



# A review on the characteristics, formation mechanisms and treatment processes of Cr (VI)-containing pyrometallurgical wastes

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## Synopsis

Pyrometallurgical wastes, such as stainless steel plant dust, ferrochrome plant dust and filter cake from the waste acid treatment facility of the stainless steel pickling plant, contain Cr (VI) that can leach into the groundwater when stockpiled or land filled. These wastes are considered to be hazardous materials and therefore need to be treated. Recycling, recovery and solidification/stabilization processes can be used to treat these wastes.

The characteristics and the formation mechanisms of electric furnace dusts and filter cake are summarized in this paper. It also reviews the present treatment processes of these wastes, and highlights the stabilization/solidification processes for the treatment of Cr(VI)-containing pyrometallurgical dusts.

Keywords: Cr(VI); pyrometallurgical wastes; dust; filter cake; stainless steel; ferrochrome; waste management; stabilization.

## Introduction

Cr(VI)-containing wastes are associated with the metallurgical, refractory, chemical, electroplating, leather tanning, pigment, welding and glass industries<sup>1</sup>. The presence of Cr(VI) in these wastes causes great concern due to the fact that Cr(VI) is a carcinogen (specifically to the lungs and in some cases to the sinonasal cavity<sup>2</sup>), is highly soluble in water, and has a high mobility in soil. Cr(VI)-containing wastes can, consequently, not simply be stockpiled or land filled, but must first be treated. In the pyrometallurgical industry Cr(VI)-containing wastes in the form of dust and sludge are produced in ferrochrome and stainless steel plants. The dust generated by ferrochrome plants typically consists of coarse dust, which is collected by the cyclone separators, and fine dust that is captured by the bag house filters. Dust that forms during the production of stainless steel is collected by a bag house filter system, while a sludge or filter cake is produced in the pickling acid treatment facility of the stainless steel plant. These dusts, as well as the waste pickling acid, have respectively been classified as hazardous wastes K061, K091 and K062 by the US Environmental Protection Agency (EPA).

In South Africa, the treatment policy of these wastes is guided by the minimum requirements for the handling, classification and disposal of hazardous waste that was published by the Department of Water Affairs and Forestry (DWAFF) in 1998<sup>3</sup>. Of all the leachable heavy metals, Cr (VI) has the strictest limits with an acceptable environmental risk concentration of 0.02 ppm<sup>3</sup>. The limits that were set by different countries on Cr (VI) species for different water sources are shown in Table I 4-6. It shows that the limits for Cr (VI) range between 0.005 and 0.1 mg/l for different kinds of water, while the total chromium limits vary from 0.0031 to 2 mg/l.

Various techniques are used in the management of Cr(VI)-containing wastes. These include the minimization of waste through source reduction (i.e. waste prevention), recycling (onsite and offsite), recovery and stabilization/solidification processes whereby the wastes are transformed into non-toxic materials, which can either be disposed or reused.

In order to understand the properties of these wastes, minimize waste formation and develop a process to treat it, numerous authors have investigated the characteristics and formation mechanisms of these wastes<sup>7-21</sup>. This paper subsequently reviews the characteristics and formation mechanisms of Cr(VI)-containing electric furnace dust and filter cake, as well as their present treatment processes. The stabilization/solidification processes of the wastes are highlighted.

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Table I

The regulation limits of Cr species for different water sources specified by different countries<sup>4-6</sup>

Country	Type of water	Concentration, mg/l	
		Cr (VI)	Cr (Tot)
France	General water	0.1	0.5
Germany	Drinking water	-	0.05
	Metal/chemical industry	0.1	0.5
Japan	Drinking water	0.05	-
	Public water systems	0.5	2
Kazakhstan	Drinking water	-	0.0031
	Liquid effluent emissions	0.005-0.03	-
South Africa	Effluent discharge	-	0.5
	Drinking water	0.05 <sup>5)</sup>	0.1
USA	Drinking water	0.1 <sup>6)</sup>	0.1
UK	Drinking water	-	0.05

- : Value not reported

Table II

Typical elemental compositions in the stainless steel plant dust and FeCr dusts (wt.%)<sup>5,22-49</sup>

Element	Stainless steel plant dust	FeCr coarse dust	FeCr fine dust
Cr	0.28~16.5 (69)	13.14~17.11 (0.4)*	1.92~7.4 (21)
Si	0.09~4.51	9.15~13.86	16.45~34.2 (298.5)
Al	0.16~0.81	5.61~6.64	1.06~5.62
Ca	0.83~14.78 (716)	0.71~1.72	0.14~0.57 (65.6)
Zn	0.04~12.76 (311)	0.59~0.64 (0.1)	1.37~12.13 (65.3~1109)
Fe	14.77~53.50 (0.3)	5.37~10.58	0.61~3.01 (1.0)
Mn	0.30~7.65	0.11~0.18 (0.2)	0.23~0.58(12~17)
Mg	0.042~10.2 (452)	4.14~7.16	1.01~13.92 (434)
Mo	0.18~1.30 (8)	-	0.008 (12)
Pb	0.03~1.9 (0.06)	0.007~0.009 (0.3)	0.06~0.123 (0.01~0.03)
Ni	0.045~5.42	0.062~0.079	0.0053~0.1
S	0.19~1.65	0.28~0.76	0.96~3.4
Cl	0.5~5.20	0.89	0.95~3.32
Na	<0.07~4.91 (320)	1.32~1.89	1.71~5.94 (2848~22400)
K	0.08~2.99 (650)	0.84~0.91	1.0~7.58 (632~1919)
Ti	0.03~0.21	0.31~0.4	0.03~0.12
P	0.02~0.82	0.013~0.044	0.013~0.044
C	0.0~1.3	9.97~15.5	1.1~1.58
Cu	0.11~0.65	0.024	0.008~0.018
F	0.012~0.016	0.01	0.04~0.9
Ga	-	0.015	0.026~0.39

\*: Values in brackets are the elemental concentrations in ppm in the TCLP leachate

## The characteristics of electric furnace dusts and filter cake

The treatment policy of waste is closely associated with the characteristics of the wastes. It is therefore important to know the physical and chemical properties of the wastes before a treatment method is developed or chosen.

