

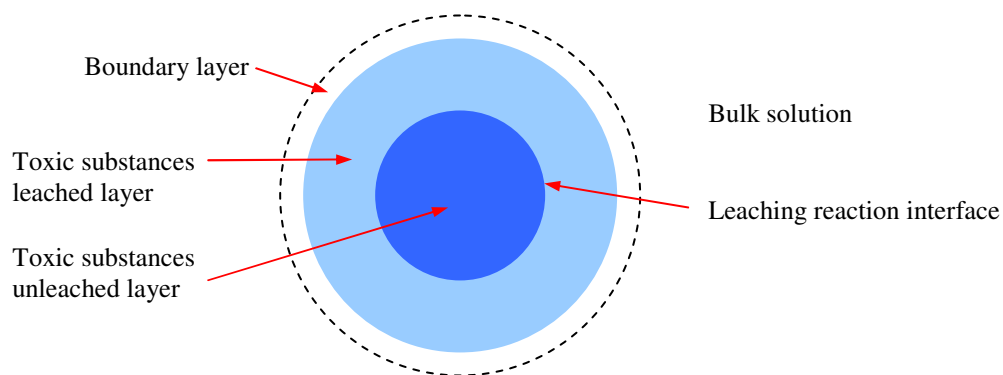
## **Chapter 5 The leachability of the Cr (VI)-containing electric furnace dust and filter cake from a stainless steel waste treatment plant**

### **5.1 Introduction**

The leachability of toxic substances from waste materials directly influences the treatment policy of the wastes. TCLP and ASTM D 3987-85 tests [21,146], which were respectively developed by the Environmental Protection Agency (US EPA) and American Standards Tests for Materials (ASTM), are widely used to understand the leachability of toxic substances from wastes. The TCLP test is also used to evaluate the risk of wastes to groundwater.

The TCLP and ASTM D 3987-85 tests, however, address neither the leachability of toxic substances over time, nor the leaching kinetics of the toxic substances. The shrinking core model can be used to understand the leaching mechanisms of toxic substances from wastes (Figure 5.1) [147,148]. According to this leaching model, the leaching steps can be divided into the following [147,148]:

- 1) Diffusion step of the leachant to the surface of the solid particle through the boundary layer.
- 2) Diffusion of the leachant to the leaching reaction interface.
- 3) Reaction step which can remove the toxic substances from the interface into the leachate via a set of physical and/or chemical processes such as dissolution, de-absorption and ion-exchange.
- 4) Diffusion step inside the leached layer of the particle which can transport the toxic substances to the surface of the particles through the matrix inside the particles.
- 5) Diffusion step in the aqueous boundary layer which can move the species into the bulk solution.
- 6) Bulk aqueous transport via diffusion or advective transport.



**Figure 5.1** Leaching model of the toxic substances from the waste particles

The rate controlling step of the overall leaching reaction is the slowest step of the leaching process. However, the rate of steps (1) to (6) can be altered by changing the leaching parameters. For example, reducing the particles size of the wastes increases the surface areas of the wastes, and therefore increases the interface of the leaching reaction and the rate of step (1), while the temperature or pressure of the leaching system and the presence of a catalyst can change the rate of reaction (3). To change the rate of step (4), one can change the temperature, pH and the concentration of the leachant. Increasing the agitating speed of the impellers increases the rates of step (5) and step (6) [147,148].

In the present chapter, the leachability of Cr (VI) from the wastes was investigated using the TCLP and ASTM D 3987-85 tests. Distilled water and nitric acid leaching tests were also used to further understand the leaching behaviour of Cr (VI) from these wastes.

## 5.2 Experimental

### 5.2.1 Sample preparation

The samples used in this study and the methods of sample preparation are the same as that described in Chapter 3.

## **5.2.2 Experiment methods**

### *5.2.2.1 TCLP test and ASTM D 3987-85 test*

The TCLP test was used to evaluate the leachability of the toxic substances from the wastes. In the preliminary evaluation of the TCLP test, 5.0 g of waste was added to 96.5 ml of distilled water (DW) and stirred with a magnetic stirrer. It was found that the pH values of the solutions are all larger than 5. After the addition of 3.5 ml of 1N HCl, the solutions were heated up to 50°C and kept at 50°C for 10 minutes. The pH values of the resultant solutions of FCD1, FCD2, FCD3, SPD and FC were found to be 6.99, 6.76, 3.15, 12.17 and 7.56, respectively. This confirmed that TCLP solution 2 (pH=2.88±0.05) is the appropriate test solution for SPD, FCD1, FCD2 and FC, whereas TCLP solution 1 (pH=4.93±0.05) should be used to test FCD3. In the extraction step, 100g samples (in triplicate) were added to 2 l of the appropriate TCLP solution, contained in borosilicate glass bottles. These bottles were then continuously rotated at 30 rpm for 20 hours, after which the slurries were filtered (using a glass fibre filter) and the pH of the leachate measured.

The ASTM D 3987-85 test was employed in this study to further understand the leachability of the wastes. 70 g samples (in triplicate) were added to 1400ml of distilled water and agitated continuously for 18 hours at 23°C. The mixtures were filtered with a glass fibre filter by vacuum, and the pH of the leachate determined.

