Chapter 1 Introduction

1.1 Background

Stainless steel is typically smelted in an electric arc furnace (EAF) from scrap, molten or lump ferrochrome and slag formers (lime, fluorspar and dolomite), after which it is refined in an argon oxygen decarburisation (AOD) or Creusot-Loire Uddeholm (CLU) converter. Ferrochrome however, is produced by the carbothermic reduction of chromite ore in a submerged-arc furnace (SAF) or direct current furnace (DC).

The emissions from these pyrometallurgical plants, which consist of NO_x, CO_x, SO_x, organic compounds and particulate dust, pose a potential threat to human health and the environment. The particulate furnace dust contains valuable components (e.g. chromium, zinc and iron) as well as significant toxic substances [e.g. chromium (VI), lead], which can leach into the groundwater when stockpiled or land filled. Of these toxic substances, chromium (VI) is both toxic and carcinogenic and exceeds the regulation thresholds in many countries [1]. According to Cox et al. [2], about 20% of the total chromium in the ferrochrome dust is present as Cr (VI), which is leachable. The US Environmental Protection Agency (US EPA) has classified the electric arc furnace dust as hazardous material (K061) as it exceeds the Toxicity Characteristics Leaching Procedure (TCLP) test limits for Pb, Cd and Cr [3]. Typically, approximately 18 to 25kg of dust or slurry per ton of ferrochrome produced is collected by the abatement systems in ferrochromium plants, and approximately 18 to 33 kg bag house filter dust is generated per ton of stainless steel produced [4-8].

Filter cake, which is the precipitate after the treatment of waste pickling acid (classified as K062 by the US EPA) in stainless steel plants, also contains significant Cr (VI) species and inorganic salts [9]. It is also potentially harmful to the environment.

Currently, there are two possible methods by which this electric furnace dust and filter cake can be managed: Landfilling or stockpiling in the waste site is the simplest and easiest method. However, this could lead to the contamination of the soil and

groundwater by toxic substances. The maximum acceptable concentrations of chromium species, zinc and lead in the leachate from these wastes, as specified by different countries, are listed in Table 1.1 [10-15]. It shows that the limits and test methods vary from country to country. However, the Cr (VI) species has the lowest limits (0.02~1.5mg/l) and is considered to be the most harmful species in the dust due to its high solubility in water and carcinogenic properties. These wastes therefore cannot be disposed without prior treatment. Thus, the existence and treatment of wastes from stainless steel and ferrochrome production remain a challenge and an issue of concern. The increase of environmental legislation globally and the trend towards sustainable development are drives for alternatives to landfill.

Table 1.1 The maximum acceptable concentrations of Cr species, Zn and Pb in leachate from the wastes specified by different countries [10-15]

Country	Leachate	Regulation limits (mg/l)				References
		Cr (III)	**Cr (VI)**	**Zn**	**Pb**	
Spain	DIN[a] leachate	4	0.5	20	0.5	10
Germany	Leachate	-	0.5	-	-	11
Japan	Leachate	-	1.5(0.5[b])	-	-	
Italy	TCLP leachate	2[c]	0.2	2	0.2	12,13
USA	TCLP leachate	5[c]	-	10	5	11,14
South Africa	ARL[d]	4.7	0.02	0.7	0.1	15

[a]Deutsches Institut fűr Normung;   [b]The maximum concentration for ocean disposal;
[c]Cr total;   [d]Acceptable risk levels.

Various alternative methods have been developed to manage these wastes. Figure 1.1 shows the waste minimisation techniques that can be used to manage the Cr (VI)-containing pyrometallurgical wastes. It shows that waste can be minimised through source reduction (i.e. waste prevention) as well as recycling (on site and off site). The choice of input materials, products, and technology changes, as well as good operational practices can also efficiently reduce the generation of wastes. Recovery is another method whereby the problem of wastes can be minimised. In South Africa, the

ferrochromium industry produces approximately 68,000 t bag house filter dust and 28 000 t slurry, while the stainless steel industry produces 24 000 t of dust annually [5,16,17]. A very strong need therefore exists to investigate the problem comprehensively and develop an appropriate treatment process.
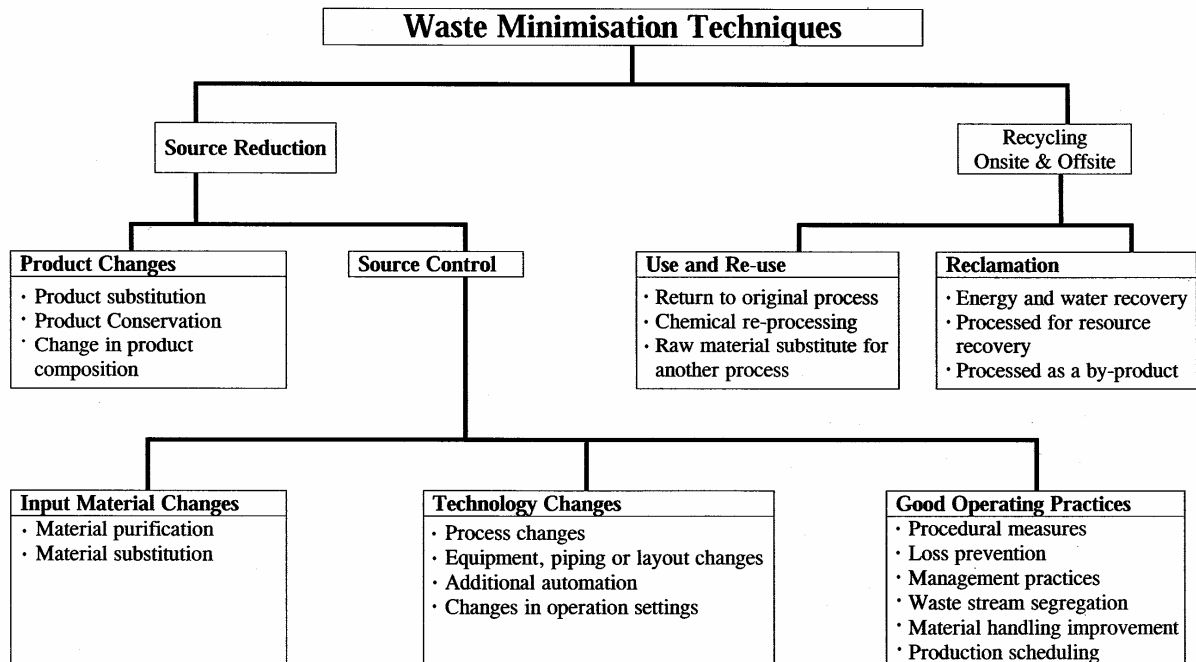

Figure 1.1 Various waste minimisation techniques that can be used to manage the Cr (VI)-containing pyrometallurgical wastes [15]

1.2 Objectives of this project

The aim of this project was to minimise the generation of the Cr (VI)-containing electric furnace dust and filter cake and develop an appropriate method to treat these wastes. This was done by studying the -

➢ characteristics of the wastes,

➢ formation mechanisms of the wastes,

➢ leachability of the wastes,

➢ aging behaviour of Cr (VI)-containing electric furnace dust and filter cake,

➢ stabilisation of Cr (VI) by silica-rich clay, and

➢ leaching mechanisms of chromium species from the stabilised wastes.