### Electric furnace dust

#### Macrostructure

Stainless steel dust is typically chocolate-brown in colour, and emits foul gases (presumably acetylene)<sup>22,23</sup>. It consists of very fine and agglomerated metal and oxide particles in the form of hollow and solid spheres, as well as metal and oxide particles that are coated with a slag layer<sup>22-27</sup>.

The ferrochrome fine dust is grey, while the coarse dust appears black in colour. The fine dust mostly consists of agglomerated particles that are constituted of oxide, metallic and carbon-based phases, while the coarse dust mainly consists of oxide and carbon-based particles that are irregular in shape<sup>22,26</sup>.

#### Chemical and phase chemical compositions

The typical compositional ranges and crystalline phases that are present in the stainless steel plant dust, ferrochrome coarse dust and ferrochrome fine dust are shown in Tables II and III.

The chemical compositions of, and crystalline phases present in the dusts vary considerably, depending on the steel grade produced, raw materials used, operational parameters, furnace type and heats. Compared to carbon steel

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Table III

Typical crystalline phases present in the stainless steel plant dust and FeCr dusts<sup>5,22-49</sup>

Element*	Stainless steel dust	FeCr coarse dust	FeCr fine dust
Cr	FeCr <sub>2</sub> O <sub>4</sub> , chromium oxide (CrO), (Mg, Fe, Mn, Cr) <sub>3</sub> O <sub>4</sub> and MgCr <sub>2</sub> O <sub>4</sub>	Chromite (Fe, Mg)(Al, Fe, Cr) <sub>2</sub> O <sub>4</sub>	Chromite and FeCr metal
Cr (VI)	-	-	CrO <sub>3</sub> , (K, Na) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> or (K, Na) <sub>2</sub> CrO <sub>4</sub>
Si	Quartz (SiO <sub>2</sub> ), indialite (Mg <sub>2</sub> Al <sub>4</sub> Si <sub>5</sub> O <sub>18</sub> ), mullite (3Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> ), SiC and fayalite (Fe <sub>2</sub> SiO <sub>4</sub> )	Quartz and anorthite (Ca, Na)(Si, Al) <sub>2</sub> O <sub>8</sub>	Quartz, forsterite (Mg <sub>2</sub> SiO <sub>4</sub> ) Fe, Mn, Cr) <sub>3</sub> O <sub>4</sub> and MgCr <sub>2</sub> O <sub>4</sub> aluminium silicate (Mg <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub> and Al <sub>2</sub> SiO <sub>5</sub> )
Al	Alumina (Al <sub>2</sub> O <sub>3</sub> ), indialite, mullite or substitute for spinel	Chromite and anorthite	Chromite
Ca	Lime (CaO), fluorite (CaF <sub>2</sub> ) and CaCO <sub>3</sub> , Ca(OH) <sub>2</sub>	Dolomite (Ca, Mg)(CO <sub>3</sub> ) <sub>2</sub> and anorthite	-
Zn	Zincite (ZnO), zinc ferrite (ZnFe <sub>2</sub> O <sub>4</sub> ), zinc metal, ZnCl <sub>2</sub> and ZnCl <sub>2</sub> ·4Zn(OH) <sub>2</sub>	-	ZnO, NaZn <sub>4</sub> (SO <sub>4</sub> )Cl(OH) <sub>6</sub> ·6H <sub>2</sub> O and Zn <sub>4</sub> SO <sub>4</sub> (OH) <sub>6</sub> ·5H <sub>2</sub> O
Mn	Jacobite (MnFe <sub>2</sub> O <sub>4</sub> ) and (Mg, Fe, Mn, Cr) <sub>3</sub> O <sub>4</sub>	-	-
Fe	Magnetite (Fe <sub>3</sub> O <sub>4</sub> ), zinc ferrite, jacobite, fayalite, chromite, hematite (Fe <sub>2</sub> O <sub>3</sub> ), (Mg, Fe, Mn, Cr) <sub>3</sub> O <sub>4</sub> and iron	Chromite and hematite	Chromite and FeCr metal
Mg	Indialite, MgCr <sub>2</sub> O <sub>4</sub> , (Mg, Fe, Mn, Cr) <sub>3</sub> O <sub>4</sub> and MgO	Dolomite and chromite	Chromite, forsterite, MgO and aluminium silicate (Mg <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub> )
Pb	PbO, PbCl <sub>2</sub> and PbSO <sub>4</sub>	-	-
Ni	Bunsenite (NiO) and Ni metal	-	-
S	Sulphates	-	NaZn <sub>4</sub> (SO <sub>4</sub> )Cl(OH) <sub>6</sub> ·6H <sub>2</sub> O and Zn <sub>4</sub> SO <sub>4</sub> (OH) <sub>6</sub> ·5H <sub>2</sub> O
Cl	KCl, NaCl, ZnCl <sub>2</sub> and ZnCl <sub>2</sub> ·4Zn(OH) <sub>2</sub>	-	Halite and NaZn <sub>4</sub> (SO <sub>4</sub> )Cl(OH) <sub>6</sub> ·6H <sub>2</sub> O
Na	NaCl	-	Halite and NaZn <sub>4</sub> (SO <sub>4</sub> )Cl(OH) <sub>6</sub> ·6H <sub>2</sub> O
K	KCl	-	-
C	Graphite, SiC and CaCO <sub>3</sub>	Coal, coke and charcoal	Coal, coke and charcoal
F	Fluorite	-	-