The Cr (VI) concentrations of the leachates from the TCLP and ASTM D 3987-85 tests were measured by the colorimetric method with a S20D spectrophotometer. The total chromium concentrations were also analysed after Cr (III) was oxidised to Cr (VI) by potassium permanganate in an acid solution. The analytical method is attached in Appendix I. The concentrations of zinc and lead were measured with a GBC909 flame atomic absorption spectrometer (AAS), by respectively using US EPA methods 7950 and 7420 [149].

### 5.2.2.2 Nitric acid and distilled water leaching

Static distilled water (DW) and nitric acid (NA) leaching tests were also conducted in order to study the surface composition of the particles. In these tests, 50g of dust was added to 1l of distilled water or nitric acid (to obtain a solid:liquid ratio of 1:20), for 2 hours at  $25\pm 1^{\circ}\text{C}$ . The slurries were then filtered and dried. The crystalline phases in the residues were identified with a Siemens D-501 X-ray diffraction (XRD) instrument and the atomic concentrations on the surfaces of the leaching residues were determined with a X-ray photoelectron spectrometer.

The leachability of Cr (VI) was also determined at different stirring speeds and temperatures (Table 5.1). The effect of stirring speed was studied at 600, 800 and 1000 rpm, while the effect of temperature at 25, 40 and  $55^{\circ}\text{C}$  was studied at a stirring speed of 800 rpm. The effect of pH was investigated by using pH buffer solutions of 5 and 9 at a stirring speed of 800rpm. In these experiments a 50 g sample was again added to 1l of distilled water. Approximately 2~3 ml leachate was sampled at different intervals and filtered using a  $0.22\ \mu\text{m}$  membrane filter. Thereafter, the same amount of distilled water was added back to the solution. The leachate samples were immediately analysed. Zinc concentrations in the leachate of FCD2 were also determined using the US EPA method 7950 [149].

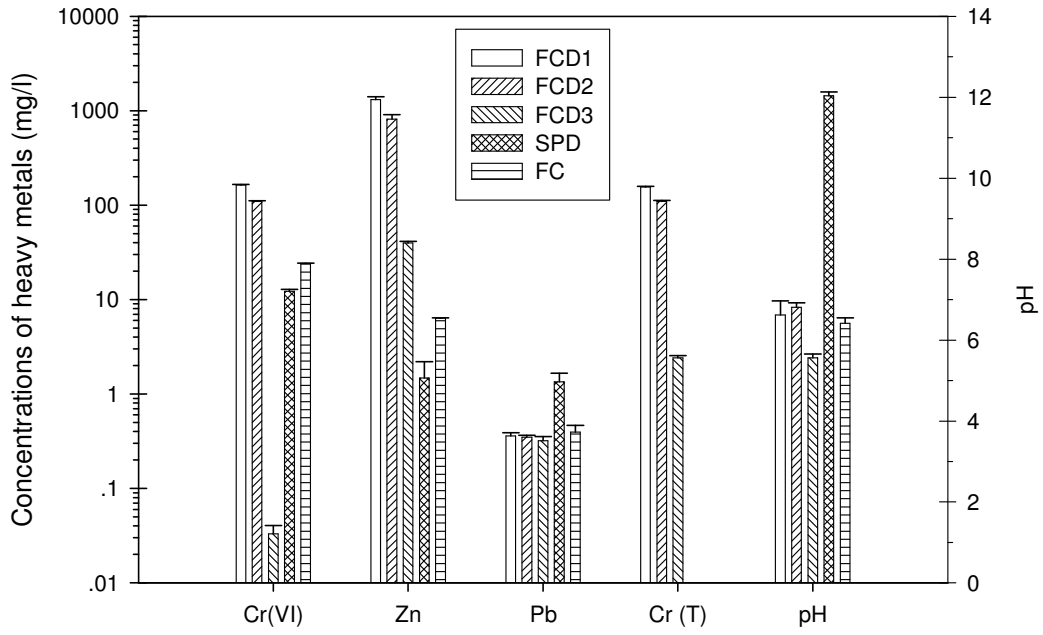
**Table 5.1** Experimental conditions of the Cr (VI) leaching tests

Parameters	SPD	FCD1, 2, 3 and FC
Stirring speed (rpm)	600, 800, 1000	800
pH of the leach solutions	5, Distilled water, 9	Distilled water
Leaching temperature ( $^{\circ}\text{C}$ )	25, 40, 55	25
Total leach time (hours)	24	168
Solid waste/leach solution (g/ml)	1/20	1/20

