

## **Chapter 9 Stabilisation of Cr (VI) through sintering using silica-rich clay, Part III: Leaching behaviour of chromium from the stabilised wastes**

### **9.1 Introduction**

Stabilisation treatment processes are effective technologies through which pyrometallurgical wastes can be disposed. It can both immobilise the toxic substances and transform the wastes into non-hazardous commercial products such as construction materials [5,14,17,43,44,56,57].

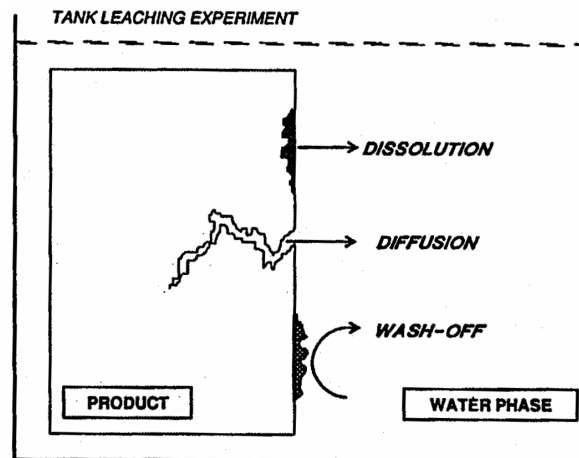
The controlling leaching mechanisms of the toxic substances from the stabilised waste products have been investigated by several workers. Shin et al. studied the leaching behaviour of Si, Ca, Sr and Cs from vitrified radioactive incineration ash, using the International Organization for Standardisation (ISO)-6961-1982 leaching test [187]. Based on more than 820 days of leaching experiments, it was proven that the dominant leaching mechanisms of these elements are dissolution and diffusion. According to Andres et al. [188], leaching of Pb and Zn from steel foundry dusts which were stabilised by cement and anhydrite ( $\text{CaSO}_4$ ) as binders were controlled by an initial wash-off followed by the diffusion process. TCLP tests showed that the stabilised products meet the regulatory limits on Zn, Pb, Cr and Cd. The treated products are therefore environmentally acceptable and can be used in the construction industry [188].

In the present chapter, the predominant leaching mechanisms of chromium species from the stabilised electric furnace dust and filter cake, using a semi-dynamic leaching test, are reported on. Two empirical models were used to evaluate the major leaching mechanisms of the chromium species. The values of the semi-empirical model parameters were used to evaluate the controlling leaching mechanisms of the chromium species from the stabilised products.

## 9.2 Background

Different leaching tests have been developed to evaluate the leaching behaviour of toxic substances from wastes. These include the Toxicity Characteristics Leaching Procedure (TCLP) test [21], the DIN 38414 (4) test [189], the ASTM D 3987-85 test [146] and the semi-dynamic leaching test [190-194]. The TCLP, DIN 38414 (4) and ASTM D 3987-85 tests, which are also called availability tests [192], are often used to assess the leachability of the toxic substances from the wastes.

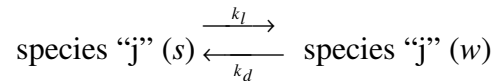
A semi-dynamic leaching test can be used to study the controlling leaching mechanisms of toxic substances from the stabilised/solidified products. The leaching models which can be used to evaluate the leaching mechanisms of the toxic substances from the stabilised/solidified wastes are well documented [192-195]. The leaching mechanisms of the toxic substances from the products are schematically shown in Figure 9.1. [192]. It shows that leaching of the toxic substances from the stabilised/solidified wastes can be controlled by surface wash-off (interface reaction kinetics), matrix diffusion and dissolution or corrosion [192-195]. The initial wash-off is often due to the soluble components on the surface of the product, while matrix diffusion occurs when the components leach through the matrix of the stabilised/solidified product. The dissolution process dominates if toxic substances dissolve at a higher rate from the edge of the stabilised product than due to diffusion through the matrix of the stabilised product [192].



**Figure 9.1** Leaching mechanisms of toxic elements from the stabilised product [192]

### 9.2.1 Leaching model based on initial wash-off or interface reaction kinetics

This model describes the mass exchange between the surface of the stabilised wastes and the aqueous solution [192,193,195]. It is relevant during the initial period of the leaching process and is also called initial surface wash-off. It can be described in terms of the exchange kinetics of a species “j” on the surface of the solid.