\* The elements such as Cr, Si, Al, Ca, Fe, Mn, Mg, Na, K and Ti can also exist in the glassy slag phase that is present in the dusts

plant dust, stainless steel plant dust has a low zinc concentration, but is enriched in metallic components since high alloy scrap is used in the production of stainless steel<sup>24,25</sup>. Stainless steel dust consists mainly of oxide phases that are rich in Fe, Cr, Ca, Zn, Mg, Mn and Ni, with minor amounts of phases that contain alkaline metals (K, Na), halogens (Cl, F), Si, Mo, Pb and S<sup>22-42</sup>. Chromium and iron oxides (CrO and Fe<sub>2</sub>O<sub>3</sub>) as well as spinel phases (such as FeCr<sub>2</sub>O<sub>4</sub>, (Mg, Fe, Mn, Cr)<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>, MnFe<sub>2</sub>O<sub>4</sub> and ZnFe<sub>2</sub>O<sub>4</sub>), and some raw materials (CaO, CaF<sub>2</sub> and CaCO<sub>3</sub>) are the major crystalline phases present in the stainless steel plant dusts. Minor phases include pure metallic particles (iron, zinc and nickel), oxide phases (NiO, MgO, PbO, SiO<sub>2</sub> and ZnO), halogens (PbCl<sub>2</sub>, ZnCl<sub>2</sub>, KCl and NaCl), SiC, fayalite (Fe<sub>2</sub>SiO<sub>4</sub>), sulphates and hydrates (ZnCl<sub>2</sub>·4Zn(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>) (Table III)<sup>22-27,29-42</sup>.

The ferrochrome coarse dust is also oxide based and contains high levels of Cr, Si, Fe, Al, Mg and C, while the oxide-based ferrochrome fine dust is enriched in Si, Zn, Na, K, Mg, S and Cl, with lower concentrations of Cr, Fe and C than in the coarse dust<sup>5,9,22,43-49</sup>. The coarse dust mostly consists of chromite ore, carbon, silica and anorthite ((Ca, Na)(Si, Al)<sub>2</sub>O<sub>8</sub>), while the fine dust is mainly associated with vaporized substances such as silica, NaCl, ZnO and Mg<sub>2</sub>SiO<sub>4</sub><sup>22,26</sup>. Small amounts of hydrates are also found in ferrochrome fine dust, i.e., NaZn<sub>4</sub>(SO<sub>4</sub>)Cl(OH)<sub>6</sub>·6H<sub>2</sub>O and Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>·5H<sub>2</sub>O<sup>22</sup>.

The leachable Cr (VI) concentrations in both the stainless steel and ferrochrome fine dusts are reported to exceed the

regulation limits of 0.05ppm for Cr(VI) in drinking water in South Africa. It is reported that between 6 and 13 ppm Cr(VI) leaches from the stainless steel dust<sup>28,42</sup>, and between 75 and 175 ppm<sup>5,28</sup> from ferrochrome bag house dust.

#### Physical properties

The particle size distribution of the dust particles ranges from sub-micron to more than 200 μm<sup>9,22,47,50</sup>. The d<sub>50</sub> values range from 0.7 to 21.5 μm for the stainless steel dust, between 0.7 and 13.2 μm for the ferrochrome fine dust, and are approximately 80 μm for the ferrochrome coarse dust (Table IV). The electric furnace dusts are therefore very fine, and can easily be airborne.

The bulk densities of the electric furnace dusts range from 0.49 to 2.53 g/cm<sup>3</sup>, while the true densities of the stainless steel dust range from 3.01 to 5.22 g/cm<sup>3</sup><sup>22,51</sup>. The specific surface areas of the dust are high (4.09–13.2 m<sup>2</sup>/g)<sup>22,51</sup>. This implies that many voids exist inside the dusts, and that they would require big storage and transportation volumes.

The electric furnace dusts have low moisture contents (0.19–1.06 wt%) and generate basic solutions (pH: 8–12.4) when leached in water<sup>22,51</sup>. The soluble fraction, due to the presence of salts in the dusts, is 6.7 wt% for the stainless steel dust and between 3.34 and 11.86 wt% for the ferrochrome dusts<sup>22,51</sup>. This means that stockpiling or land filling of the dusts without prior treatment can induce the basification of soil and groundwater.

