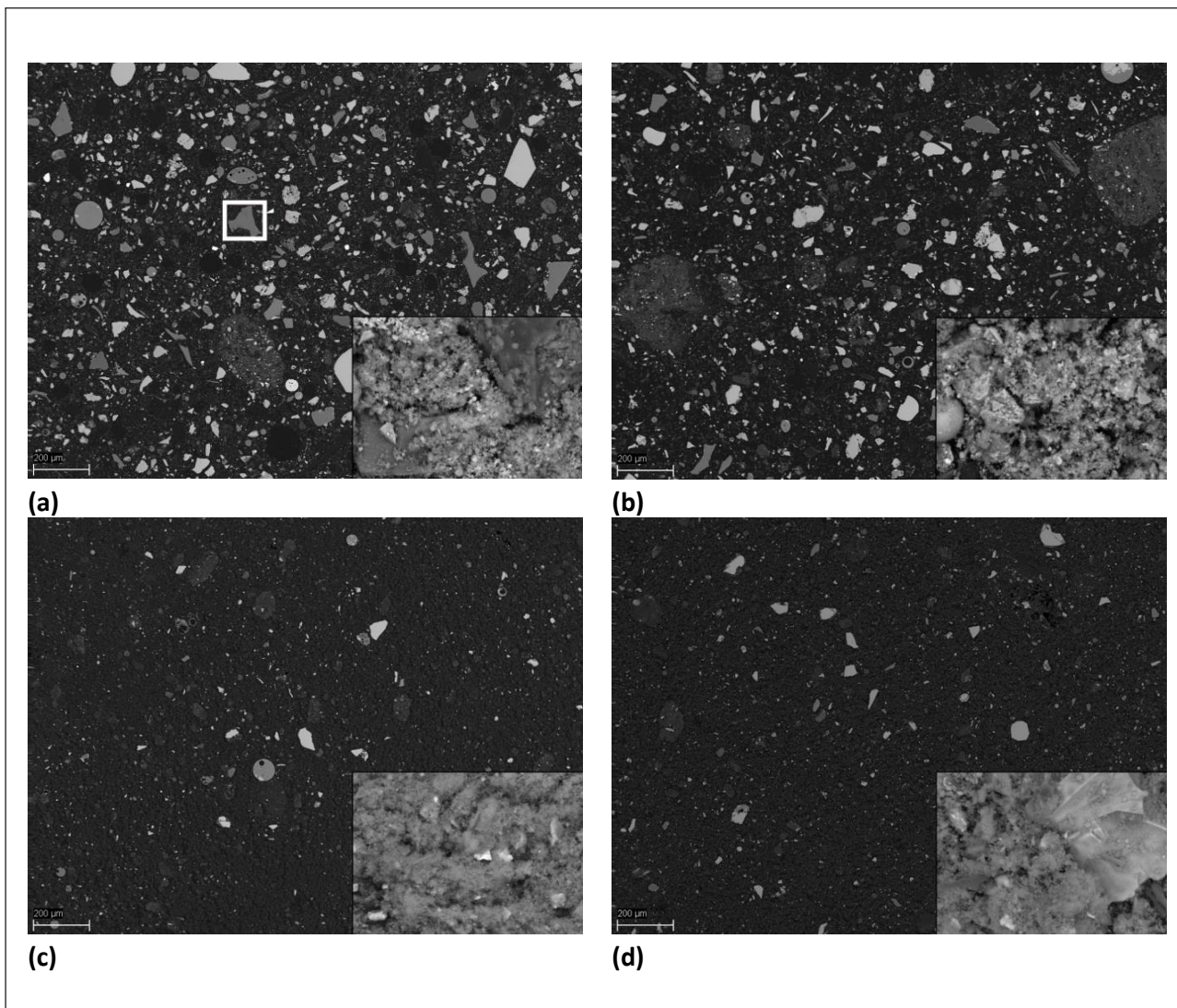


Figure 1
SEM micrographs for BFDs A (a), B (b), C (c) and D (d), at 2 000 (larger image) and 100 (smaller image) times magnification. The larger particle with an uneven morphology, marked by the white box in (a), is an example of an un-reacted chromite particle.

TABLE 2 SEM-EDS analyses of cross-sectional polished BFDs												
BFD	Detected elements (%)											Total
	Mg	Al	Si	S	Cl	K	Ca	Cr	Fe	Zn	O	
A	6.24	3.38	11.71	1.55	5.38	3.11	1.29	6.81	7.97	18.66	33.91	100
B	6.66	2.98	11.75	1.63	4.67	3.01	1.06	7.62	8.47	18	34.2	100
C	12.3	2.26	21.77	1.18	1.6	2.66	0.59	3.28	2.85	9.4	42.09	100
D	13.23	2.58	20.12	1.33	1.57	2.36	0.92	3.84	3.76	8.57	41.71	100

are typically associated with actual off-gas particles, such as magnesium (Mg), aluminium (Al), silicon (Si) and zinc (Zn), were present in significant concentrations in all of the BFD samples. Of particular interest was that no noteworthy amounts of Na were detected in any of the BFD samples. It is well known that alkali roasting of chromite is an industrial process for the production of sodium chromate, the formation efficiency of which depends on the amount of O_2 and alkali present, as well as the temperature during the production process (Antony et al., 2001). Maine et al. (2005) proposed that Cr(VI) could mainly be associated with alkali metals in FeCr BFD, but did not present any evidence to support this statement. However, the lack of Na in the BFD samples cannot be considered as evidence that anionic Cr(VI) (CrO_4^{2-}) is not associated with significant amounts of Na since the SEM-EDS technique has limitations with respect to Na analysis.