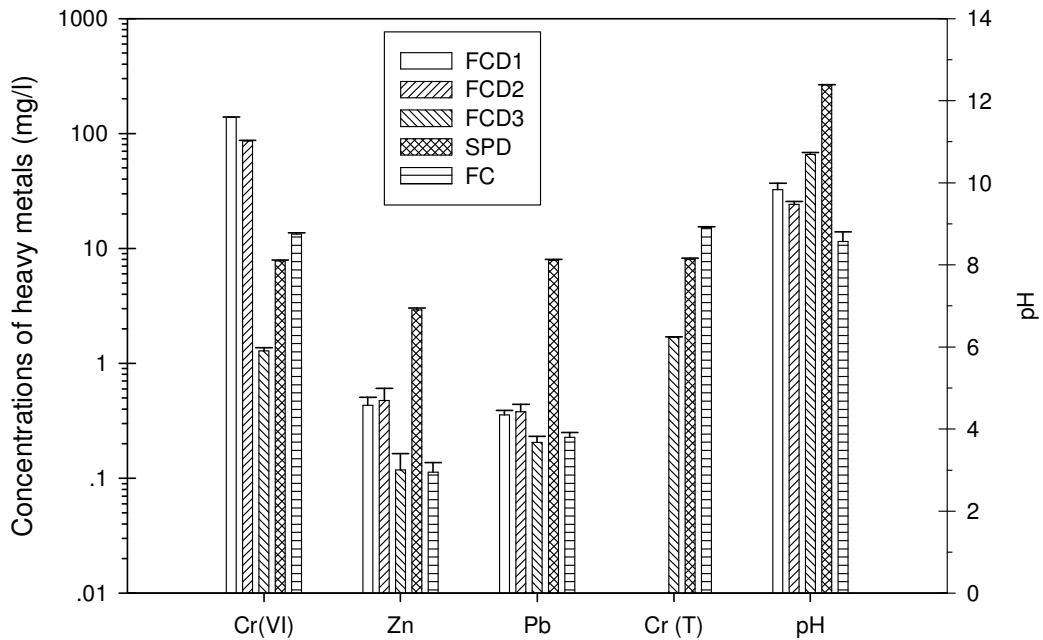
## 5.3 Results and discussion

### 5.3.1 TCLP and ASTM D 3987-85 tests

The results of the TCLP and ASTM D 3987-85 tests of the wastes are shown in Figures 5.2a and 5.2b, respectively. It shows that all the wastes are hazardous materials



(a) TCLP test



(b) ASTM D3987-85 test

**Figure 5.2** The concentrations of toxic substances in TCLP test(a) and ASTM D3987-85 test(b)

according to South African legislation. It also shows that most of the leachable chromium exists in the form of Cr (VI). High levels of chromium are present in the TCLP leachate of FCD3 although the concentration of Cr (VI) is substantially lower than that determined by the ASTM D 3987-85 test. This is possibly due to the reduction of Cr (VI) by metal ions such as  $\text{Fe}^{2+}$  that are present in the TCLP leachate ( $\text{pH} < 6$ ), while it is precipitated at a pH of approximately 11 during the ASTM D 3987-85 test [150]. The zinc concentrations in the TCLP leachate of FCD1, 2 and 3 (approximately 1314, 810 and 40 mg/l, respectively) are much higher than those of the ASTM D 3987-85 test (less than 0.5 mg/l), since zinc is mostly present as zinc oxide, which cannot be extracted by distilled water, but by glacial acetic acid.

All the leachates from the ASTM D 3987-85 tests form basic solutions, while the TCLP leachates are acidic except for the SPD ( $\text{pH} \approx 12$ ). The high pH value of the TCLP leachate from the SPD is due to the existence of  $\text{Ca}(\text{OH})_2$  in the dust.

### ***5.3.2 Static distilled water and nitric acid leaching tests***

The static distilled water and nitric acid leaching tests were only conducted on the EF dusts. After leaching these dusts with either 1M  $\text{HNO}_3$  or distilled water for 2 hours, the dusts were examined by XRD (Figures 5.3 and 5.4). XRD analyses of the leaching residues of the ferrochrome dust show that chromite particles, quartz, cristobalite, ZnO, MgO,  $\text{Mg}_2\text{SiO}_4$  and ferrochrome particles still exist after the 2h distilled water leaching test, while  $\text{NaZn}_4(\text{SO}_4)\text{Cl}(\text{OH})_6 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$  as well as NaCl dissolved (Figure 5.3). Only chromite particles, quartz, cristobalite,  $\text{Mg}_2\text{SiO}_4$  and ferrochrome particles are present in the nitric acid leach residue of the ferrochrome fine dust. It indicates that the nitric acid leach dissolves  $\text{Ca}(\text{OH})_2$  and oxidises parts of the nickel particles from the SPD (Figure 5.4). Spinel phases, fluorite and silica still exist. Small gas bubbles are liberated from the stainless steel plant dust during the nitric acid leach. This is possibly hydrogen. The nitric acid leachate is light brown in colour (possibly due to  $\text{Fe}^{3+}$  species), while the distilled water leachate is light yellow in colour (presumably  $\text{Cr}^{6+}$  species). The analysis results show that the Cr (VI) concentration in the NA leachate (0.13mg/l) is lower than that in the DW leachate (6.4mg/l).