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Table IV

Physical properties of electric furnace dusts<sup>5,22-41</sup>

	Stainless steel dust	FeCr fine dust (coarse dust)
Particle size, d <sub>50</sub> , (µm)	0.7~21.52	0.71~13.23 (79.76)
Moisture (wt%)	0.19~0.62	0.93~1.06 (0.48)
Specific surface area (m <sup>2</sup> /g)	4.09~5.73	5.31~13.2
Bulk density (g/cm <sup>3</sup> )	0.90~2.53	0.49~0.93
Density (g/cm <sup>3</sup> )	3.01~5.22	-
Water soluble fraction (wt%)	6.7	3.34~11.86
pH	11.96~12.4	8.08~8.48 (11.18)

## Filter cake from the waste acid treatment plant

The filter cake from the waste pickling acid treatment plant consists of very fine particles with 90% of particles smaller than 12 µm, and a d<sub>50</sub> of approximately 3.7 µm<sup>51-53</sup>. It mainly contains calcium, fluorine and iron, which amount to approximately 49–64 wt% of the filter cake, while nickel, chromium and sulphur are present in lower concentrations<sup>22,52</sup>. When the filter cake is heated to 1000°C, a mass loss of between 10 to 15 wt% is obtained due to the dehydration of the metal hydroxides<sup>22,52,53</sup>.

High proportions of amorphous phases that are rich in Cr, Fe and Ni are found<sup>22,52</sup>, while calcium fluoride (CaF<sub>2</sub>), calcium sulphate (CaSO<sub>4</sub>), Cr<sub>2</sub>O<sub>3</sub> and FeCr<sub>2</sub>O<sub>4</sub> are present as crystalline phases<sup>22,52-56</sup>. It is reported that between 15 and 43 ppm Cr(VI) leaches from the filter cake<sup>28</sup>.

## Formation mechanisms

Reducing the formation of Cr(VI)-containing waste and deciding on either a recycling procedure or stabilization method requires an understanding of the formation mechanisms of the wastes.

### Stainless steel plant dust

The formation of stainless steel plant dust proceeds through<sup>7-21</sup>:

- ▶ The vaporization of elements or compounds from the high temperature zones, i.e. arc zone, oxygen blowing zone and the reaction zone during decarburization. Zinc, lead and cadmium as well as alkaline metals and oxides can vaporize from these areas in the furnace. Metal oxides such as ZnO subsequently form through the oxidation of these vaporized species in the off-gas duct<sup>13</sup>
- ▶ The ejection of slag and metal by CO gas bubbles that burst during decarburization and the force of the arc. CO gas bubbles that form in the decarburization reaction enter the slag layer with a thin steel film. Dust particles can form through fragmentation of this bubble film cap, whereby small film droplets form. The remaining crater could close up and form jet droplets. Huber *et al.* concluded that the formation of film droplets is the major dust formation mechanism, while the jet droplets are in general larger in size and therefore mostly drop down to the bath<sup>7</sup>.
- ▶ The direct capturing of charged fines of quartz, lime, fluorite, calcite, nickel metal and graphite in the off-gas during the course of charging. Ca(OH)<sub>2</sub> forms in the off-gas duct due to the hydration of lime.

Different authors reported that the respective formation mechanisms contribute to different extents to dust formation: Huber *et al.* reported that approximately 60 wt% of the total dust consists of ejected metal and slag droplets, while volatiles in the dust contribute about 27 wt%<sup>7</sup>. Dalhaes *et al.* however, showed that about 3 wt% of the total dust formed through vaporization in the AOD converter, while the ejection of metal and slag by the bursting of gas bubbles is the main dust forming mechanism (about 91 wt% of the total dust)<sup>8</sup>. Ohno *et al.* found that dust formation is mostly due to the bursting of gas bubbles<sup>9</sup>. There is therefore general agreement, however, that the ejection of slag and metal by the bursting of gas bubbles is the major mechanism of dust formation in the steelmaking plant.

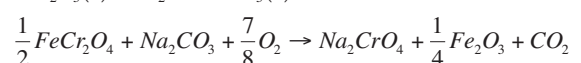
## Ferrochrome plant

Dust formation mechanisms in semi-closed submerged arc furnaces (SAFs) can be divided into four categories<sup>28</sup>:

- ▶ Vaporization of elements or compounds from high temperature zones in the SAF, e.g. halite (NaCl), cristobalite (SiO<sub>2</sub>), periclase (MgO) and ZnO are the oxidation products of oxide species that are fumed through reduction reactions with carbon or carbon monoxide
- ▶ Ejection of slag and metal through the holes of the electrodes
- ▶ Charge materials such as fine carbon-bearing particles, quartz and chromite particles that are captured in the off-gas
- ▶ Phases and reaction products that form in the off-gas duct from species in the off-gas. These include anorthite ((Ca,Na)(Si,Al)O<sub>8</sub>), aluminium silicates (Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> and Al<sub>2</sub>SiO<sub>5</sub>), forsterite (Mg<sub>2</sub>SiO<sub>4</sub>), NaZn<sub>4</sub>(SO<sub>4</sub>)Cl(OH)<sub>6</sub>·6H<sub>2</sub>O and Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>·5H<sub>2</sub>O<sup>28</sup>.