XRD analysis

XRD of the BFDs indicated that all of the samples comprised mainly of the same crystalline compounds. In the order of decreasing abundance, they are chromium spinel ($(Fe^{2+},Mg)(Cr,Fe^{3+})_2O_4$), quartz (SiO_2), halite ($NaCl$), anorthite ($CaAl_2Si_2O_8$), osakaite ($Zn_4SO_4(OH)_6 \cdot 5H_2O$) and forsterite (Mg_2SiO_4). The

similarities in crystalline phases of the investigated BFDs indicate that the samples originated from a similar type of process (i.e. FeCr production with BFD off-gas cleaning).

XAS characterisation

As is evident from Fig. 2(a) XAS spectra of the BFD samples collected at Cr K-edge indicate that they are broadly similar. The spectral features at the edge and above are similar to those of chromite from the upgraded upper group 2 (UG2) chromite layer of the Bushveld Complex in South Africa, suggesting that the unreacted chromite is the dominant Cr carrier in the furnaces where the BFD samples A, B and C were collected. BFD sample D was not characterized by XAS. Other important sources of Cr in the BFD samples include ferrochrome and slag. Figure 2(b) presents the least squares fitting of the Cr K-edge XANES spectra, indicating that the BFD samples consists of chromite, FeCr and FeCr slag, as represented by reference materials, i.e., UG2 chromite, FeCr and FeCr slag obtained from a FeCr smelter in South Africa. The BFD samples are dominated by chromite in terms of Cr concentrations, with chromite abundances ranging from 72% to 82% by weight (Table 3). The remaining Cr concentrations are tied to FeCr and slag.