1.3 Structure of the thesis

The dissertation starts with a review chapter (Chapter 2) in which previous work on electric furnace dust and waste pickling acid are discussed. It reviews the characteristics, formation mechanisms and treatment processes of Cr (VI)-containing pyrometallurgical wastes (stainless steel plant dust, ferrochrome dust and filter cake).

Chapter 3 focuses on the investigation of the characteristics of the electric furnace dust and filter cake samples collected from a South African stainless steel plant and ferrochrome plant. The particle size distribution, bulk density, moisture content, pH, chemical composition and phase composition of the wastes were studied. TG/DTA analysis, Raman spectrometry and X-ray photoelectron spectrometry (XPS) were also used to further understand the basic properties of these wastes.

The microstructures and formation mechanisms of the wastes are presented in Chapter 4. In this Chapter, the formation mechanisms of these wastes are postulated from the observed microstructures and the production processes of stainless steel, high-carbon ferrochromium and filter cake. Chapter 5 describes the leachability of the wastes based on the TCLP test, ASTM D 3987-85 test and static leaching test results. Chapter 6 deals with the aging behaviour of Cr (VI)-containing stainless steel plant dust and filter cake. Chapters 7 and 8 investigate the stabilisation of Cr (VI) by silica-rich clay, using synthetic and electric furnace dust and filter cake samples. The leaching mechanisms of the chromium species from the wastes that were stabilised with clay were also studied using a semi-dynamic test, and are presented in Chapter 9. Finally, a summary of the results are given and conclusions are drawn in Chapter 10. Recommendations for future work are also made in Chapter 10.

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Chapter 2 The characteristics, formation mechanisms and treatment processes of Cr (VI)-containing pyrometallurgical wastes: a review

Chapter 2 The characteristics, formation mechanisms and treatment processes of Cr (VI)-containing pyrometallurgical wastes: a review

2.1 Introduction

Cr(VI)-containing wastes are produced by stainless steel and ferrochrome plants. These wastes include dust, sludge and waste acid from stainless steel pickling plants. Stainless steel plant dust contains significant levels of valuable elements such as chromium, nickel and iron [4], while the electric furnace 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. The ferrochrome coarse dust mostly consists of chromite ore, silica particles, carbon-bearing particles and ejected slag particles. The ferrochrome fine dust is however mainly associated with vaporised substances such as zinc oxide [9].

The stainless steel waste pickling acid, which contains Cr (VI), iron and nickel salts and waste nitric and hydrofluoric acid, is treated by either recycling or precipitation. The waste acid recycling processes include the diffusion dialysis separation process [18], the distillation-crystallisation process [19], the solvent extraction process [19] and the ion exchange process [20]. In the precipitation process lime is typically used to precipitate the metal ions as metal hydroxides under alkaline conditions, whereby a filter cake is formed. All these pyrometallurgical wastes contain leachable Cr(VI) salts and other toxic substances, which can potentially pollute the ground water and soil when stockpiled or land filled [9].

The potential leachability of the toxic substances from these wastes into the ground water is often evaluated by the Toxic Characteristics Leaching Procedure (TCLP) test that was developed by the US Environmental Protection Agency (US EPA) [21]. 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 (DWAF) in 1998 [15]. Of all the leachable

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toxic substances, Cr (VI) has the strictest limits with an acceptable environmental risk concentration of 0.02 ppm [15]. The limits that were set by different countries on Cr (VI) species for different water sources are shown in Table 2.1 [13,17,22]. It shows that the limits for Cr (VI) are 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.

Table 2.1 The regulation limits of Cr species for different water sources specified by different countries [13,17,22]

Country	Type of water	Concentration, mg/l	
		Cr (VI)	Cr (Tot)
France	General water	0.1	0.5
Germany	Drinking water	nr*	0.05
	Metal/chemical industry	0.1	0.5
Japan	Drinking water	0.05	nr
	Public water systems	0.5	2
Kazakhstan	Drinking water	nr	0.0031
	Liquid effluent emissions	0.005-0.03	nr
South Africa	Effluent discharge	nr	0.5
	Drinking water	0.05 [17]	0.1
USA	Drinking water	0.1 [22]	0.1
UK	Drinking water	nr	0.05

*nr: not reported

In order to understand the properties of the wastes, minimise waste formation and develop an appropriate process to treat them, the characteristics and formation mechanisms of the wastes have been investigated by numerous researchers [23-37]. Over the past decades, different treatment processes have also been developed to treat these wastes. This chapter subsequently reviews the properties and formation mechanisms of Cr(VI)-containing pyrometallurgical wastes. The present treatment processes of the wastes are also summarised and the solidification/stabilisation processes of the wastes are highlighted.

2.2 The characterisation of electric furnace dust and filter cake

The treatment policy of wastes 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.
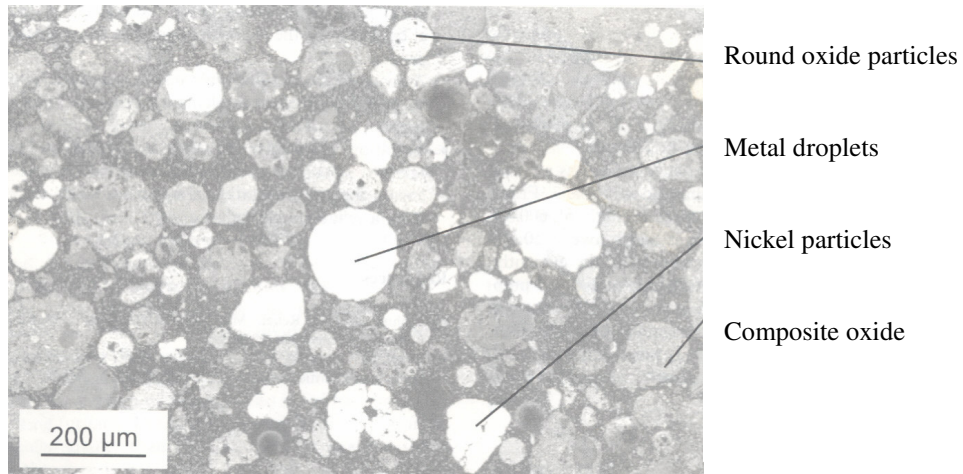
2.2.1 Electric furnace dust