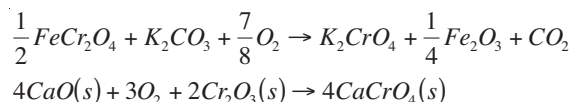
## The formation of Cr (VI) in electric furnace dust

XPS analysis of ferrochrome dust indicated that chromium in oxidation states 3+ and 6+ are present on the surface of the dust<sup>22,44</sup>. Since conditions in the SAF are reducing, with a typical oxygen partial pressure of less than 10<sup>-8</sup> atm<sup>26</sup>, it can be assumed that Cr (VI) is generated from Cr (III) when the dust is removed from the furnace to the cyclone separators and the baghouse filters, as the oxygen partial pressure increases. Beukes reported that chromium (III)-containing particulate substances can be oxidized into Cr (VI) by flare in the off-gas duct<sup>57</sup>. Thermodynamic calculations confirm that dry Cr(III) precipitates can be converted into Cr(VI) when heated in the presence of oxygen<sup>58</sup>. It is also reported that increased lime contents are conducive to the formation of Cr (VI) species<sup>51,57,59</sup>, and that Cr (VI) formation is interrelated with the alkali metal oxides in the charge<sup>5</sup>. It can therefore be assumed that Cr(VI) in the dust forms either by oxidization or through both oxidation and reaction with CaO or alkali oxides according to the following reactions:





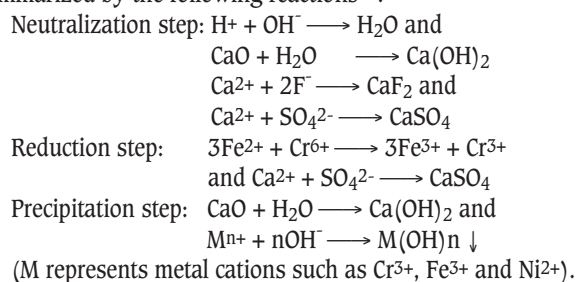
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### The formation of filter cake in the waste acid treatment plant

The scale of hot rolled or annealed stainless steel strip predominantly contains  $Fe_xO$  ( $x=0.67, 0.75$  and  $1$ ),  $Cr_2O_3$ ,  $NiO$ ,  $SiO_2$ ,  $NiCr_2O_4$  and  $FeCr_2O_4$ <sup>56</sup>. The surface quality of stainless steel is improved through either acid pickling, fused salt bath conditioning followed by acid pickling, or acid pickling following electrolytic neutral pickling<sup>60</sup>. The acid pickling following electrolytic neutral pickling process is displacing the two former conventional processes due to the good condition of the pickled strip surface, the lower operation and maintenance cost, and the simplicity of the process<sup>60</sup>. The typical electrolytic neutral pickling solution is sodium sulphate, while the pickling acids are nitric, hydrofluoric, sulphuric and hydrochloric acids<sup>60,61</sup>. After the pickling process waste acid which is highly acidic with a typical pH of 1, and which contains high concentrations of fluorine, iron, nickel and chromium, remain<sup>46</sup>. The Cr(VI) concentration in solution is influenced by the potential of the solution, pH and reductants in the solution<sup>62-64</sup>.

The standard treatment process for this waste pickling acid includes three steps, namely the neutralization of the waste acid through the addition of lime, the reduction process of Cr(VI) with ferrous sulphate and the precipitation of metallic species with lime. The last step of the process involves the collection of the precipitate, whereby filter cake is produced and a leachate which has a pH of approximately 10<sup>22,46</sup>. The formation of the filter cake can therefore be summarized by the following reactions<sup>28</sup>:



### Treatment processes of electric furnace dust and filter cake

Increasing costs of waste disposal and stricter environmental regulations imply that attention should first be given to the minimization of dust, then to the possibility of recycling or partial recycling after segregation, and only then should metal recovery or stabilization of the remaining waste materials be considered.

A number of issues influence the choice of treatment method of the Cr(VI)-containing electric furnace dust and filter cake: (a) The composition of the dust varies considerably due to changes in heats, raw materials, grade and operational parameters which require all-purpose technologies; (b) Volatile substances in the dusts can affect the normal operation of the furnace if they are simply charged back to the furnace; (c) Leachates from the electric

furnace dusts are highly basic, and therefore require large volumes of acid in order to adjust the pH<sup>65</sup>; (d) The filter cake cannot be recycled back to the steelmaking plant due to its high fluorite and sulphate contents.

Because the coarse ferrochrome dust contains low concentrations of volatile substances (Zn, S and alkali metals), but also usable carbon, quartz and chromite particles (which amount to approximately 48–71 wt%), it can be recycled back to the SAF.

Zinc is the valuable element that can potentially be recycled from the ferrochrome fine dust. The concentration of the zinc is, however, too low to be economically recycled. Pyrometallurgical recovery methods will, however, be hampered by the high concentrations of Na, K, S, F and Cl-containing compounds, which will vaporize together with the zinc (Table II)<sup>5,28,45-47</sup>. Hydrometallurgical recovery methods would conversely generate a secondary waste that contains Cr(VI) and soluble salts. The amount of fine dust that forms during the production of ferrochrome can therefore be controlled by controlling the quality of the raw materials, especially the volatile components in the coal, coke and charcoal.

### Minimization of dust formation

In order to minimize dust formation, it is suggested that violent carbon boils should be limited<sup>15</sup>, the size of the bursting bubbles be reduced by controlling the decarburization reaction (and therefore controlling the ratio of chemical to electrical energy in the EAF)<sup>7,11</sup>, the position of the oxygen lance, blowing time<sup>20</sup> and intensity of blowing should be optimized<sup>19</sup>, a slag layer that covers the metal bath should be formed early on in the heat<sup>8</sup> (a foamy slag practice would therefore be beneficial as well as slags of higher viscosities<sup>15</sup>), slopping should be limited, and friable additives and fluxes should be bottom injected<sup>7-11</sup>.