Where  $k_l$  and  $k_d$  are the rate constants describing the kinetics of releasing a species (“j”) from the surface of the solid (s) and attaching a species (“j”) from the aqueous solution (w).

The leach rate of a species from the stabilised waste can be expressed as an exponential function of the rate constants [192,193,195]:

$$L(t) = f \left\{ \exp \left[ -\left( k_l + \frac{S}{V_l} k_d \right) t \right] \right\} \quad (9.1)$$

Where S is the surface area of the stabilised waste form and  $V_l$  is the volume of the leachant.

The leaching process can also be expressed in terms of the cumulative fraction leached,  $F(t)$ , which is related to the leaching rate  $L(t)$ :

$$L(t) = \frac{M_0}{S} \frac{dF(t)}{dt} \quad (9.2)$$

Where  $M_0$  is the initial amount of a species in the stabilised waste and S is the surface area of the stabilised waste.

Replacing  $L(t)$  in equation (9.1) into equation (9.2) and integrating with time, the cumulative fraction leached of a species can be expressed as an exponential function [192,193,195], i.e.,

$$F(t) = k_l \left\{ 1 - \exp \left[ -\left( k_l + \frac{S}{V_l} k_d \right) t \right] \right\} \quad (9.3)$$

Where  $k_1$  is a constant term. If the rate of the initial surface wash off is fast enough, the equation (9.3) can be further simplified as  $F(t) = k_1$ , which is the initial fraction leached.

### 9.2.2 Leaching model based on matrix diffusion

A species which is transported from the stabilised waste to the solution through diffusion can be described using Fick's second law:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \quad (9.4)$$

Where  $C$  is the concentration of the diffusing species and  $D_e$  is an average effective diffusion coefficient. In this study, the leaching behaviour of a species from the cylinder products can be assumed as a semi-infinite medium ( $x > 0$ ). Furthermore, a species in the stabilised waste is postulated to have a zero surface concentration and a constant effective diffusion coefficient [190-193,195]. In this case, the leaching rate of a species, which is a solution of equation (9.4), can be expressed as [190-193,195,196]:

$$L(t) = C_0 \left( \frac{D_e}{\pi} \right)^{\frac{1}{2}} \quad (9.5)$$

Where  $C_0$  is the initial concentration of the species in the stabilised waste.

Therefore, replacing  $L(t)$  in equation (9.2), the cumulative leached fraction of a species that has been leached at time  $t$  can be derived as:

$$F(t) = 2 \frac{S}{V} \left( \frac{D_e t}{\pi} \right)^{\frac{1}{2}} \quad (9.6)$$

Where  $S$  is the surface area of the stabilised waste and  $V$  is the volume of the sample.

It shows that the leached fraction has a linear relationship with the square root of the leaching time. It can therefore be written that:

$$\text{Log } F(t) = \frac{1}{2} \log(t) + \log \left( 2 \frac{S \sqrt{D_e}}{V \sqrt{\pi}} \right) \quad (9.7)$$

### 9.2.3 Leaching model based on dissolution or corrosion

According to Cote et al., the leaching rate of a species from the stabilised waste can be expressed as [193]:

$$L(t) = L_0 \left[ 1 - \frac{C^{(w)}(t)}{C_{sat}^{(w)}} \right] \quad (9.8)$$

Where  $L_0$  is the maximum leaching rate,  $C^{(w)}(t)$  is the concentration of a species in the aqueous solution and  $C_{sat}^{(w)}$  is the concentration of a species at saturation in the aqueous solution.

This process can also be expressed using the network dissolution velocity  $u$ , if the matrix breakdown due to the leaching of a species from the stabilised waste:

$$u(t) = \frac{L(t)}{C_0} \quad (9.9)$$

Where  $C_0$  is the initial concentration of a species in the stabilised waste. Replacing equation 9.8 into equation 9.9 gives:

$$u(t) = u_0 \left[ 1 - \frac{C^{(w)}(t)}{C_{sat}^{(w)}} \right] \quad (9.10)$$

In the case where the concentration of a species is much less than the saturation concentration of a species in aqueous solution, i.e.,  $C_{sat}^{(w)} \gg C^{(w)}(t)$ , it follows that  $u(t) = u_0$ . Thus a linear function exists between the cumulative fraction of a released species and leaching time is [193]:

$$F(t) = \frac{S}{V} u_0 t \quad (9.11)$$

The cumulative leached fraction of the toxic substances from the stabilised wastes can be therefore expressed as a function of leaching time, i.e.,