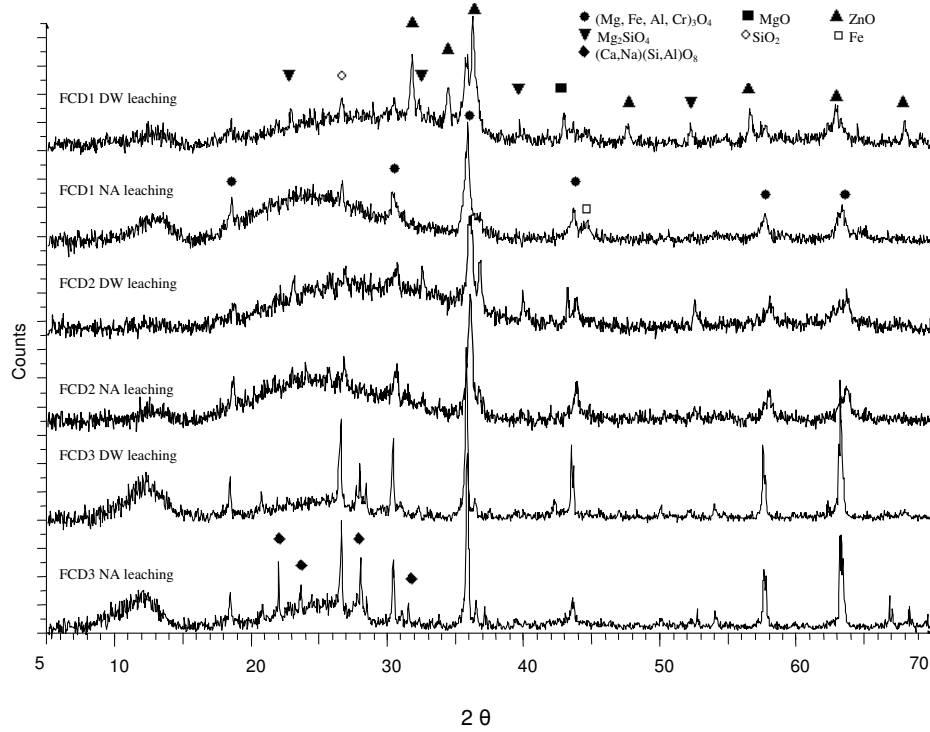


Figure 5.3 XRD patterns of FCD 1,2 and 3 after DW and NA leach for 2 h

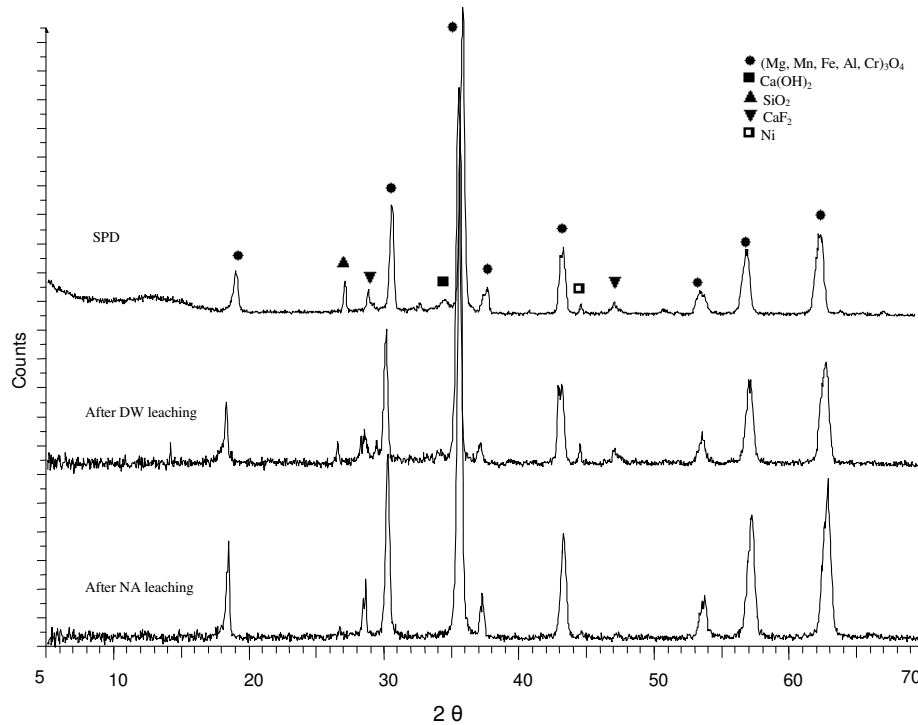


Figure 5.4 XRD patterns of SPD before and after DW and NA leach for 2 h

The elements that exist on the surface of the electric furnace dust and the residue of the distilled water and nitric acid leaching tests of ferrochrome dust are shown in Table 5.2. The major elements on the surface of the SPD are Zn, O, Si and Mg, while Na, F, Cr, K, C, Cl, Ca and Fe are present in minor amounts. Before the leaching experiments, zinc, halogens (F, Cl), alkali metals (K, Na) and the elements O, Cr, S and Si are present on the surface of the ferrochrome dust. It shows that the elements that can easily vaporise are the major components on the surface of the dust particles.