2.2.1.1 Macro and microstructure

The stainless steel dust is typically chocolate-brown in colour, and emits foul gases (possibly acetylene) [38], especially when coming in contact with water. The high carbon ferrochrome fine dust however, is grey, while the coarse dust appears black in colour due to the significant levels of chromite ore particles and carbon-bearing materials [9].
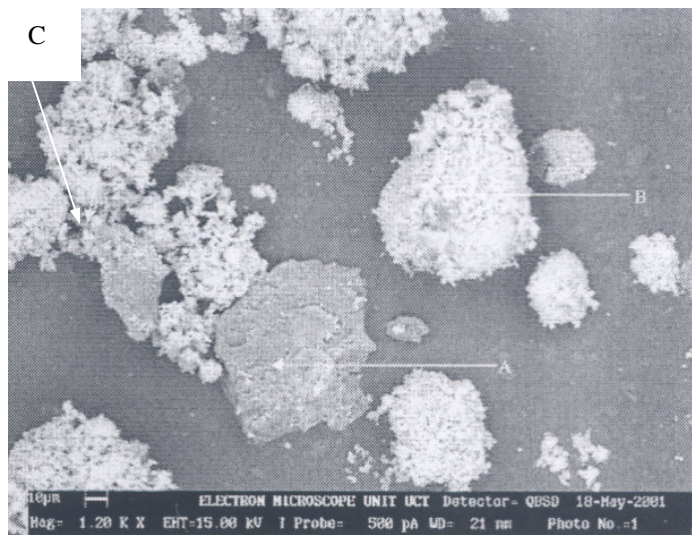
The micrographs of electric furnace dust from a South African stainless steel plant and ferrochrome plant are shown in Figure 2.1 [39,40]. The electric furnace dust includes metal and oxide particles that are present in either spherical or angular shape [4,38,39,41,42]. The stainless steel plant dust contains very small spherical particles, slag spheres, metal particles that are coated with a slag layer, as well as oxide particles that contain dendritic crystals [4,38,39,41]. The ferrochrome bag house filter dust is very fine and is constituted of agglomerated particles. It consists of chromite ore, char particles (phase A in Figure 2.1), ferrochrome particles (phase C in Figure 2.1) and particles with significant levels of Mg, Si, Cr and Zn (phase B in Figure 2.1) [2,40].

2.2.1.2 Physical properties

The particle size distribution of the stainless steel plant dust ranges from sub-micron to 200μm [41]. The mean particle diameters (d_{50}) range from 0.7 to 21.52 μm for the stainless steel dust, and between 0.71 and 13.23 μm for the ferrochrome bag house filter dust (Table 2.2). The electric furnace dust has low moisture contents (0.19-0.63 wt%) and high specific surface areas (4.09-13.2 m^2/g).

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Round oxide particles

Metal droplets

Nickel particles

Composite oxide

200 µm

(a)

(b)

Figure 2.1 Micrographs of electric furnace dust from a South African stainless steel plant (a) [39] and ferrochrome plant (b) [40]

The bulk densities of the stainless steel dust range from 0.90 to 2.53 g/cm^3, while the true densities of the dust range from 3.01 to 5.22 g/cm^3. This implies that many voids exist inside the dusts, and that they would require big storage and transportation volumes.

The stainless steel dust generates a basic solution with a pH of about 12 when leached in water [12,38,43]. It is believed that this is due to the presence of the lime in the dust. The

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Table 2.2 Physical properties of electric furnace dust [2,4,6,9,12,14,17,38-51]

	Stainless steel dust	Ferrochrome dust
Particle size, d_{50}, (μm)	0.7-21.52	0.71-13.23
Moisture (wt%)	0.19-0.62	nr*
Specific surface area (m^2/g)	4.09-5.73	5.31-13.2
Bulk density (g/cm^3)	0.90-2.53	nr
Density (g/cm^3)	3.01-5.22	nr
Water soluble fraction (wt%)	6.7	3.34-11.86
pH	11.96-12.4	nr

*nr: not reported

soluble fraction, due to the presence of salts in the dust, is 6.7 wt% for the stainless steel dust, whereas for the ferrochrome dust it ranges between 3.34 and 11.86 wt% [17,42].

2.2.1.3 Chemical composition and phases

Compared to carbon steel 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 [4,39]. The chemical composition of and crystalline phases present in the dust vary considerably, depending on the steel grade produced, raw materials used, operational parameters, furnace type and heats. Due to the same reasons, the compositions of ferrochrome dust as well as the crystalline phases present in them vary. 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 Table 2.3. It shows that stainless steel dust consists mainly of oxide phases that are rich in Ca, Cr, Fe, Ni, Mn, Zn and Mg, with minor amounts of Si, Al, Mo, Pb, Ti, Cu, P, S, alkaline metals (K, Na) and halogens (Cl, F) [2,4,6,9,14,17,38-53]. The ferrochrome coarse dust from the cyclone separators is also oxide-based and contains significant levels of Si (9.15-13.86wt.%), Al (5.61-6.62wt.%), Cr (13.14-17.11wt.%), Fe (5.37-10.58wt.%), Mg (4.14-5.4wt.%) and C (9.97-15.5wt.%), while the oxide-based ferrochrome fine dust

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from the baghouse filter is relatively high in Si, Zn, Na, K, Mg, Cl and S, but lower in Cr, Fe and C concentrations [9,16,17,54-58]. Chromium and iron oxides (CrO and Fe_2O_3) as well as spinel phases, such as $FeCr_2O_4$, Fe_3O_4, $MnFe_2O_4$ and $ZnFe_2O_4$, and their solid solutions are the major crystalline phases present in the stainless steel plant dust, while the minor phases are pure metallic particles (iron, zinc and nickel), oxide phases (NiO, MgO, PbO, SiO_2 and ZnO), halogens ($PbCl_2$, $ZnCl_2$, KCl and NaCl), indialite ($Mg_2Al_4Si_5O_{18}$), mullite ($3Al_2O_3 \cdot 2SiO_2$), SiC, fayalite (Fe_2SiO_4), sulphates, hydrates ($ZnCl_2 \cdot 4Zn(OH)_2$, $Ca(OH)_2$) and some raw material particles (CaO, CaF_2 and $CaCO_3$) [4,6,14,38-53].