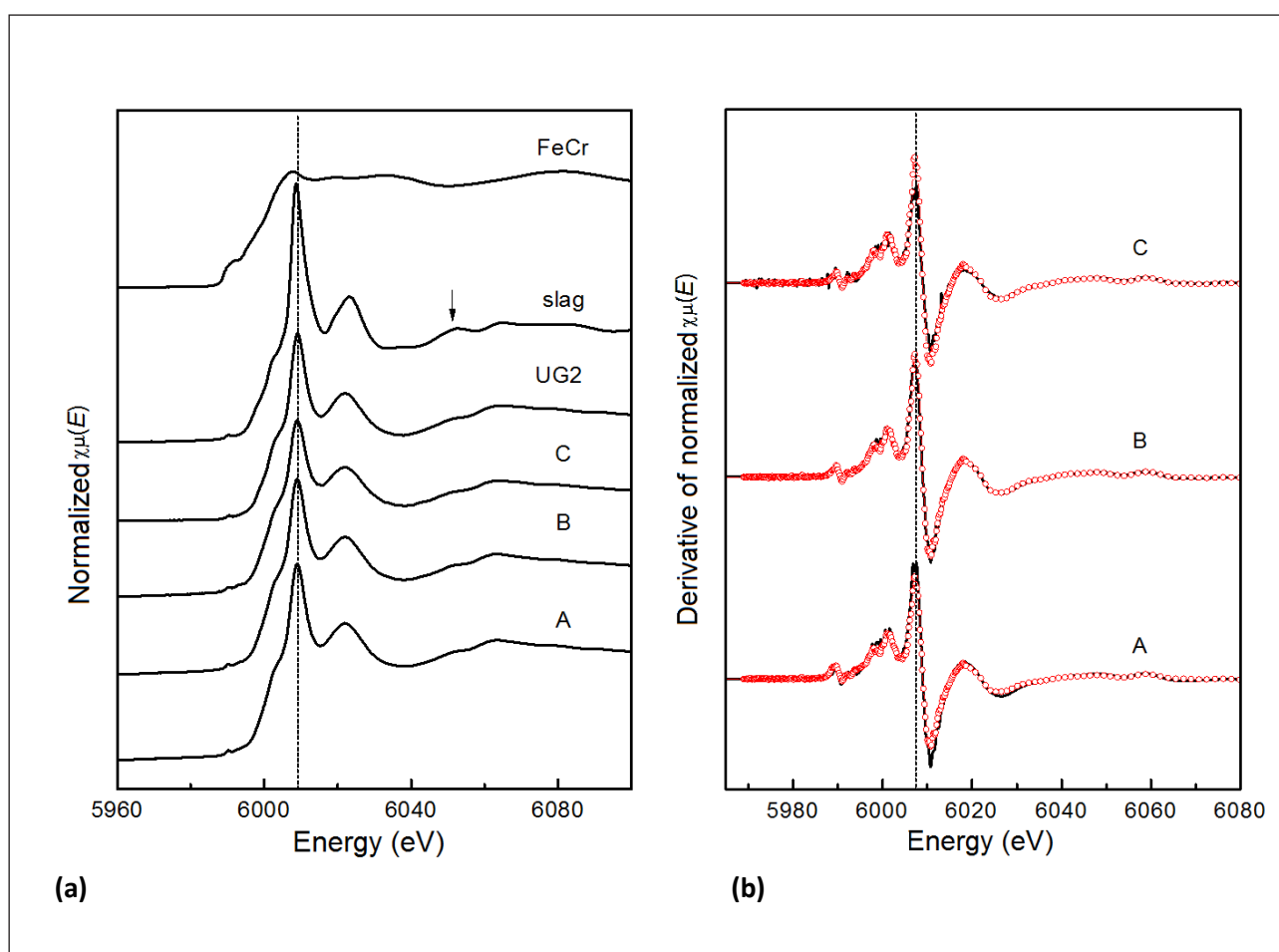


Figure 2

Cr K-edge XANES spectra of the BFD samples and their comparison to the UG2 chromite, slag and FeCr reference samples obtained from a South African FeCr producer (a). Least squares fitting of the derivative of the normalized BFD samples with end member compositions of chromite, slag and FeCr. Measured spectra are shown in black and the fits are indicated by the red circles (b).

TABLE 3 Cr-containing constituents present in BFD samples determined from least square fitting of the XANES spectra			
BFD	% Cr constituent, compared to reference materials		
	UG2 chromite	FeCr	Slag
A	81.6	10.1	8.3
B	80.6	11.8	7.6
C	71.6	25.4	3.0

Trace metal leachability

It is generally accepted that higher concentrations of most heavy and transitional metals will leach out of a solid matrix (e.g. waste and soil) at low pH values (Ding et al., 2014; Lee et al., 2012). This was also observed experimentally, as indicated in Figs. 3 and 4, which present the log concentrations of alkali and alkali earth (Fig. 3), as well as transition and heavy (Fig. 4) metals as a function of leach solution pH. The higher solubility at lower pH was especially evident at pH ≤ 3 . Elements occurring in low concentrations in the BFD samples ($< 10 \text{ mg}\cdot\text{kg}^{-1}$ BFD) were excluded from all figures to prevent congestion of the graphs, and Na contents were excluded from Figs 3(a) and (b) at pH > 7 , since NaOH solution was used to increase the pH of the leach solutions.