**Table 5.2** XPS analysis of the EF dusts (atomic%)

Element	Chemical state	FCD1	FCD2	FCD3	FCD1 (DW)*	FCD1 (NA)**	SPD
Na	Na <sup>+</sup>	7.21	5.80	1.63	2.33	0.86	4.47
Zn	Zn <sup>2+</sup>	9.74	6.38	2.63	9.24	0.75	5.19
F	F <sup>-</sup>	5.18	0.49	0.34	4.03	0.39	2.35
Cr	Cr, Cr <sup>3+</sup> , Cr <sup>6+</sup>	1.52	1.37	0.81	1.27	0.62	0.89
O	Oxides	53.07	54.98	44.53	60.64	64.54	55.10
K	K <sup>+</sup>	1.49	2.12	0.32	0.45	0.16	1.00
C	C, CO <sub>3</sub> <sup>2-</sup>	5.93	9.86	37.53	5.35	3.76	3.98
Cl	Cl <sup>-</sup>	1.46	2.13	0.81	0.32	0.15	0.95
S	SO <sub>4</sub> <sup>2-</sup>	1.32	2.61	1.32	0.46	Nd	0.09
Si	Si <sup>4+</sup>	13.09	14.27	10.06	15.91	28.53	6.24
Ca	Ca <sup>2+</sup>	nd***	nd	nd	nd	nd	3.08
Mg	Mg <sup>2+</sup>	nd	nd	nd	nd	nd	12.05
Fe	Fe <sup>2+</sup> , Fe <sup>3+</sup>	nd	nd	nd	nd	nd	2.96

\* distilled water leach residue; \*\* nitric acid leach residue; \*\*\* not determined.

The Na, Zn, K, total Cr and Cl concentrations are higher on the surface of the ferrochrome fine dusts, than those of the ferrochrome coarse dusts. After distilled water leaching of FCD1 the concentrations of sodium and chlorine decrease noticeably, while



after leaching with nitric acid the atomic concentrations of Na, Cl, Zn and F on the surface are reduced. Tables 3 also shows that the most abundant elements are Si and O with a ratio of 1:2 after nitric acid leaching. It confirms that some of the ferrochrome dust particles have a core of SiO<sub>2</sub> with an out layer of vaporised substances such as ZnO and NaCl. In contrast to the XRD results, it shows that most of the NaCl condensed on the surface of the particles and are easy to leach out, while zinc is present in the form of zinc oxide.

### ***5.3.3 Effect of stirring speed on the leachability of Cr (VI) from stainless steel dust***

The effect of the stirring speed on the leachability of Cr (VI) is shown in Figure 5.5. It shows that approximately 65% Cr (VI) (7.8mg/l) leached out in 5 min, and that stirring speed has no effect on the leaching of Cr (VI). This indicates that most of Cr (VI) exists on the surface or near the surface of the dust particles, and that it will easily leach out when it rains or snows. It cannot simply be stockpiled at the waste site, since Cr (VI) can leach out and thereby contaminate surface water, ground water and soil. It also means that the leaching of Cr (VI) is not controlled by either step (4) or step (5) of the described leaching model, since agitation does not have an effect on the leaching rate of Cr (VI) from the waste particles. In addition, it shows that the Cr(VI) content of the stainless steel plant dust can substantially be reduced in a simple washing process.

Figure 5.5 also shows that the Cr (VI) concentration firstly increases and reaches a maximum after 1 hour of leaching. Then the Cr (VI) concentration starts to decrease, which can be explained by the transformation of Cr (VI) to Cr (III). It seems that the Cr (VI) concentration remains stable after 9 hours of leaching.

### ***5.3.4 Effect of temperature on the leachability of Cr (VI) from stainless steel dust***

The effect of temperature on the leachability of Cr (VI) from SPD is shown in Figure 5.6. It was found that Cr (VI) dissolution increases with an increase in temperature of the leachate. At 55°C, with a stirring speed of 800 rpm, approximately all of the Cr (VI) leached out within 24 hours. It is therefore believed that the Cr (VI) leaching reaction is controlled by either diffusion of Cr (VI) inside the Cr (VI) leached layer and/or chemical