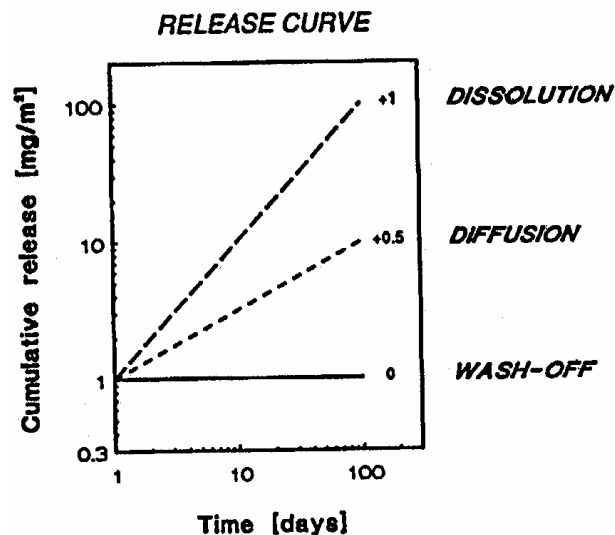
$$F(t) = k_1 \left[ 1 - \exp\left\{-\left(k_l + \frac{S}{V_l} k_d\right)t\right\} \right] + 2 \frac{S}{V} \left( \frac{D_e t}{\pi} \right)^{\frac{1}{2}} + \frac{S}{V} u_0 t \quad (9.12)$$

Equation (9.12) can also be simplified as:

$$F(t) = k_1[1 - \exp(-k_2t)] + k_3t^{\frac{1}{2}} + k_4t \quad (9.13)$$

Where  $k_1[1 - \exp(-k_2t)]$  is the term contributed by initial surface wash-off,  $k_3t^{\frac{1}{2}}$  is based on matrix diffusion from the porous product media and  $k_4t$  is the leached fraction due to the dissolution or corrosion of the matrix.

The dominant leaching mechanisms of a species from the stabilised waste can also be obtained by empirically analysing the slope of the logarithm of the cumulative fraction released versus the logarithm of the leaching time [192]. Figure 9.2 shows the theoretical curves of the different leaching mechanisms [192]. It shows that the controlling mechanism is surface wash off if the slope of the logarithm of cumulative fraction release versus the logarithm of leaching time is zero. If it is 0.5, the major leaching mechanism is diffusion. Dissolution controls the leaching process if the slope is 1.



**Figure 9.2** The theoretical curves of the different leaching mechanisms [192]

From the slope of the different leaching mechanisms, De Groot et al. derived that if the slope is below 0.4, the release of a species is controlled by initial surface wash-off [192]. The diffusion of a species from the solid matrix is the controlling mechanism when the

slope is between 0.4 and 0.6, while dissolution or corrosion of the network can control the leaching process with a slope of more than 0.6 [192].

### 9.3 Experimental

#### 9.3.1 Sample preparation

Approximately 40 g mixtures with different ratios of clay and waste were well mixed and pressed into cylinders with diameters of 2.5 cm and  $4.0 \pm 0.36$  cm in height. These cylinders were dried at  $110^\circ\text{C}$  for 48 hours. Thereafter, they were sintered at 1000 or  $1100^\circ\text{C}$  in a Muffle furnace for 5 hours in order to obtain a dimensionally stable product. The heating rate of the furnace was  $\sim 4^\circ\text{C}/\text{min}$  and the furnace was cooled down to room temperature at a rate of  $\sim 1.6^\circ\text{C}/\text{min}$ . The different types of samples and the experimental conditions are listed in Table 9.1.

**Table 9.1** Samples and experimental conditions

Sample	Composition (wt.%)	Sinter temp. ( $^\circ\text{C}$ )	Sinter time (h)
M1	50%SPD+50%AS	1100	5
M2	50%SPD+50%MR	1100	5
M3	20%FCD1+80%AS	1000	5
M4	20%FCD2+80%AS	1000	5
M5	20%FC+80%AS	1000	5