No data, to the author's knowledge, have been published on the phase compositions of ferrochrome dust. The characterisation of ferrochrome dust was therefore an important part of this study because it is essential to know the phase compositions before a method can be developed to treat it.

The Cr (VI) concentrations (0.035-0.6wt%) in the stainless steel plant dust and ferrochrome fine dusts are enough to be harmful to human health and the environment (Table 2.3). Cox et al. reported that Cr (VI) exists in the form of $Cr_2O_7^{2-}$ or CrO_4^{2-} on the surface of ferrochrome dust particles, and indicated that more than 75% of the Cr (VI) originates from particles that are less than 10μm in diameter [2]. These particles constitute approximately 28 % of the dust by mass.

The concentrations of sodium, potassium and zinc are extremely high in the TCLP leachate of the ferrochrome dusts (Na 2848-22400 mg/l, K 632-1919 mg/l, Zn 65.3-1109mg/l) [9,17,55,56]. This further increases the treatment difficulties of these wastes [58]. Since the sulphur content in the ferrochrome dust ranges from 0.28 to 3.4wt% [9], it would not be viable to recycle it directly to the furnace due to the harmful impact, which it would have on the quality of the metal products.

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Table 2.3 Typical elemental compositions and crystalline phases present in the stainless steel plant dust and ferrochrome dust [2,4,6,9,14,17,38-58]

Element [a]	Composition range of element, wt.%			Phases that contain the element
	Stainless steel dust	FeCr coarse dust	FeCr fine dust	Stainless steel dust
Cr	0.28-16.5 (69)	13.14-17.11 (0.4) [b]	1.92-7.4 (21)	Chromite ($FeCr_2O_4$), chromium oxide (CrO), $(Mg,Fe,Mn,Cr)_3O_4$ spinel and $MgCr_2O_4$
Cr (VI)	0.14-0.6	0.0005-0.0017	0.035-0.122	-
Si	0.09-4.51	9.15-13.86	16.45-34.2 (298.5)	Quartz $(SiO_2)^d$, indialite ($Mg_2Al_4Si_5O_{18}$), Mullite ($3Al_2O_3 \cdot 2SiO_2$), SiC and fayalite (Fe_2SiO_4)
Al	0.16-0.81	5.61-6.64	1.06-5.62	Alumina (Al_2O_3), indialite ($Mg_2Al_4Si_5O_{18}$), Mullite ($3Al_2O_3 \cdot 2SiO_2$) or substitute for spinel phase
Ca	0.83-14.78 (716)	0.71-1.72	0.14-0.57(65.6)	Lime (CaO), fluorite (CaF_2) and $CaCO_3$, $Ca(OH)_2$
Zn	0.04-12.76 (311)	0.59-0.64 (0.1)	1.37-12.13 (65.3-1109)	Zincite (ZnO), zinc ferrite ($ZnFe_2O_4$), zinc metal, $ZnCl_2$ and $ZnCl_2 \cdot 4Zn(OH)_2$
Fe	14.77-53.50 (0.3)	5.37-10.58	0.61-3.01 (1.0)	Magnetite (Fe_3O_4), zinc ferrite ($ZnFe_2O_4$), jacobite ($MnFe_2O_4$), fayalite (Fe_2SiO_4), chromite ($FeCr_2O_4$) hematite (Fe_2O_3), $(Mg,Fe,Mn,Cr)_3O_4$ spinel and iron
Mn	0.30-7.65	0.11-0.18 (0.2)	0.23-0.58(12-17)	Jacobite ($MnFe_2O_4$) and $(Mg,Fe,Mn,Cr)_3O_4$ spinel
Mg	0.042-10.2 (452)	4.14-7.16	1.01-13.92 (434)	Indialite ($Mg_2Al_4Si_5O_{18}$), $MgCr_2O_4$, $(Mg,Fe,Mn,Cr)_3O_4$ spinel and periclase (MgO)
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)	Lead oxide (PbO), lead chloride ($PbCl_2$) and lead sulphate ($PbSO_4$)
Ni	0.045-5.42	0.062-0.079	0.0053-0.1	Bunsenite (NiO) and nickel metal
S	0.19-1.65	0.28-0.76	0.96-3.4	Sulfates
Cl	0.5-5.20	0.89	0.95-3.32	Potassium chloride (KCl), sodium chloride (NaCl) and $ZnCl_2$ and $ZnCl_2 \cdot 4Zn(OH)_2$
Na	<0.07-4.91 (320)	1.32-1.89	1.71-5.94 (2848-22400)	Sodium chloride (NaCl)
K	0.08-2.99 (650)	0.84-0.91	1.0-7.58 (632-1919)	Potassium chloride (KCl)
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	Graphite, SiC and $CaCO_3$
Cu	0.11-0.65	0.024	0.008-0.018	-
F	0.012-0.016	0.01	0.04-0.9	Fluorite (CaF_2)
Ga	-	0.015	0.026-0.39	-

Note: [a] :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 dust.

[b] :Values in brackets are the elemental concentrations in ppm in the TCLP leachate.

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2.2.2 Filter cake from the waste pickling acid treatment plant

In order to improve the surface quality of stainless steel three different methods are used, namely acid pickling, fused salt bath conditioning followed by the acid pickling and acid pickling following electrolytic neutral pickling [59]. The acid pickling following electrolytic neutral pickling is displacing the two former conventional processes due to the good condition of the pickled strip surface, the lower operation and maintenance cost [59]. The typical electrolytic neutral pickling solution is sodium sulphate, while the pickling acids are nitric, hydrofluoric, sulphuric and hydrochloric acids [20,59]. The waste pickling acids are acidic with a typical pH of 1 and contain significant concentrations of fluorine, iron, nickel and chromium [9]. The typical composition range of the spent HNO_3/HF pickling acid is shown in Table 2.4 [19]. The standard treatment process for the waste pickling acid includes three steps, i.e. the neutralisation 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 is the collection of the precipitate, whereby the filter cake is produced [9].

Table 2.4 The typical compositions of the stainless steel pickling acid wastes [19]

Acids or elements	Composition range, kg/m^3
HNO_3	100-200
HF	10-80
Fe	30-70
Ni	3-10
Cr	3-12
Mo	0-0.5

The original filter cake is constituted of very fine particles with a d_{50} of approximately 3.7 um [60]. It mainly contains calcium, fluorine and iron which amount to approximately 49 wt% to 64 wt% of the filter cake [60]. The remainder are nickel (approximately 1-3 wt%), chromium (approximately 2-3 %), sulphur (approximately 3 wt%) and oxygen [60]. After being heated up to 1000^oC, the total weight loss of the filter cake is between 10 to 15 wt% due to the dehydration of the metal hydroxides [60].