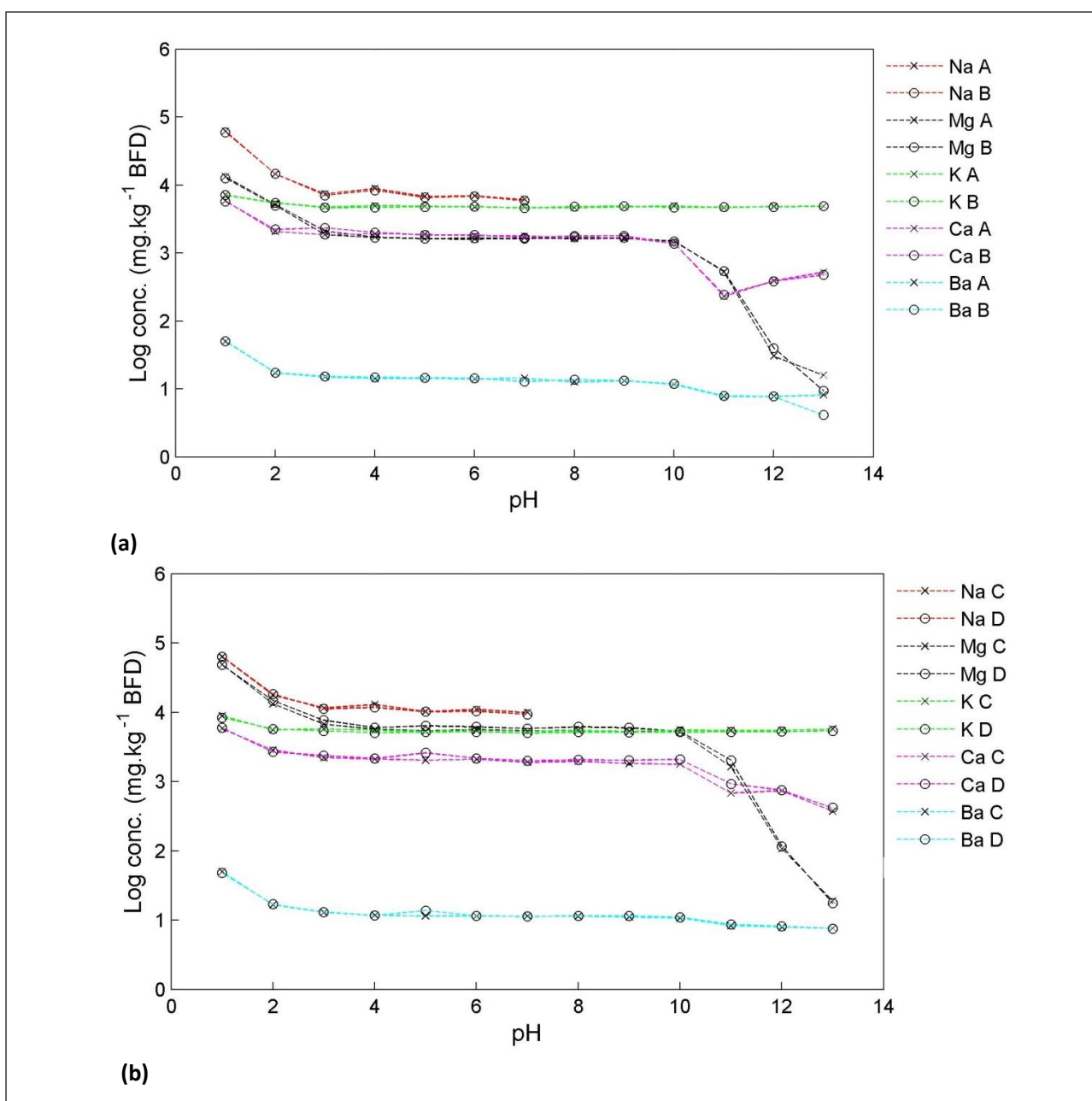


Figure 3

Log concentration of alkali and alkali earth metals in (a) BFDs A and B, as well as (b) BFDs C and D, as a function of leach solution pH.