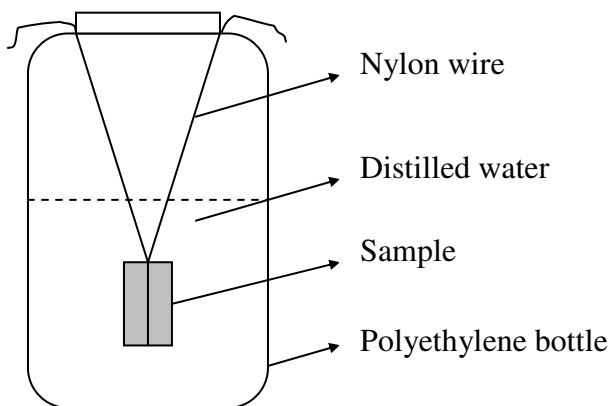
#### 9.3.2 Leaching test

Duplicated sintered samples were immersed into distilled water at  $25 \pm 1^\circ\text{C}$  after being stored for approximately 2 days in a desiccator. The ratio of the surface area of the cylindrical specimens to the volume of leachant (distilled water) was  $1:10 \text{ (cm}^{-1}\text{)}$ . The distilled water was replaced at designed intervals according to [192]:

$$t_n = n^2 t_1 \quad (n = 1, 3, 5, 7, 9, \dots)$$

Where  $t_n$  is the time at the end of the leaching period,  $t_1$  is the time at the end of the first leaching period, where  $t_1 = 1$  hour. The leaching setup of the semi-dynamic experiment is

shown in Figure 9.3. It shows that the cylindrical specimens were suspended using nylon wire in the centre of the leaching solution (distilled water).



**Figure 9.3** Experimental set-up of the leaching test

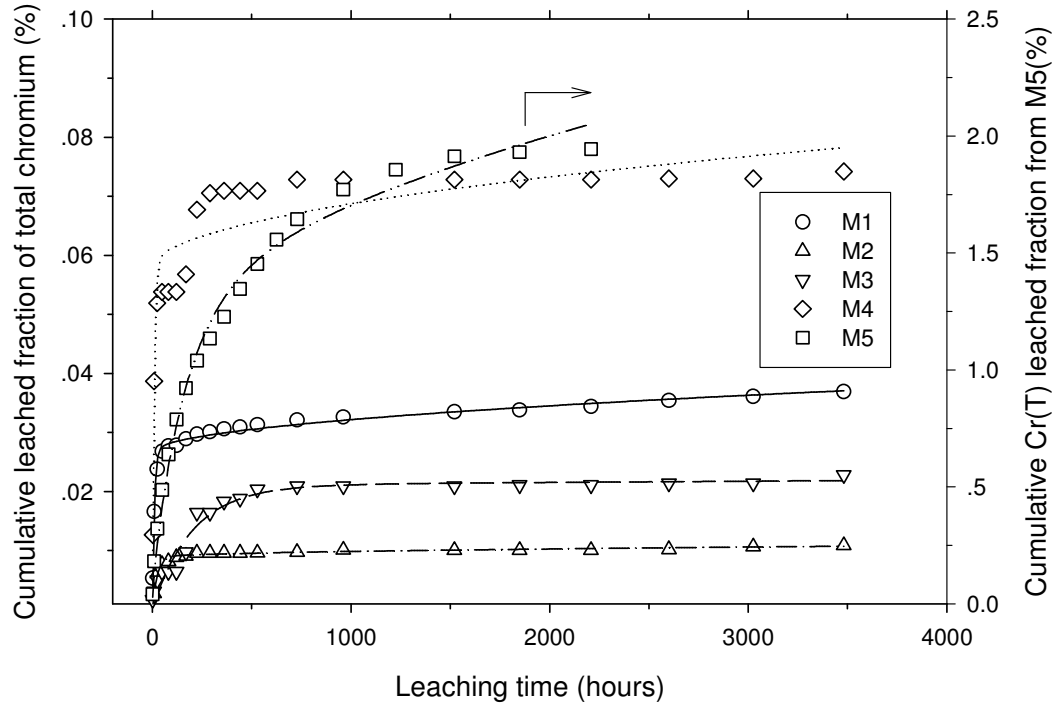
The Cr (VI) and total chromium concentrations in the leachates were analysed with the methods that are described in Appendix I. The pH of the leachate was also recorded.