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The X-ray diffraction analysis shows that the filter cake contains high proportions of amorphous phases that include metal ions such as Cr, Fe and Ni [60]. It also contains the crystalline phases calcium fluoride (CaF_2) [60,61] and calcium sulphate ($CaSO_4$) [61], and stainless steel scale which include the phases Cr_2O_3 and $FeCr_2O_4$ [62]. The high fluorite and sulphate contents in the filter cake seem to restrict the reuse of the filter cake in the steelmaking plant. It is therefore suggested that the wastes from the pickling bath and the neolyte tank should be treated separately [63].

2.3 Formation mechanisms of electric furnace dust and filter cake

2.3.1 Dust formation in the stainless steel plant

The formation of stainless steel plant dust includes in general two steps, i.e., emission of dust from the electric arc furnace or converter, followed by escape from the furnace to the bag house filters. In the first step, the dust is carried off by the off-gas, whereas the chemical and physical transformation of the particulate matter, such as chemical reactions between gaseous, liquid and solid phases and the agglomeration of fine particles, occur during the second step [23].

The formation mechanisms of dust in the electric arc furnace are shown schematically in Figure 2.2 [23-37]. The following mechanisms contribute to dust formation in electric arc furnaces:

1) Vaporisation of the elements or compounds from the high temperature zones, i.e. arc zone (1), oxygen blowing zone (1') and the reaction zone of decarburisation. Zinc, lead and cadmium as well as alkaline metals and oxides can vaporise in these areas in the furnace. Metal oxides phases such as ZnO are then the oxidation products in the off-gas duct [29].

2) Ejection of slag and metal, by CO gas bubble bursting due to decarburisation (3), oxygen blowing (2'), the force of the arc (2) and the ejection of the bursting droplets (4) when the burst metal droplets (3) decarburise in contact with the oxidised atmosphere.
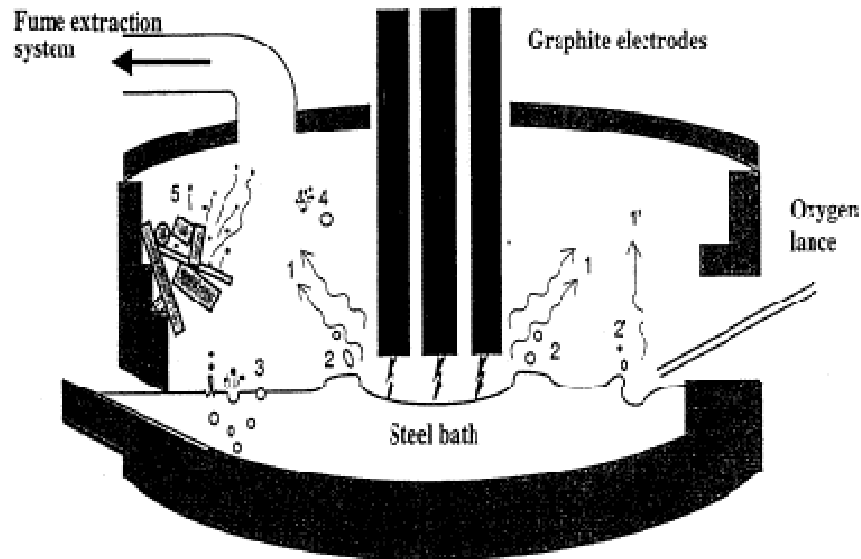
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Figure 2.2 Formation mechanisms of dust in the EAF [23]

The formation mechanisms of fine droplets due to bubble bursting in the melt bath is shown in Figure 2.3. The CO gas bubbles formed by the decarburisation reaction enter the slag layer with a thin steel film (a). The dust droplets can form through fragmentation of the bubble film cap, whereby small film droplets form (b and c). The remaining crater would close up and form jet droplets (d, e, f and g). However, these droplets do not have enough kinetic energy to carry them out of the furnace and are often captured by the off-gas [64]. Huber et al. concluded that the formation of film droplets is the major dust formation mechanism, while the jet droplets are larger in size and therefore drop down to the bath [23].

3) Direct capturing of charged fines such as lime, quartz and ferroalloy particles (5, Figure 2.2) by the off-gas. Quartz, lime, fluorite, calcite, nickel metal and graphite in the dust are directly captured by the off-gas during the course of charging. $Ca(OH)_2$ forms in the off-gas duct due to the hydration of lime.
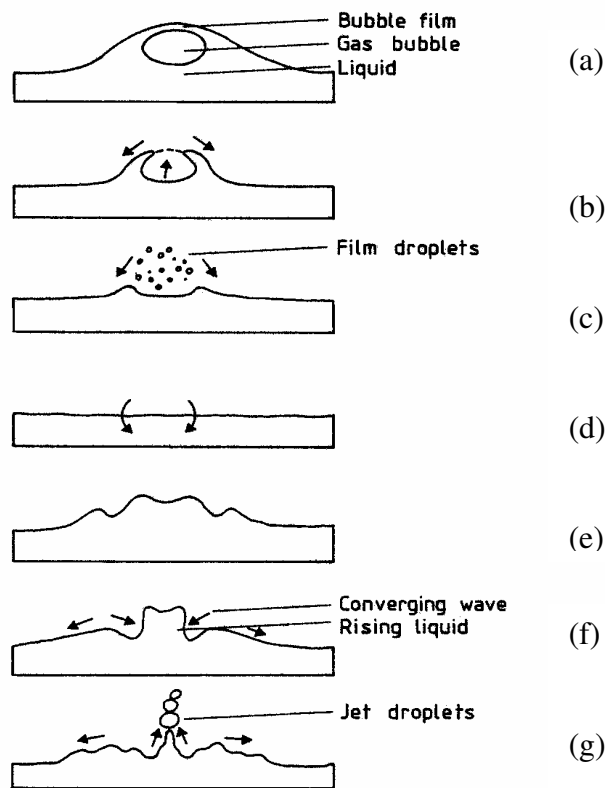
Figure 2.3 Formation mechanisms of fine droplets due to bubble bursting [24]

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 are metal and slag droplets, while volatiles in the dust contribute about 27 wt% [23]. It is also found that dust emission is closely associated with the emission of CO gas [23].   Dalhaes et al. however showed that about 3 wt% of the total dust formed through vaporisation 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) [24]. Ohno et al. found that most of the dust is less that 5 μm in diameter and caused by the bursting of gas bubbles [25]. There is general agreement however that the ejection of slag and metal by gas bubble bursting is the major mechanism of dust formation in the steelmaking plant.