### Recycling

Methods can be developed to recycle dust back to the melting furnace by minerals processing methods (gravity separation and magnetic separation) due to the different densities and magnetic properties of the particles. However, toxic substances such as Cr(VI) can leach out during the minerals processing and hydrometallurgical operations, which implies that the wastewater of these processes would require further treatment.

Direct recycling of electric furnace dust back to the blast furnace and electric furnace typically use agglomeration or pneumatic injection technologies<sup>66-70</sup>. In the pneumatic injection technologies the dust is either injected on its own, or together with coal or coke in order to foam the slag<sup>66-70</sup>. In the process the zinc content of the resultant electric furnace dust is increased by up to more than 30 wt%, and then needs to be recovered<sup>67</sup>. The disadvantage of recycling the dust back to the blast furnace is that if the dust contains high concentrations of vaporized species such as zinc, cadmium, lead and alkaline metals (Na and K), these species would circulate in the blast furnace and induce blockages. In the case of EAF operation it might increase the energy consumption and affect the refractory materials. However, it has been proven that recycling of EAF dust through direct injection of briquettes or micro-pellets, is economically viable

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in Armco melt shops. In a trial at one of the local ferrochrome plants, pelletized ferrochrome bag house dust was charged back to the SAF<sup>46</sup>. However, it induced blockages and led to an enrichment of chemicals in the off-gas as well as corrosion of the off-gas duct due to the high temperatures employed. It is therefore clear that dust that contains significant concentrations of volatile components is not suitable to be recycled directly back to the SAF. The volatile content should first be reduced (e.g. by washing with water), before the remaining dust is charged back to the furnace.

## Recovery

Recovery processes include both hydrometallurgical<sup>44,65,71-86</sup> and pyrometallurgical methods<sup>87-109</sup>. In the hydrometallurgical recovery processes leach solutions such as caustic soda, sulphuric acid, mononitritotriacetate anion (NTA<sup>3-</sup>) and hexahydrated ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O), hydrochloride, acetic acid as well as NH<sup>3</sup>·(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solutions are used, depending on the variation of the chemical compositions and crystalline phases present in the electric furnace dust<sup>43,44,71-86</sup>. Microwave and ultrasound wave technology can be used to improve the reaction rates in these processes<sup>65,73</sup>. The major product of these recovery processes is zinc metal. However, the main problem associated with these processes is the detoxification of the leach residues<sup>84</sup>.

In the pyrometallurgical treatment processes, electric furnace dust is refined or reduced by either a gaseous (methane, hydrogen) or solid (coke, coal, waste carbon products, iron powder) reductant to produce a crude Zn, Cd, Pb, Cr and Ni bearing ferroalloy at high temperatures<sup>87-109</sup>. Power is supplied by either plasma arc, electricity, solar or microwave energy. The disadvantages of these pyrometallurgical methods are the high energy consumptions and investment costs, as well as the molten slag and off-gas that are generated as secondary waste, which need to be treated further.

## Stabilization/solidification processes

Treatment methods for the stabilization of Cr(VI) have been and are developed for wastes that are currently been generated, but also for the remediation of polluted sites. In stabilization/solidification processes the hazardous wastes can either be chemically transformed into a non-toxic form or additives can bond with the waste, whereby the mobility of the heavy metals are reduced and value added to the waste<sup>110,123</sup>. Typical stabilization/solidification treatment processes include cementation and vitrification or glassification processes<sup>110-122</sup>. Cementation is commonly used in waste treatment as it is inexpensive, and can incorporate wet wastes<sup>124</sup>. Vitrification, on the other hand, is an attractive option as it is associated with large volume reductions<sup>125</sup>.

Clay, lime, Ordinary Portland Cement (OPC) and other generated wastes (such as coal fly ash, blast furnace slag and ferrochrome slag) have been reported to stabilize and solidify heavy metals in the electric furnace dust and filter cake, with different degrees of success<sup>110-120</sup>. The resultant waste mixture is a non-toxic material, which has structural integrity and can be land-filled, or can be used as a raw material for other industries (e.g. fertilizer, glass and pigment industries).

The stabilization/solidification processes are, from an environmental and economic viewpoint, the most promising methods to treat electric furnace dusts and filter cake.

## Cementation processes

Cements are intrinsically porous, with associated pore water. The porosity and permeability of the stabilized/solidified waste therefore play major roles in its performance in the environment.

Bethlehem Steel Corporation developed the Super Detox process, which was marketed by EnviroSource and has been commercialized since 1989<sup>111-112</sup>. In this process, the electric furnace dust, lime, aluminasilicates and other additives are well mixed into a concrete-like material. The heavy metals in the dusts are either precipitated or oxidized/reduced into their least soluble components and thereafter immobilized in the aluminasilicate matrix. The process therefore relies on complex pozzolanic chemistry to change the metal components into their least soluble form. Both wet and dry electric furnace dusts can be treated, and the stabilized dust can then be disposed of as a non-hazardous waste.

Another commercial solidification process successfully treats carbon steel and alloy steel electric furnace dust as well as waste pickling acid at Atlas Steel<sup>113-114</sup>. It uses spent pickling acid, slag and lime to treat electric furnace dust. The treatment process includes (a) the acidification of waste with iron and silicon containing materials (slag) and (b) the addition of lime to adjust the pH in order to solidify the metal silicates. Laboratory, pilot and industrial scale tests show that the leachable concentrations of lead, cadmium and chromium (VI) from this precipitate are below the limits of the Ontario drinking water standard and the US EPA. It is an economical and safe way to treat electric furnace dust and spent pickling acid.