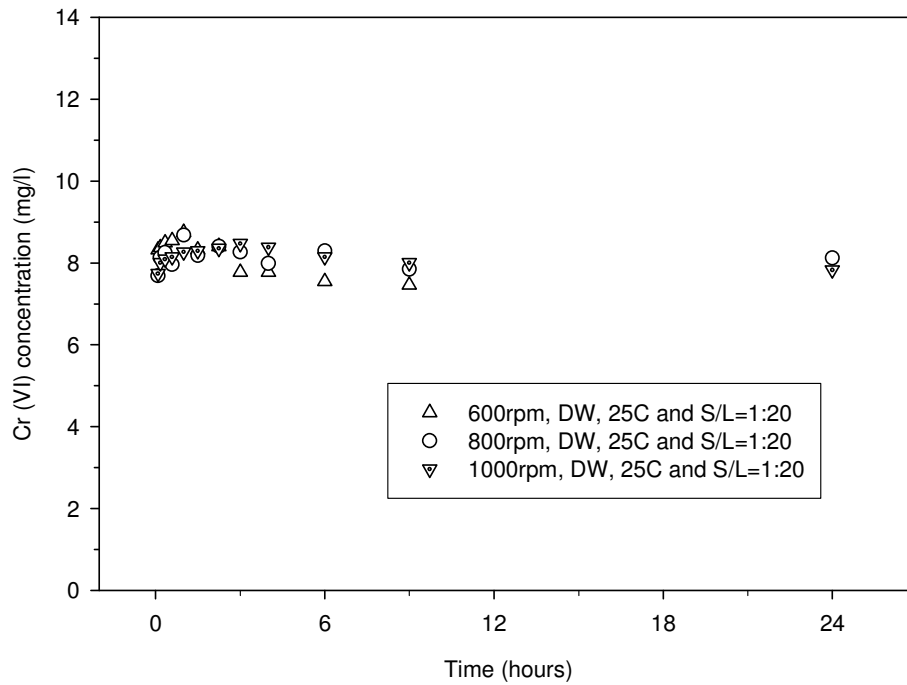


Figure 5.5 Effect of stirring speed on the leachability of Cr (VI) from SPD

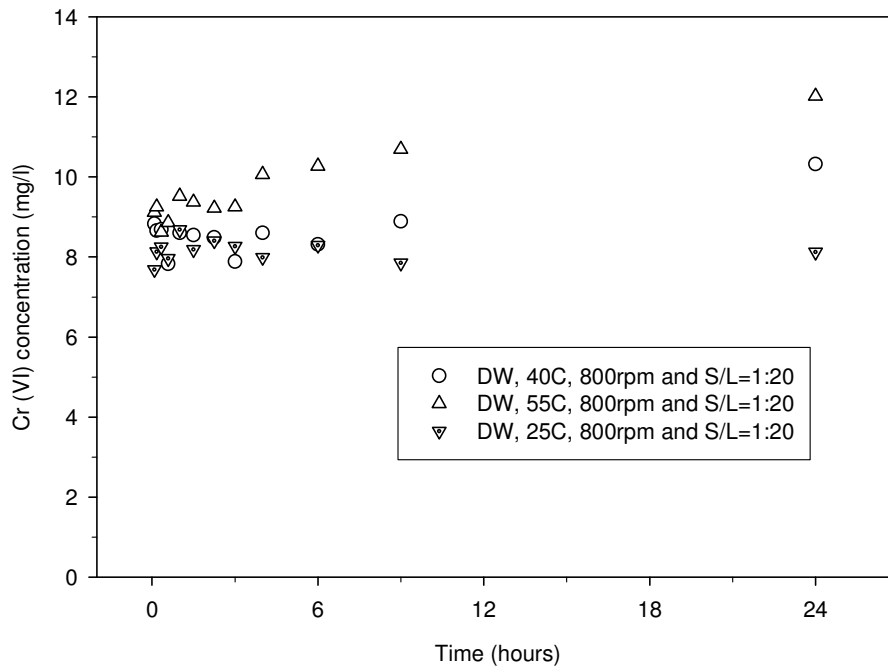


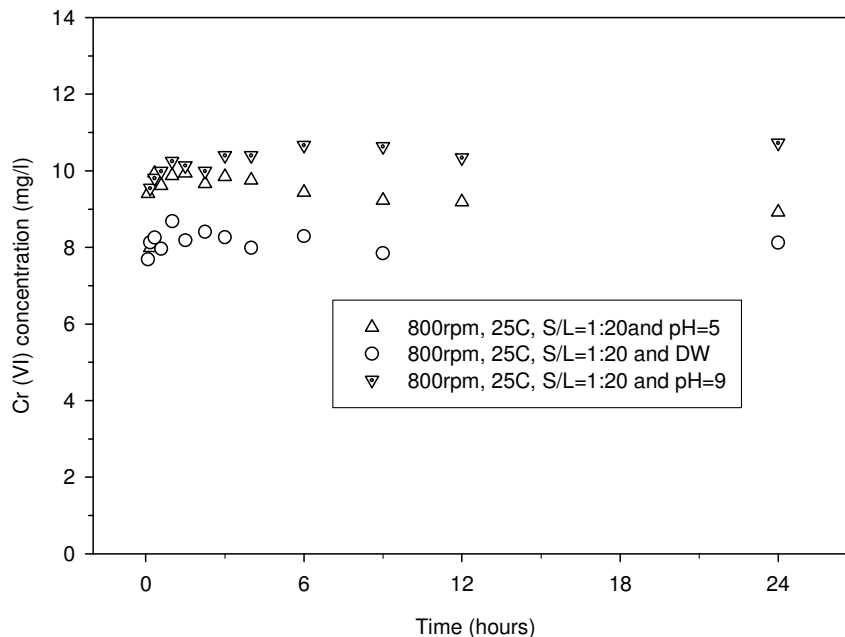
Figure 5.6 Effect of temperature on the leachability of Cr (VI) from SPD

reactions whereby Cr (III) is transformed into Cr (VI). The latter reactions are influenced by the pH of the aqueous solution and redox potential.

Since the chemical and phase composition of the stainless steel dust is complex, it is difficult to fully understand the leaching mechanisms of Cr (VI) from the waste. Certain components in the dust can influence the Cr (VI) concentration in the leachate. These include reducing agents, such as Fe (II), which can influence the redox potential of the solution, and lime which can change the pH of the solution. These components can over time change the Cr (VI) concentration in the leaching solution, and therefore make the leaching mechanisms of Cr (VI) complicated to understand.