In order to minimise dust formation, it is suggested that:

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a. The size of the bubbles is reduced by controlling the decarburisation reaction in the EAF [23];

b. Operational issues such as the foamy slag practice, the pre-heating of the scrap, slopping, the position of the oxygen lance and the bottom injection of additives or fluxes should be optimised [23-27];

c. The energy input (electrical and chemical) should be optimised [23,27].

2.3.2 Dust formation in the ferrochrome plant

Ferrochrome dust formation mechanisms in submerged arc furnaces (SAFs) has not been reported in the literature. It is suggested that the vaporisation of elements or compounds from high temperature zones of the SAF and the charge materials that are directly captured in the off-gas could be involved in dust formation [40]. Carbon-bearing particles, quartz and chromite particles that are angular in shape present in the dust presumably originated from charge fines that were entrained in the off-gas.

The reported leachable Cr(VI) concentration of ferrochrome bag house dust range between 0.035 and 0.122 ppm [17,55,56]. Beukes reported that chromium (III)-containing particulate substances can be oxidised into Cr (VI) by flare in the off-gas duct [65]. Maine et al. also assumed that Cr (VI) formation is interrelated with the alkali metals in the charge [17]. Moreover, lower temperatures and higher lime contents are conducive to the formation of Cr (VI) species [65]. The presence of alkaline bearing materials therefore impacts strongly on Cr (VI) formation, and should be reduced in the charge [65].

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

The scale of the 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 $FeCr_2O_4$ [66]. The formation mechanisms of the filter cake vary according to the treatment process. For the traditional three step treatment process, the filter cake contains amorphous phases which consist of metal ions such as Cr, Fe, Ca and Ni, crystalline phases such as calcium fluoride (CaF_2) [60,61], calcium sulphate ($CaSO_4$) [61], Cr_2O_3 and spinel phase ($FeCr_2O_4$) [62]. Based on

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an analysis of the production process, the amorphous phases are mixtures of the metal hydroxides that precipitated from the alkaline solution. CaF_2 and $CaSO_4$ however might precipitate due to their low solubilities (solubility limits of 0.016g/l and 2.09g/l respectively [67]). Cr_2O_3 and the spinel phases (e.g. $FeCr_2O_4$) are associated with stainless steel scale that remained after pickling.

2.4 Treatment processes of electric furnace dust and filter cake

A number of problems currently hamper the treatment of Cr(VI)-containing electric furnace dust and filter cake: (a) The variation in composition of the dusts (as shown in Table 2.3) due to changes in heats, raw materials, grade and operational parameters which require that the technology can treat all kinds of dusts; (b) Volatile substances in the dusts can impact on the normal operation of the furnace if it is 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 [68]; (d) the high sulphur content in the filter cake makes it difficult to recycle back to the steelmaking plant [63]. (e) Cr (VI) is highly soluble, and has very low regulation limits. As an alternative to land filling or stockpiling, different methods have been developed to deal with these wastes:

1) Minimisation of the wastes at source by optimising the operational parameters;
2) Direct recycling of the dust back to the electric furnace by injection with air [69-73];
3) Recovery processes, which include hydrometallurgical methods [68,74-89] and pyrometallurgical methods [90-112];
4) Solidification/stabilisation methods, for instance, cementation and vitrification or glassification processes [3,5,113-123]; and
5) Use as a raw material for fertiliser, glass and pigment plants [124,125].

2.4.1 Recycling

Direct recycling of electric furnace dust back to the blast furnace and electric furnace typically use agglomeration or pneumatic injection technologies [69-73]. In the pneumatic injection technologies the dust is either injected on its own, or together with

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coal or coke [69-73]. Figure 2.4 shows the typical direct injection process. The dust is pelletised and screened, and then injected into the furnace. The powder mixture of dust and/or carbon is used to foam the slag, but in the process the zinc content of the resultant electric furnace dust is increased by up to more than 30 wt%, which then needs to be recovered [70]. The disadvantage of recycling back to the blast furnace is that if the dust contains significant concentrations of vaporised species such as zinc, cadmium, lead and alkaline metals (Na and K), these species circulate in the blast furnace and induce blockages [86]. For EAF operation, it would increase the energy consumption. In a trial at one of the local ferrochrome plants, pelletised ferrochrome bag house dust was charged back to the SAF [9]. However, it induced blockages and corrosion of the off-gas duct due to the high temperatures employed and enrichment of chemicals in the off-gas.
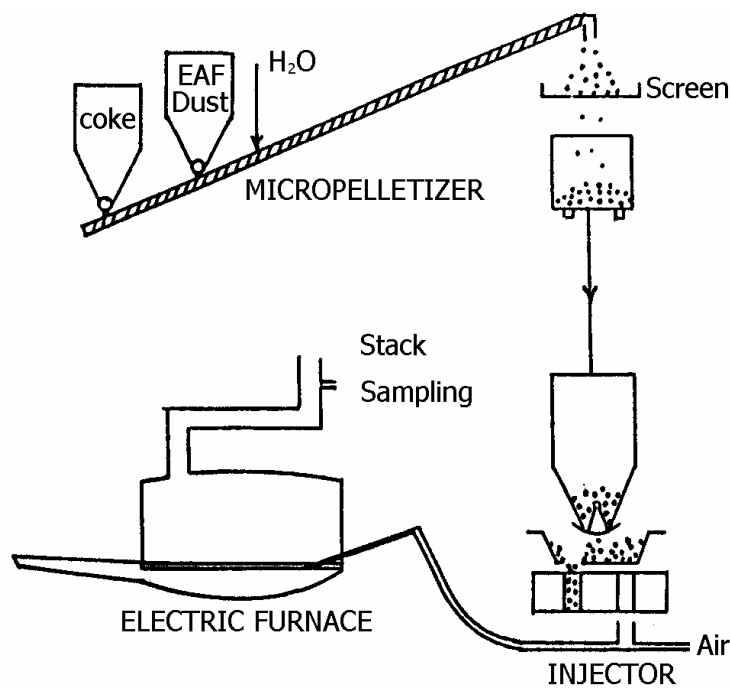
Figure 2.4 The direct recycling process [70]

2.4.2 Recovery

In the past decades, a number of methods have been developed to recover EAF dusts. It includes pyrometallurgical methods such as the Waltz and Enviroplas processes,

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hydrometallurgical methods such as the ZINCEX and EZINEX processes, and combinations of hydro and pyrometallurgical methods (MRT and IBDR-ZIPP processes). Table 2.5 shows the available recovery processes and the main products formed in these processes. It shows that most of them are pyrometallurgical methods, in which mainly Zn and Fe bearing products are formed.