The advantages of these processes are the minimization of transportation costs since the stabilization/solidification is done on-site, secondary emissions to the environment are minimal, and capital costs are low.

Stabilization/solidification of chromium(VI), using OPC, ground granulated blast furnace slag, ferrochrome slag and fly ash has also been investigated, but with different degrees of success. Giesecke *et al.* have studied the production of cement blocks from ferrochrome dust and electric arc furnace slag with different ratios of OPC<sup>49</sup>. The results showed that approximately 95% of the Cr (VI) and 30-55% of the salts (Na, K, SO<sub>4</sub> and Cl) were stabilized. The addition of FeCl<sub>2</sub> and electric arc furnace slag to the mixture improved the stabilization ratio of Cr (VI), although the Cr (VI) concentration in the leachate was still higher than the regulation limits of 0.05 mg/l set for drinking water in South Africa<sup>5</sup>. Cohen and Petrie also examined the possibility of stabilizing ferrochromium dust with OPC<sup>47,126</sup>. They found that for effective setting of the cement-waste product, the dust need to be washed first, whereby soluble chromium, Zn, Mg, K and Na were removed. Improved retention was achieved through longer curing times and increased cement contents. Cr(III) precipitated in the alkaline pore solution as the insoluble hydroxide or was incorporated into the hydration products of the cement. Approximately 1% of the total chromium remained soluble as Cr(VI) in the pore solution.

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## *Vitrification or glassification processes*

The Inorganic Recycling Corporation (IRC) developed a process that can completely transform EAF dusts into commercial products<sup>115,116</sup>. This process includes three parts, i.e., mixing, vitrification and off-gas treatment. The electric furnace dusts are first mixed with I/R chemicals and silicates such as silica sand, clay and cullet. The mixture is then melted in the vitrification furnace at 816–1371°C, poured into a mould or quenched into particulate materials. Particulate material in the off-gas is fed back to the mixer. The products, which are environmentally friendly, can be used in architectural applications or as abrasives. The waste water is also recycled back to the mixing step, thereby creating a zero-waste process. The cost of the process was reported to be between \$110 and \$135/ton of dust in 1993<sup>116</sup>.

The glassification process that was developed by Glassification International use pyrometallurgical wastes such as electric furnace dust, slag, spent refractory and mill scale, to produce a non-hazardous product<sup>117</sup>. In this process the waste and glass-forming materials are blended and melted at approximately 1371°C. Vaporized species are condensed and charged back to the furnace in order to prevent air pollution. The glassy product can be either quenched into granules or cast into different kinds of products such as tiles and sheets for architectural purposes. The cost to glassify was reported in 1993 to be approximately US\$80 per ton of glass produced from 12 000 tons of dust<sup>117</sup>. The unit cost of the process depends on the production capacity and the type of the final product produced.

## *Stabilization/solidification using clay and other by-products*

The stabilization of Cr (VI) in stainless steel plant dust by clay has also been investigated<sup>51,118</sup>. Bricks were prepared by mixing different ratios of dust to clay, followed by drying at 110°C and sintering between 1000 and 1200°C for different time periods. Cr (VI) in the stainless steel dust was effectively stabilized when a 5:5 ratio of clay to stainless steel dust was used at a sintering temperature of 1200°C. The amount of Cr (VI) that leached from the sintered brick decreased with an increase in sintering time and sintering temperature, while it increased with decreasing clay:dust ratio.

Peng *et al.* also used clay as additive to vitrify stainless steel flue dust in order to stabilize the heavy metals<sup>51</sup>. The softening temperature of the mixture decreased to 1200°C when a 1:1 mass ratio of clay to dust was used. TCLP tests on the vitrification product indicated that the concentration of heavy metals in the leachate is lower than the US EPA limits. TG/DTA and FT-IR analysis showed that the vitrification product is very stable, with only a 0.3% weight loss when heated to 1000°C.

Gericke reported that heavy metals in ferrochrome dust can be immobilized through mixing 20% of ferrochrome dust with 80% of clay or 50% clay with 30% ferrochrome dust and 20% ferrochrome slag<sup>48</sup>. TCLP tests indicated that Cr (VI) concentrations in the leachate are less than 0.03 ppm.

Maine *et al.* also used 50% of clay and 50% ferrochrome baghouse filter dust, and sintered it at 1200°C to stabilize the

Cr (VI) and salts in the ferrochrome dusts<sup>5</sup>. The results showed that more than 99% of Cr (VI) and 90% of salt in the ferrochrome dusts were stabilized. The Cr (VI) concentration in the leachate was also decreased with an increase in sinter temperature.

## *Long-term stability of the stabilized Cr (VI)*

A prescribed test method for the evaluation of the leachability of Cr(VI) from stabilized waste does not exist. Three main types of leaching tests are used to evaluate stabilized/solidified wastes namely batch or agitated extraction tests, diffusion or flow-around tests and column leach or flow-through tests<sup>127</sup>. Of all the available leaching tests, the TCLP (toxicity characteristic leaching procedure) test, which is a batch test, is the most commonly used to test stabilization/solidification products. The TCLP test has, however, come under criticism as it is considered to create a 'worst case scenario' for leaching, where the test material is subjected to consistent acid attack<sup>126</sup>. Other criticisms include that the acetic acid used contributes to breakdown of the test sample<sup>126</sup> and that certain cement-based stabilization products have high acid neutralizing capacity to neutralize the acidity of the leachant<sup>128,129</sup>. Neutralization of the acidity of the leachant implies that the leaching of heavy metals will be low, and the assessment of the leaching potential of the waste unrealistic. The TCLP test also does not address the leachability of toxic elements over time, nor their leaching kinetics.