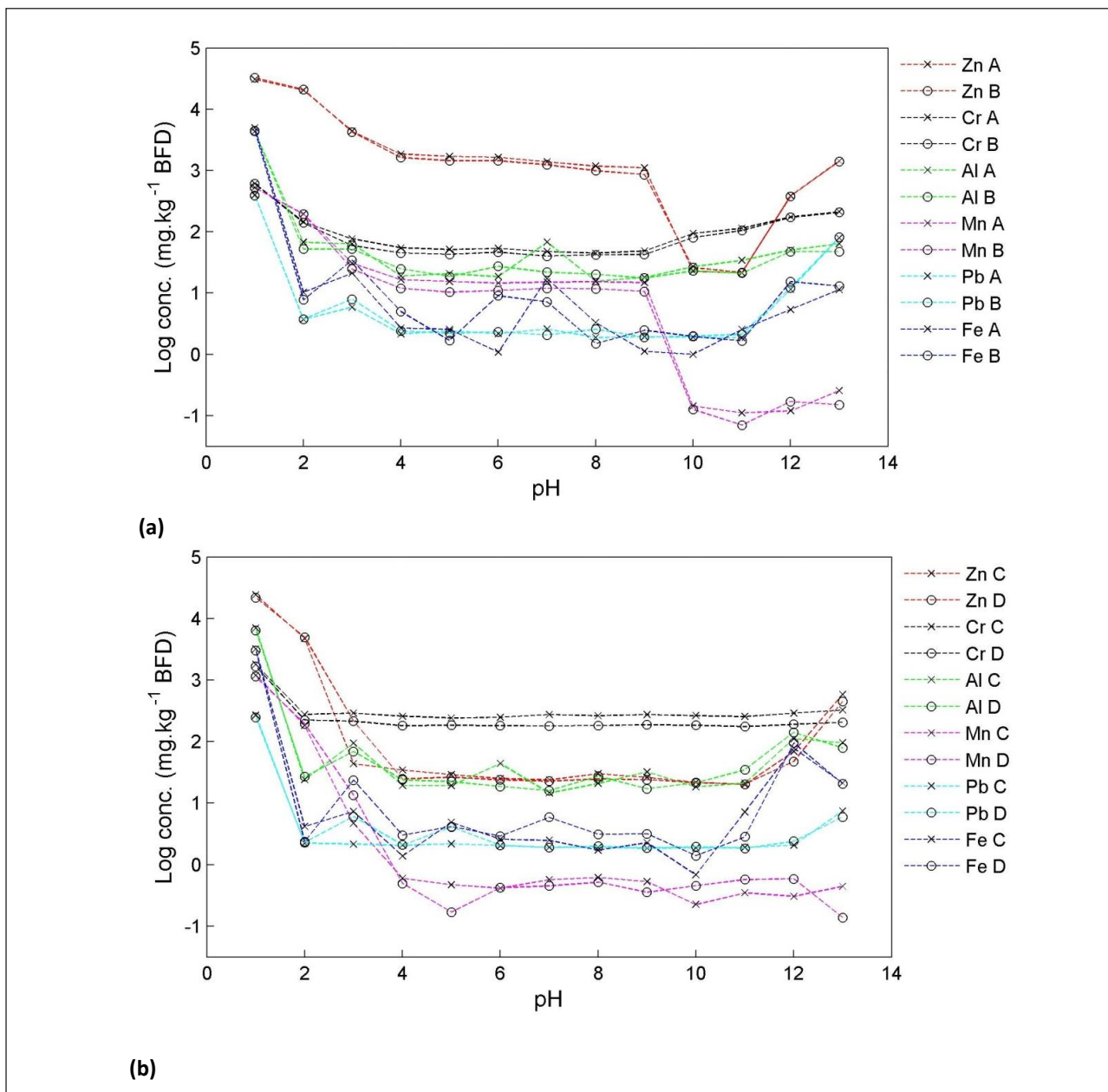


Figure 4
Log concentration of transition and heavy metals present in (a) BFD A and B, as well as (b) C and D as a function of leach solution pH

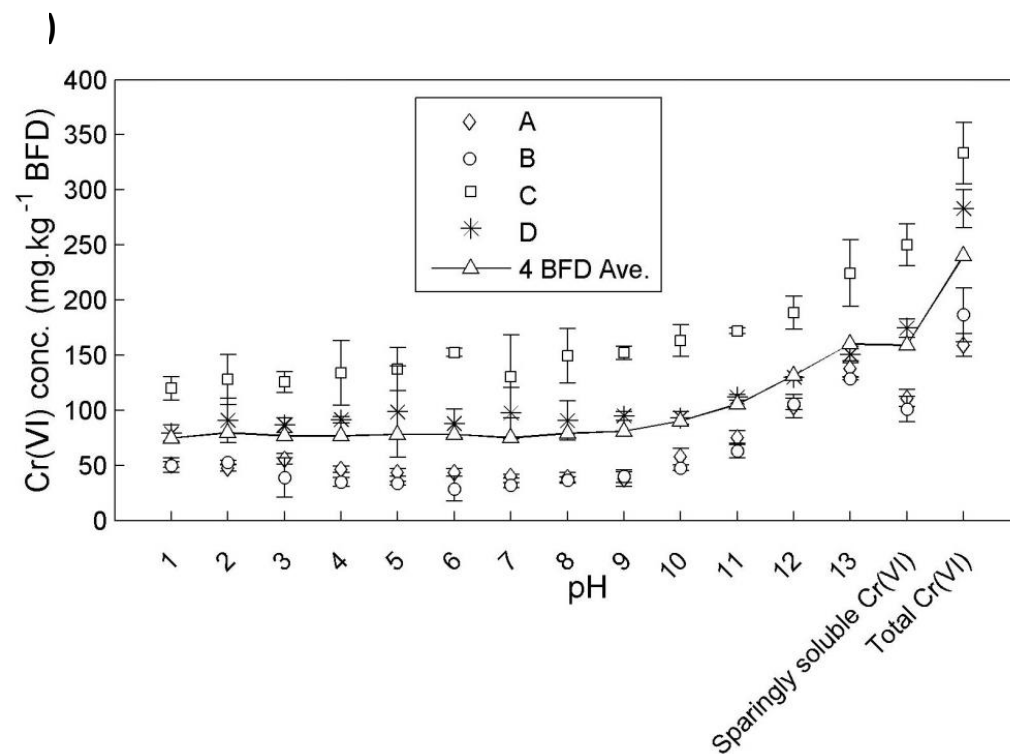
When comparing metal concentrations presented in Fig. 3 to concentrations presented in Fig. 4, it is evident that most alkali and alkali earth metals, excluding Ba, were present in much higher concentrations than transition and heavy metals, except for Zn that had concentrations comparable to alkali and alkali earth metals, especially at very low pH. The results presented in Figs 3 and 4 will be contextualized further in the following sections.

Cr(VI) leachability

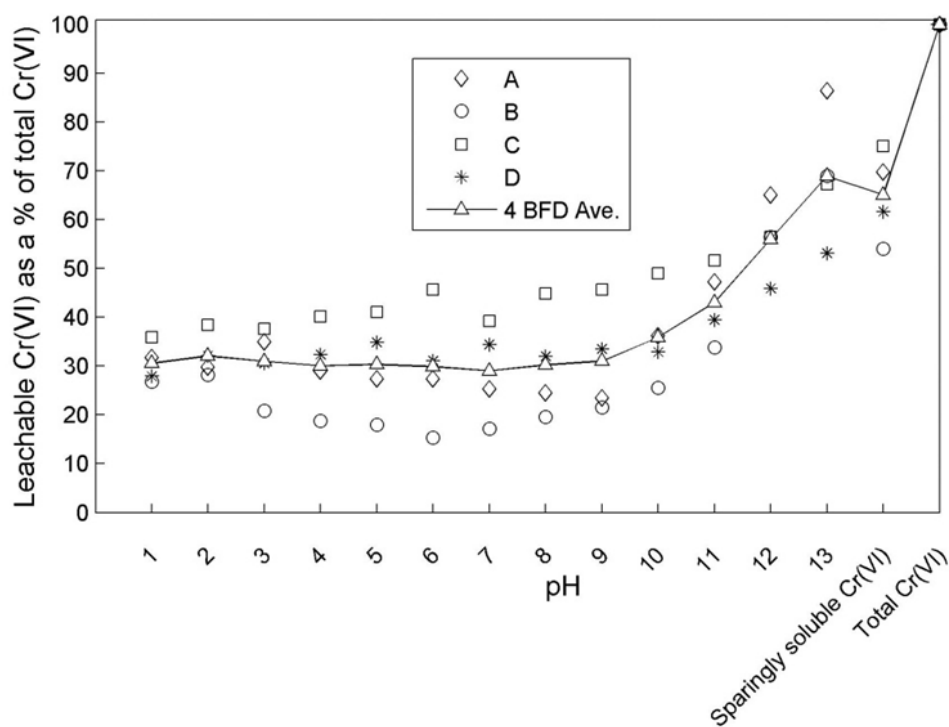
Figure 5(a) presents the leachable Cr(VI) concentrations as a function of leach solution pH, as well as the two solubility fractions, i.e., combined water-soluble and sparingly water-soluble Cr(VI), as well as total Cr(VI) determined. Figure 5(b) indicates the same data normalized to percentage, based on the