In hydrometallurgical recovery processes leaching solutions such as caustic soda, sulphuric acid, mononitrilotriacetate anion (NTA^{3-}) and hexahydrated ferric chloride ($FeCl_3 \cdot 6H_2O$), hydrochloride, acetic acid as well as NH_3-$(NH_4)_2CO_3$ solutions are used, depending on the variation of the chemical compositions and crystalline phases present in the electric furnace dust [74-89]. Microwave and ultra sound wave technology can be used to improve the reaction rates in these processes [68,76]. The major product of these recovery processes is zinc metal. However, the main problem associated with these processes is the detoxicification of the leach residues [87].

In the pyrometallurgical treatment processes, electric furnace dust is refined or reduced by a gaseous (methane, hydrogen) or solid (coke, coal, iron powder) reductant to produce a crude Zn, Cd, Pb, Cr and Ni bearing ferroalloy at high temperatures [90-112]. Power is supplied by either plasma arc, electricity, solar or microwave heat 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.

2.4.3 Solidification/stabilisation

In solidification / stabilisation 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 toxic substances are reduced and value added to the waste [113]. The solidification/stabilisation processes are, from an environmental and economic viewpoint,

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Table 2.5 Electric furnace dust management methods [3,114]

Process name	Process type	Zn-bearing product	Fe-bearing product	Other products
Waelz kiln (2-stage)	Pyro	ZnO	Iron oxide/metallized iron	$PbCl_2/CdCl_2$ fume
Waelz kiln (1-stage)	Pyro	ZnO	Iron oxide/metallized iron	-
Flame reactor	Pyro	ZnO	Slag	-
ZTT Ferrolime	Pyro	ZnO	Ferrolime	Salt mixture
MR/Electrothermic	Pryo	ZnO	Slag/residue	-
MRT	Hydro/pyro	High purity ZnO	Iron oxide/metallized iron	Pb/Cd metals
Laclede Steel	Pyro	Zn metal	Slag	-
EZINEX	Hydro	Zn metal	Iron oxide	Salt mixture
Ausmelt	Pyro	ZnO	Slag	-
MetWool	Pyro	ZnO	Pig iron	Mineral wool
Enviroplas	Pyro	Zn metal or ZnO	Slag	-
AllMet	Pyro	Zn metal	Fe/Fe_3C	Salt mixture
IBDR-ZIPP	Pyro/Hydro	ZnO	Pig iron	Salt mixture
ZINCEX	Hydro	Zn metal	Residue	Pb/Cd cement
Rezada	Hydro	Zn metal	Iron oxide	Salt mixture, Pb/Cd cement
Cashman	Hydro	High purity ZnO	Iron oxide/metallized iron	Salt mixture, Pb/Cd cement
Terra Gala	Hydro	ZnS	Iron oxide	$PbCl_2$, Pb/Cd cement
Elkem	Pyro	Zn metal	Iron oxide slag	-
IMS	Pyro	Zn metal	Iron oxide slag	-
Hi-Plas	Pyro	Zn metal	Pig iron	-

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the most promising methods to treat electric furnace dust and filter cake. It can use clay and waste that are generated by other industries (such as incinerator fly ash, coal fly ash and blast furnace slag) to stabilise or solidify the toxic substances in the electric furnace dust and filter cake [3,113-121]. The resultant waste mixture is a non-toxic material, which can be used by the building and glass industries. The solidification/stabilisation treatment processes of the electric furnace dust and filter cake can typically be divided into cementation, vitrification or glassification processes:

2.4.3.1 Cementation process

The Super Detox process, which was marketed by EnviroSource and commercialised since 1989, was developed by Bethlehem Steel Corporation [3,114]. In this process, the electric furnace dust, lime, aluminosilicates and other additives are well mixed into the concrete-like material. The toxic substances in the dust are either precipitated or oxidised/reduced into the least soluble components and thereafter immobilised by the alumino-silicate matrix. Both wet and dry electric furnace dusts can be treated. The product is very impermeable.

Another commercial solidification process successfully treats carbon steel and alloy steel electric furnace dust as well as waste pickling acid at Atlas Steels [115,116]. It uses spent pickling acid, slag and lime to treat electric furnace dust. The treatment process is schematically shown in Figure 2.5. It includes (a) the acidification of waste with iron and silicon containing materials (slag) and (b) using lime to adjust the pH in order to solidify the metal silicates. The laboratory, pilot and industrial 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 economic and safe way to treat electric furnace dust and spent pickling acid.

The production of cement blocks that use ferrochrome dust as raw material have been studied by Giesekke et al. [16]. The mixtures consisted of ferrochrome dust and electric arc furnace slag with different ratios of ordinary Portland cement (OPC), which were cured for 56 days. The German DIN 38414 procedure was used to evaluate the
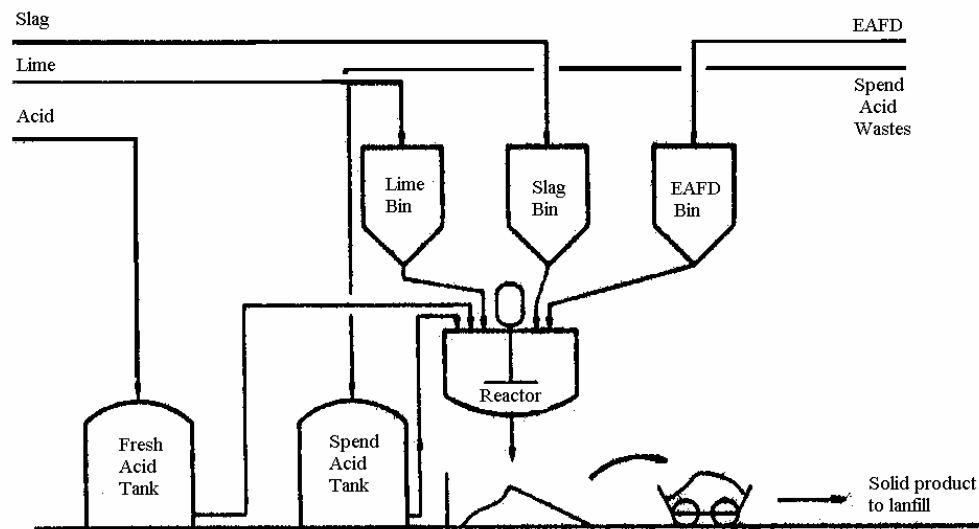
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Figure 2.5 The solidification process for treating EF dust with spent acid [115]

leachability of these cement blocks after it was crushed to less than 10 mm. The results show that about 95% of the Cr (VI) and 30-55% of the salts (Na, K, SO_4 and Cl) were stabilised. The addition of $FeCl_2$ and electric arc furnace slag improved the stabilisation ratio of Cr (VI). However, the Cr (VI) concentration in the leachate was higher than the regulation limits (0.05 mg/l) set for drinking water in South Africa [17].