### 5.3.5 Effect of pH on the leachability of Cr (VI) from stainless steel dust

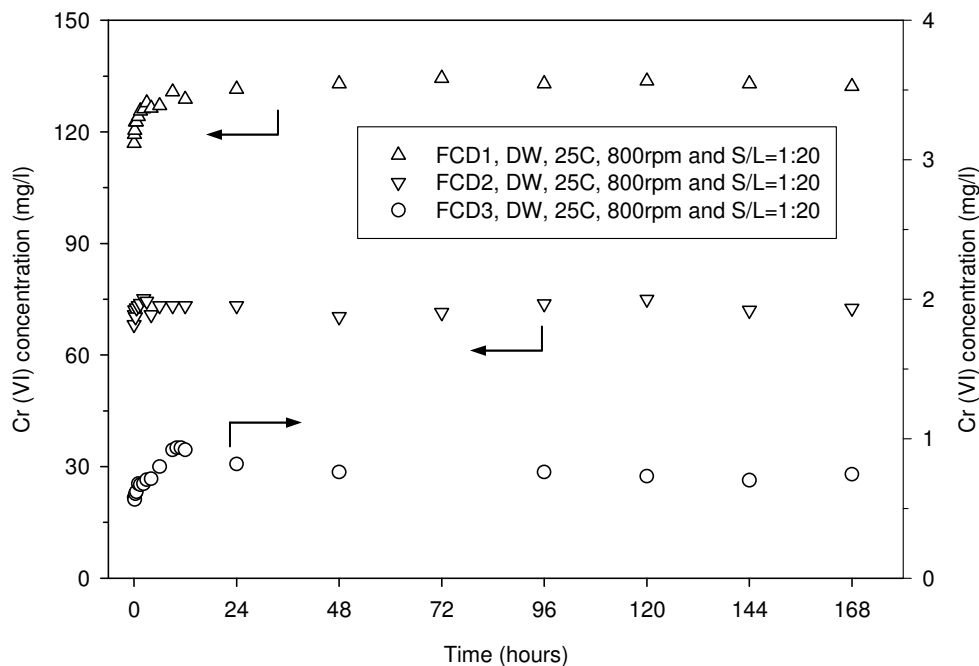
The leachability of Cr (VI) from SPD, using solutions of different pH, is shown in Figure 5.7. At 25°C and a stirring speed of 800rpm more Cr (VI) is leached from acidic and basic solutions than from distilled water with a pH of approximately 6.5. Under the current experimental conditions more Cr (VI) is leached from basic solutions than from acidic solutions.



**Figure 5.7** Effect of pH on the leachability of Cr (VI) from SPD

### 5.3.6 The leachability of Cr (VI) from ferrochrome dusts and filter cake

In order to understand the leaching behaviour of Cr (VI) from ferrochrome dust and filter cake, a seven day leaching test was performed with distilled water at 25°C. The results are shown in Figures 5.8 and 5.9. It shows that approximately 72% and 62% of Cr (VI), present respectively in dust samples FCD1 and FCD 2, were leached out by distilled water under 1 min. This is presumably due to “wash-off” of Cr (VI) from the surface of the dust particles. The maximum Cr (VI) concentration (~132mg/l) was reached after 24 hours for sample FCD1, while the peak value of ~73mg/l Cr (VI) was reached within an hour for sample FCD2. Ferrochrome fine dusts are therefore very harmful to the environment, and should not come in contact with water before being processed. The Cr (VI) in the ferrochrome fine dust can also be lowered by washing the dusts. However, the wastewater needs to be treated further due to the significant levels of Cr(VI).

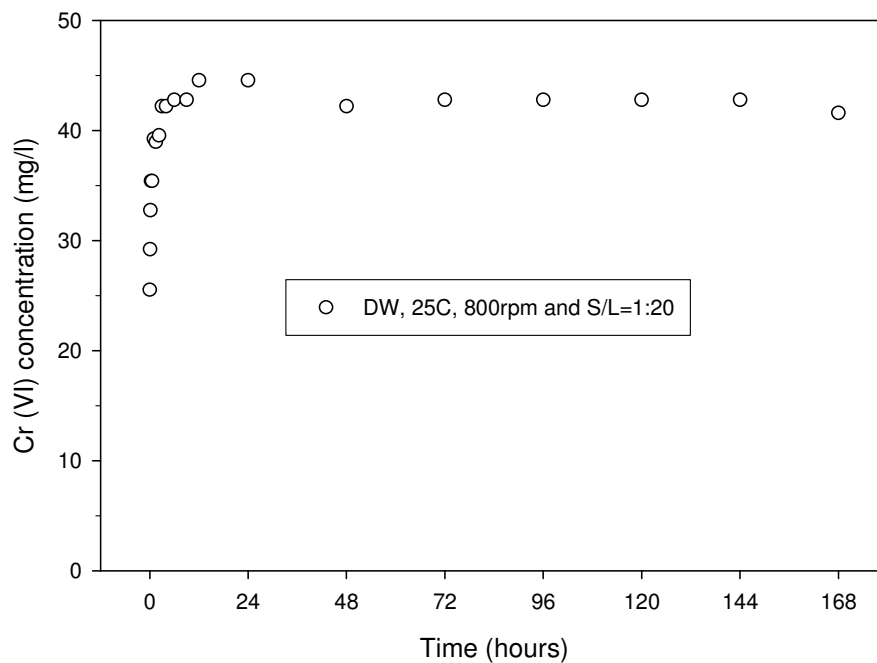


**Figure 5.8** The leachability of Cr (VI) from ferrochrome dust, using distilled water

The amount of Cr (VI) that was leached from sample FCD3 was below 1 mg/l Cr(VI), and increased with time up to 9 hours, after which it slightly decreased when the leaching

time exceeded 9 hours. It is assumed that this is due to the reduction of Cr (VI) by  $\text{Fe}^{2+}$  in the leachate. Since the ferrochrome coarse dust (sample FCD3) contains low concentrations of volatile substances and hazardous Cr (VI), but also exploitable quartz and chromite, it is suitable to be recycled back to the furnace after being agglomerated by briquetting or pelletising using binders.