total extractable Cr(VI) of each sample. From these results, it is evident that the amount and percentage of leachable Cr(VI) increased with an increase in leach solution pH at $\text{pH} \geq 9$. This is in contrast to the results obtained for all the other metals (Figs 3 and 4) for which the leachability increased as the leach solution pH decreased.

From the data presented in Figs 3, 4 and 5, it is impossible to shed any light on the possible association of anionic CrO_4^{2-} with cations, to indicate the identity of the Cr(VI) compounds that are present in the BFD samples. However, the observed increase of leachable Cr(VI) with an increase in pH (Fig. 5(b)) is an indication that not only water-soluble (e.g. Na_2CrO_4 , K_2CrO_4), but also sparingly water-soluble (e.g. CaCrO_4 , SrCrO_4) and waterinsoluble (e.g. BaCrO_4 , PbCrO_4) Cr(VI) compounds occur in the samples evaluated. This data can also be used to estimate the average water-soluble, sparingly water-insoluble and



(a)



(b)

Figure 5

Leachable Cr(VI) as a function of leach solution pH, combined water-soluble and sparingly water-soluble Cr(VI), as well as total Cr(VI) (a). The same data normalized to % Cr(VI), based on the total extractable Cr(VI) (b).

water-insoluble fractions. As is evident from Fig. 5(b), there was no statistically significant difference in the extractable Cr(VI) at $\text{pH} \leq 9$, with approximately 31% of the total Cr(VI) being extracted in this range. This represents the water-soluble Cr(VI) fraction. On average, approximately 65% of the total Cr(VI) was present as a combination of water-soluble and sparingly water-soluble compounds. The difference between these two fractions, i.e. 34%, therefore represents the percentage of sparingly water-soluble Cr(VI) compounds. The difference between the total Cr(VI) (100%) and the combined water-soluble and sparingly water-soluble fractions (65%) revealed the presence of approximately 35% water-insoluble Cr(VI) compounds in the BFD samples evaluated.

The above-mentioned results and, in particular, the presence of substantial fractions of sparingly water-soluble and water-insoluble Cr(VI) compounds, contradict the general perception that total Cr(VI) extraction from ferrochrome BFD can be achieved by neutral or acidic aqueous extractions. For instance, Maine et al. (2005) indicated that > 100 h of extraction is required with neutral water to completely extract Cr(VI) from BFD. Gericke (1995) maintained that 24 h leaching with aqueous solutions of pH 2 to 6 is adequate for Cr(VI) extraction from BFD. Bulut et al. (2009) stated that only 30 min was required to dissolve all Cr(VI) present in BFD and that the solution pH did not play a significant role. However, none of these authors used buffers and extraction methods to ensure

extraction of sparingly water-soluble and water-insoluble Cr(VI) compounds (Ashley et al., 2003).

Apart from the above-mentioned possible underestimation of the amount of Cr(VI) present in BFD by previous studies, the retention times applied in some studies (Maine et al., 2005; Gericke, 1995) are impractical. Some FeCr producers pump their BFD sludge (BFD after being contacted with water) directly to a thickener to separate the solid particles from the process water, while others might have a small surge tank to regulate the pumping of the afore-mentioned BFD sludge to the thickener. Figure 6 indicates a simplified schematic illustration to demonstrate a typical process flow of BFD.