2.4.3.2 Vitrification or Glassification processes

The Inorganic Recycling Corporation (IRC) developed a process that can completely transform EAF dusts into commercial products [117,118]. This process (Figure 2.6) 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 ^{o}C (1500-2500 ^{o}F), 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 in abrasive applications. The water waste is also recycled back to the mixing step, thereby creating a zero-waste process.
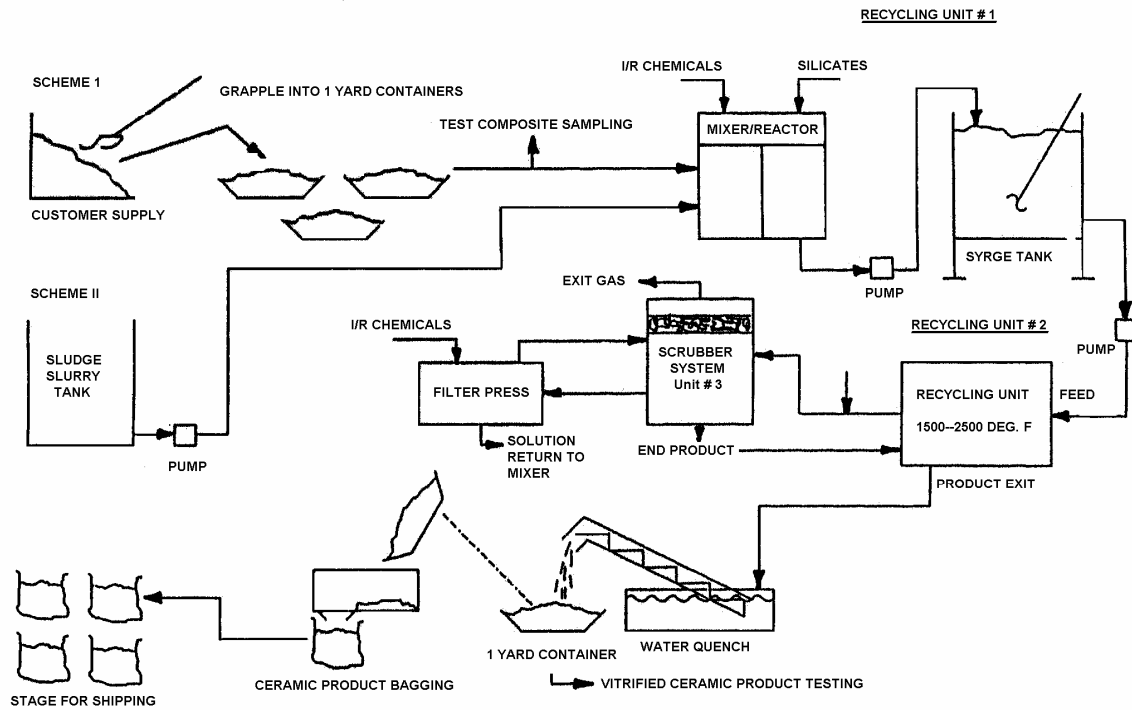
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Figure 2.6 Inorganic Recycling Corporation process in which electric furnace dust is treated [118]

The Glassification process [119], which 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. In this process, the waste and glass forming materials are blended and melted at approximately $1371°C$ ($2500 °F$). Vaporised 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 stabilisation of Cr (VI) in stainless steel plant dust by clay has also been investigated [5]. Bricks were prepared by mixing different mass ratios of dust to clay (5:5, 4:6 and 3:7), followed by drying at $110°C$ and sintering between 1000 and $1200°C$ for different time periods (1, 2, 3 and 5 hours). Cr (VI) in the stainless steel dust was effectively stabilised with a mass ratio of clay to stainless steel dust of 5:5 at $1200°C$. The Cr (VI)

concentration in the sintered brick decreased with an increase in sintering time and sintering temperature, while it increased with increasing clay:dust ratio. It was assumed that the Cr (VI) concentration decreased due to the redox reaction during the sintering period, when Cr (VI) was reduced into Cr (III), presumably by iron oxide. Peng et al. also used clay as additive to vitrify stainless steel flue dust in order to stabilise the toxic substances [44]. The softening temperature of the mixture decreased to $1200^{o}C$ when a 1:1 mass ratio of clay to dust was used. TCLP tests on the vitrification product indicated that the concentrations of toxic substances in the leachate are 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 $1000^{o}C$. Gericke reported that heavy metals in ferrochrome dust can be immobilised through mixing 20% of ferrochrome dust with 80% of clay or 50% clay with 30% ferrochrome dust and 20% ferrochrome slag [57]. 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 bag house filter dust, and sintered it at $1200^{o}C$ to stabilise the Cr (VI) and salts in the ferrochrome dusts [17]. The results showed that more than 99% of Cr (VI) and 90% of salt in the ferrochrome dusts were stabilised. The Cr (VI) concentration also decreased with an increase in sinter temperature.

2.5 Conclusions

This chapter has shown that electric furnace dust and filter cake that are produced by ferrochrome and stainless steel plants contain significant amounts of Cr(VI), which is both toxic and carcinogenic. Since unacceptable 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 dust and original filter cake are very fine particles that contain valuable elements such as Fe, Cr and Ni. The stainless steel dust is formed by the vaporisation of the 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, which is the major mechanism of dust formation in the

steelmaking plant. Vaporisation and direct capturing of charge materials are two mechanisms whereby dust forms during ferrochrome production. Filter cake is formed due to the precipitation of metal hydroxides, and super saturated salts and from remnants of stainless steel scale.

These wastes can be either minimised at source by optimising the operation parameters or be detoxified by the proper treatment methods. Direct recycling of electric furnace dust back to the ironmaking and steelmaking plant is the easiest way to treat these wastes, whereas the disadvantages of this process are blockage and corrosion of the off-gas duct and an increase in the energy consumption. Pyrometallurgical, hydrometallurgical and combinations of hydro and pyrometallurgical processes can be used to recover the valuables in the electric furnace dust. However, the main problems associated with these processes are the detoxicification of the leach residues, 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. Solidification/stabilisation 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 such as slag, spent refractory, mill scale and spent acid. The advantages of the solidification/stabilisation process include low investment costs, operational simplicity and the minimization of secondary waste residues.