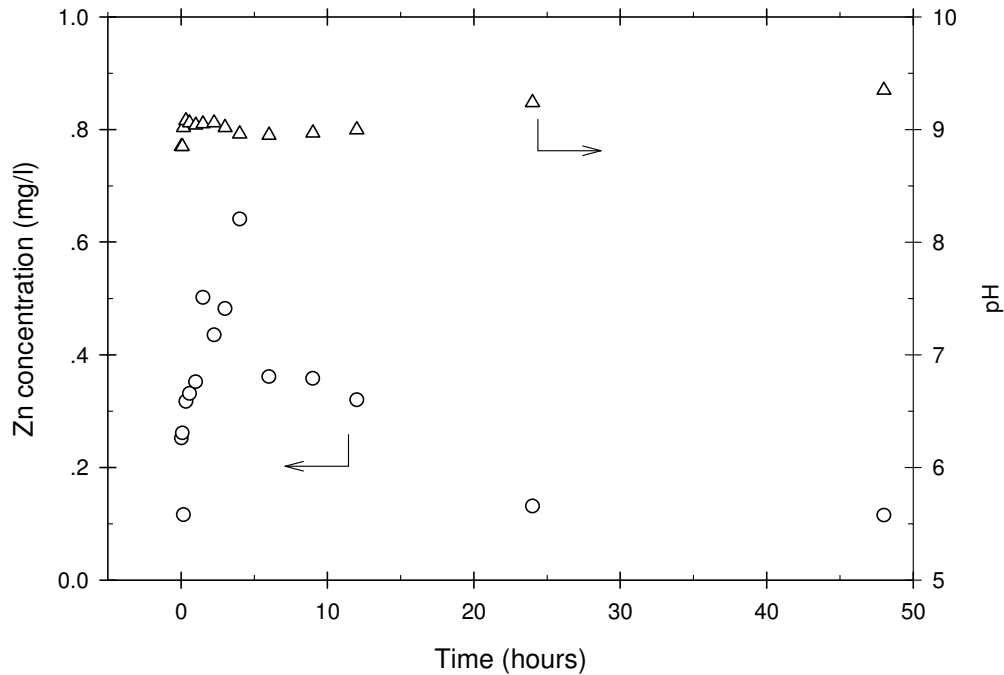
Figure 5.9 shows that approximately 25 mg/l Cr (VI) would leach out in 1 min from the FC. A maximum amount of approximately 44mg/l Cr (VI) was leached from the FC within 3 hours. It also shows that Cr (VI) is rapidly leached out.



**Figure 5.9** The leachability of Cr (VI) from FC

The change in zinc concentration and pH of the FCD2 leachate with time are shown in Figure 5.10. It was observed that the pH of the leachate did not change significantly during the leaching period. The zinc concentration in the leachate however, reached a maximum value after approximately 4 hours, after which it then decreased over time, possibly due to the precipitation of zinc in alkaline solutions ( $\text{pH} \approx 9$ ) [150]. Most of the zinc in the dust remained unaffected during the distilled water leach. If zinc would

therefore be recovered from ferrochrome fine dust, using a hydrometallurgical route, an acidic leach solution should be used.



**Figure 5.10** Zinc concentration and pH in FCD2 leachate versus time (DW, 800rpm, 25°C and S/L=1/20)

#### 5.4 Conclusions

In the present study, the leachability of Cr(VI)-containing EF dust and filter cake were studied. The following conclusions can be drawn:

- 1) TCLP and ASTM 3987-85 tests show that stainless steel plant dust, ferrochrome fine dust and filter cake are hazardous materials according to South African legislation. They therefore pose a potential threat to the environment.
- 2) Static distilled water and nitric acid leaching experiments show that the ferrochrome fine dust particles have a core of SiO<sub>2</sub> with an outer layer that consists of vaporised substances such as ZnO and NaCl.
- 3) Leaching experiments on the stainless steel plant dust show that approximately 65% of the Cr (VI) leaches out within 5 min under the current experimental

- conditions, but that the Cr (VI) leach out more easily in acidic and basic solutions than in distilled water.
- 4) Since the leaching behaviour of Cr (VI) does not change with stirring speed but with temperature, it can be concluded that the Cr (VI) leaching reaction is most probably controlled by the diffusion of Cr(VI) inside the Cr (VI) leached layer and the rate of the chemical reaction whereby Cr (III) is transformed into Cr (VI).
  - 5) Distilled water leaching experiments on ferrochrome dusts and filter cake show that Cr (VI) is easily leached by distilled water. Due to the high Cr(VI) concentration of the ferrochrome fine dust, it should not come in contact with water before being processed. The coarse ferrochrome dust is suitable to be recycled back to the SAF, as it contains low concentrations of volatile substances, but also usable carbon, quartz and chromite particles.