Typically, chemical Cr(VI) treatment takes place just prior to the BFD sludge entering the thickener. Currently, ferrous sulphate reduction of Cr(VI) is the most commonly applied treatment method (Beukes et al., 2012). However, Fe(II) that is not consumed to reduce Cr(VI) is oxidized within a couple of minutes to Fe(III), at the pH levels applicable to FeCr process water (Beukes et al., 2012; He et al., 2004; Buerge and Hug., 1997; Fendorf and Li, 1996). Therefore, the effective residence time of the BFD particles in the process water, during which Cr(VI) extraction can take place, is far less than the 2 h extraction time applied in this study. Considering the afore-mentioned description, it is evident that it is highly likely that the short extraction times associated with current Cr(VI) treatment

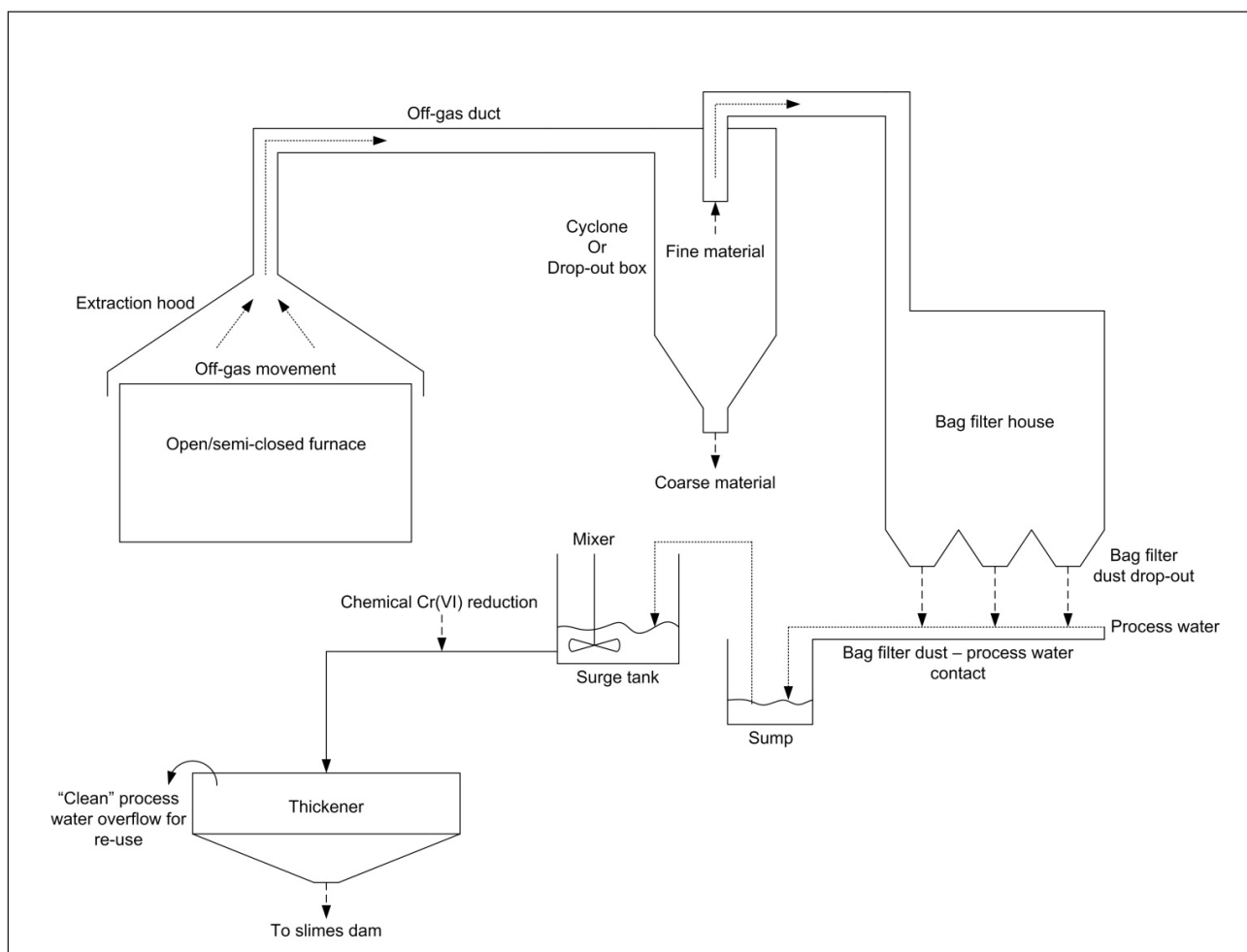


Figure 6
Schematic illustration to demonstrate a typical process flow of BFD

strategies of FeCr producers only allow the extraction of the water-soluble Cr(VI) fraction.

Previously Maine et al. (2005) attempted to explain the slow release of Cr(VI), beyond the initial fast solubilisation of a certain fraction. These authors postulated that most of the Cr(VI) condenses onto the surface of the rounded fly ash type BFD particles, which can dissolve very rapidly in water. They further suggested that a small fraction of Cr(VI) might be trapped by the glassy surface of the BFD particles, which resulted in the slow release of the remaining Cr(VI). However, the results presented in this paper prove that the slow release, following the rapid initial dissolution of a fraction of the Cr(VI), can rather be attributed to the presence of substantial fractions of sparingly water-soluble and water-insoluble Cr(VI) compounds.