Other batch tests that have been used to evaluate stabilized ferrochrome dust, stainless steel dust and pickling filter cake include the German DIN 38414 (1984) procedure<sup>49</sup>, the acid rain test<sup>49</sup>, the ASTM D 3987-85 test<sup>28,51</sup>, static distilled water and nitric acid tests<sup>28,51</sup>, EE (equilibrium extraction) test<sup>126</sup>, the SCE (sequential chemical extraction) test<sup>126</sup>, pore solution expressions<sup>126</sup> and a semi-dynamic leach test in which the leachant is replaced periodically after intervals of static leaching<sup>51</sup> (Table V). It was reported that errors associated with the SCE and pore solution expressions are too high to draw any quantitative conclusions about the stabilization of cement-stabilized ferrochrome dust<sup>126</sup>.

The main criticism of batch tests is their inability to predict the behaviour of the stabilized waste under field conditions in the long term<sup>127,130</sup>. Variables such as pH, redox potential, buffering capacity, complexation capacity, ionic strength, dielectric constant, reaction kinetics, particle size, temperature and surface area influence leachate generation<sup>131</sup>. According to Van der Sloot, leaching trends are established through laboratory tests, but factors such as life-time, temperature, pH, redox potential, geometry, water to solid contact frequency and surface reactions need to be taken into account when translating laboratory test data to field conditions<sup>130</sup>. Site-specific conditions should therefore be taken into account when selecting the appropriate leaching test.

## **Conclusions**

Very little has been published on Cr(VI) in stainless steel and ferrochrome dust, as well as the filter cake that forms during the treatment of waste pickling acid. What is known



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Table V

## Summary of the leaching tests that have been used to evaluate stabilized stainless steel dust, ferrochrome dust and pickling filter cake

Name of test	Leachant	Liquid: solid ratio	Method of mixing	Duration	Other
TCLP <sup>28,51,126</sup>	Buffered acetic acid (solution 1: pH=4.93; solution 2: pH=2.88)	1:20	Rotated head-overheels at 30rpm	20 hours	
DIN 38414 <sup>49</sup>	De-ionized water.	1:10	Shaken	24 and 48 hours	
Acid rain test <sup>49</sup>	Water, carbonated to a pH=3.95	1:20	Rotated head-overheels at 30 rpm	24 hours	
ASTM D 3987-85 <sup>28,51</sup>	Distilled water	1:20	Agitated	18 hours at 23°C	
Static distilled water/nitric acid tests <sup>28,51</sup>	Distilled water / nitric acid,	1:20	Static	2 hours at 25±1°C	
EE <sup>126</sup>	Distilled water	1:4	Agitated	7 days	Sample crushed to -149 µm
SCE <sup>126</sup>	Five consecutive extraction steps: (a) 0.25M CsCl <sub>2</sub> + 0.75M LiCl in 60% CH <sub>3</sub> OH (b) 1M CH <sub>3</sub> COONa adjusted to pH5 with CH <sub>3</sub> COOH (c) 1M NH <sub>2</sub> OH.HCl in 25% CH <sub>3</sub> COOH (d) 0.02M HNO <sub>3</sub> in 30% H <sub>2</sub> O <sub>2</sub> ; 1.2M CH <sub>3</sub> COONH <sub>4</sub> in 20% HNO <sub>3</sub> (e) acid digest		Agitated		
Pore solution extraction <sup>126</sup>	100g crushed sample is placed in a confined chamber and pressure exerted until liquid is extruded from the stabilized product				
Semi-dynamic leach test <sup>51,132</sup>	Distilled water	Ratio of surface area of cylindrical specimen to volume of leachate  1:10 cm <sup>-1</sup>	Static	Distilled water, replaced at designated intervals according to $t_n = n^2 t_1$ ( $n$ = leaching period, $t_1$ =end of the first leaching period, $t_n$ =end of the nth leaching period)	

however, is that these waste materials contain high levels of Cr(VI), which are both toxic and carcinogenic. Since unacceptable high levels of Cr(VI) can leach from these wastes into the groundwater, they first need to be treated before being stockpiled or land filled.

The electric furnace dusts and filter cake are very fine particles that contain valuable elements such as Fe, Cr and Ni. The stainless steel dust is formed by the vaporization of elements or compounds at the high temperature zones, by the direct capturing of charge fines by the off-gas and by ejection of slag and metal through the bursting of gas bubbles. Vaporization, ejection of slag and metal droplets via the electrode holes, direct capturing of charge materials and reaction products in the off-gas duct are the dust forming mechanisms in ferrochrome production. Filter cake is formed through the precipitation of metal hydroxides and super-saturated salts, and also contains remnants of stainless steel scale.

These wastes can either be minimized at source by optimizing the operational parameters or be detoxified by the proper treatment methods. Solidification/stabilization processes are effective ways to treat these pyrometallurgical wastes. The electric furnace dusts can be cemented, glassified and sintered into value-added products with other pyrometallurgical wastes. The advantages of the solidification/stabilization process include low investment costs, operational simplicity and the minimization of secondary waste residues.

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