According to a survey conducted by Beukes et al. (2012) at various FeCr producers, the pH of FeCr process waters usually varies between 6.2 and 9.0. As indicated in Fig. 5(b), as well as the discussions thereafter, approximately 31% of the total Cr(VI) is leached at $\text{pH} \leq 9$, which correlates with the water-soluble Cr(VI) fraction. In order to confirm that the currently applied Cr(VI) treatment strategies extract only the water-soluble Cr(VI) fraction, even if extended extraction times are applied, the solid residue obtained from the evaporation of 4 successive 24 h extractions of the BFD samples at pH 7 were characterized with XAS and presented in Fig. 7. The pH level of 7 was chosen to avoid potential complications from pH adjustments (i.e. addition of CO_3^{2-} and/or OH^- altering cation association of CrO_4^{2-} at higher pH levels).

As is evident from Fig. 7, the XANES spectra of the solid residue of all four BFD samples investigated (A, B, C and D)

indicated that the Cr present in the samples is dominated by Cr(VI) species. The spectra display a strong similarity to the spectrum of Na_2CrO_4 , which is a water-soluble Cr(VI) species. This does not necessarily imply that Na_2CrO_4 was the sole source of Cr(VI) in the leachate precipitates of the BFD samples. Due to the low Cr concentrations, EXAFS spectra were not optimal and the results should therefore be regarded as qualitative, rather than quantitative. These results also did not permit modelling of the local coordination environment of the Cr(VI) species. Notwithstanding the afore-mentioned limitations, the presence of Cr(VI) in all BFD leachate precipitates is unequivocal; additionally, the Cr(VI) species were similar to Na_2CrO_4 .

CONCLUSIONS

The results presented in this paper indicate that the currently applied Cr(VI) treatment strategies of FeCr producer (with process water $\text{pH} \leq 9$) only effectively extract and treat the water-soluble Cr(VI) compounds from the BFD, which represent approximately 31% of the total Cr(VI) present in the BFD samples evaluated. Extended extraction times of 4 consecutive 24 h extractions, proved futile in extracting sparingly water-soluble and water-insoluble Cr(VI) species within the afore-mentioned pH range, as confirmed with XAFS.

Considering the above-mentioned, it is critical that improved Cr(VI) treatment strategies be formulated that would extract all of the Cr(VI) from BFDs. The results presented in this paper suggest that extraction at pH 13 would be required to solubilise the sparingly water-soluble Cr(VI) species from BFD. This will ensure that sparingly water-soluble Cr(VI) compounds do not leach from the waste storage facilities (e.g. slimes dams). Otherwise, there is the potential of Cr(VI) releases over time, which has been proven to result in environmental Cr(VI) pollution (Loock-Hatting, 2016; Loock-Hatting et al., 2015; Loock et al., 2014). However, it is highly unlikely that such a high process-water pH would be economically feasible. Additionally, it is well known from literature that Fe(II), currently the most commonly employed chemical reductant of Cr(VI), oxidizes very quickly with dissolved oxygen at such high pH levels. Therefore, the effectiveness of this and other potential reductants at elevated pH levels needs to be investigated. Furthermore, the need to extract the water-insoluble Cr(VI) species prior to chemical reduction should be investigated in greater detail, in order to assess the likelihood of such species being mobilised over extended time periods relevant to waste disposal facilities.

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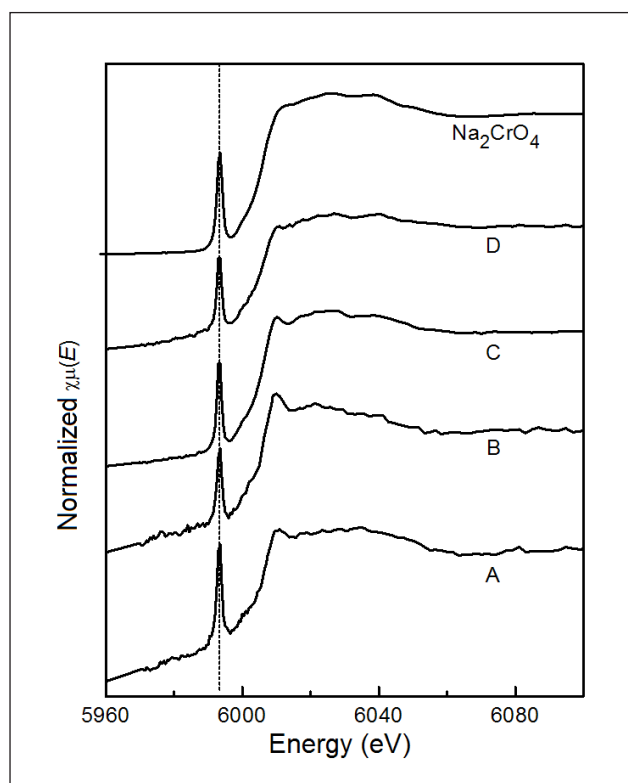


Figure 7

Normalized Cr K-edge XANES spectra of the solid residue extracted from BFD samples. The pre-edge peak characteristic of the Cr(VI) species is marked by the vertical dotted line at 5993 eV.

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