## 9.4 Results and discussion

### 9.4.1 Leaching mechanisms of chromium from the stabilised product

The cumulative fraction of total chromium that leached from the stabilised waste as well as the model calculation results using function (9.13) is shown in Figure 9.4 (the data are shown in Appendix VI). It shows that the cumulative release fraction of total chromium from samples 50%SPD+50%AS (M1), 50%SPD+50%MR (M2), 20%FCD1+80%AS (M3), 20%FCD2+80%AS (M4) and 20%FC+80%AS (M5) are approximately 0.04%, 0.01%, 0.02% 0.07% and 1.9%, respectively. It indicates that chromium does not readily leach from stabilised wastes. The cumulative leached concentrations of total chromium from stabilised wastes M1, M2, M3 and M4 are 1.91, 0.58, 0.10 and 0.32 ppm respectively (Table VI.1), which are below the acceptable limits for chromium (the acceptable risk level of Cr (III) is 4.7 ppm in South Africa [15]). Sample M5 has an average cumulative leached concentration of 6.9 ppm, and therefore exceeds the acceptable risk level of chromium in South Africa.





**Figure 9.4** Cumulative Cr(T) release and modelling results from the stabilised wastes (M1-50%SPD+50%AS; M2-50%SPD+50%MR; M3-20%FCD1+80%AS; M4-20%FCD2+80%AS and M5-20%FC+80%AS)

By fitting the data to the leach model described by Cote et al. and Shin et al. (function 9.13), coefficients  $k_i$ , where  $i = 1, 2, 3, 4$  and  $5$  were determined, and are listed in Table 9.2. It can be seen from Table 9.2 that the  $k_4$  values are at least 9 orders of magnitude smaller than the  $k_1, k_2$  and  $k_3$  values. By comparing the values of the different terms in function (9.13), i.e.,  $k_1[1-\exp(-k_2t)]$ ,  $k_3t^{\frac{1}{2}}$  and  $k_4t$ , it is therefore clear that according to this model the predominant release mechanisms of total chromium are initial surface wash-off followed by matrix diffusion. It further indicates that the controlling leaching mechanisms of chromium from M1, M2, M3 and M4 change into diffusion control from initial wash off control after approximately 81h, 121h, 81h and 49h, respectively. The average effective diffusion coefficients of chromium from the solidified wastes can be calculated based on function (9.6). These were found to be, respectively,  $2.52 \times 10^{-10}$ ,  $9.73 \times 10^{-12}$ ,  $3.43 \times 10^{-12}$ ,  $9.46 \times 10^{-10}$  and  $3.98 \times 10^{-6}$  m<sup>2</sup>/s for M1, M2, M3, M4 and M5. The

correlation coefficients ( $R^2$ ) of the cumulative release fraction as calculated from the model and the experimental values for leaching experiments M1, M2, M3, M4 and M5 are 0.99, 0.99, 0.96, 0.89 and 0.99, respectively.

**Table 9.2** Controlling leaching mechanisms of total chromium from the stabilised wastes

Sample	$k_1$	$k_2$	$k_3$	$k_4$	Controlling leaching mechanisms
M1	2.65E-02	1.01E-01	1.79E-04	1.68E-14	Wash-off and diffusion
M2	8.82E-03	4.02E-02	3.25E-05	3.49E-15	Wash-off and diffusion
M3	2.06E-02	4.98E-03	2.09E-05	6.55E-15	Wash-off and diffusion
M4	5.77E-02	1.14E-01	3.47E-04	1.89E-13	Wash-off and diffusion
M5	9.94E-01	5.97E-03	2.25E-02	5.74E-12	Wash-off and diffusion

The logarithm of cumulative total chromium release versus logarithm of leaching time of the stabilised wastes are shown in Figure 9.5. It shows that the slopes for samples M1, M2, M3, M4 and M5 are 0.17, 0.28, 0.35, 0.17 and 0.49, respectively. According to De Groot, it means that the controlling leaching mechanisms of samples M1, M2, M3 and M4 are initial surface wash-off because the slope of the regression line is lower than 0.4 [192]. Matrix diffusion controls chromium that leaches from sample M5 since the slope of the regression line is 0.49 which is in the range of 0.4-0.6 [192]. This does not fully agree with the results of the model of Cote et al. and Shin et al. [187,193] (Table 9.2). The deviations from the model results are due to the fact that the latter model can only identify one major leaching mechanism of a species, while the former model can identify the leaching mechanisms of a species during different stages of the leaching process. It is, therefore, recommended that the model of Cote et al. and Shin et al. is used if the leaching process of a species is controlled by two or three different mechanisms.

#### **9.4.2 Leaching mechanisms of Cr(VI) from the stabilised wastes**

The cumulative Cr (VI) releases from the solidified wastes (expressed in  $\text{mg/m}^2$ ) as a function of leaching time, as calculated from equation 9.13 are presented in Figure 9.6

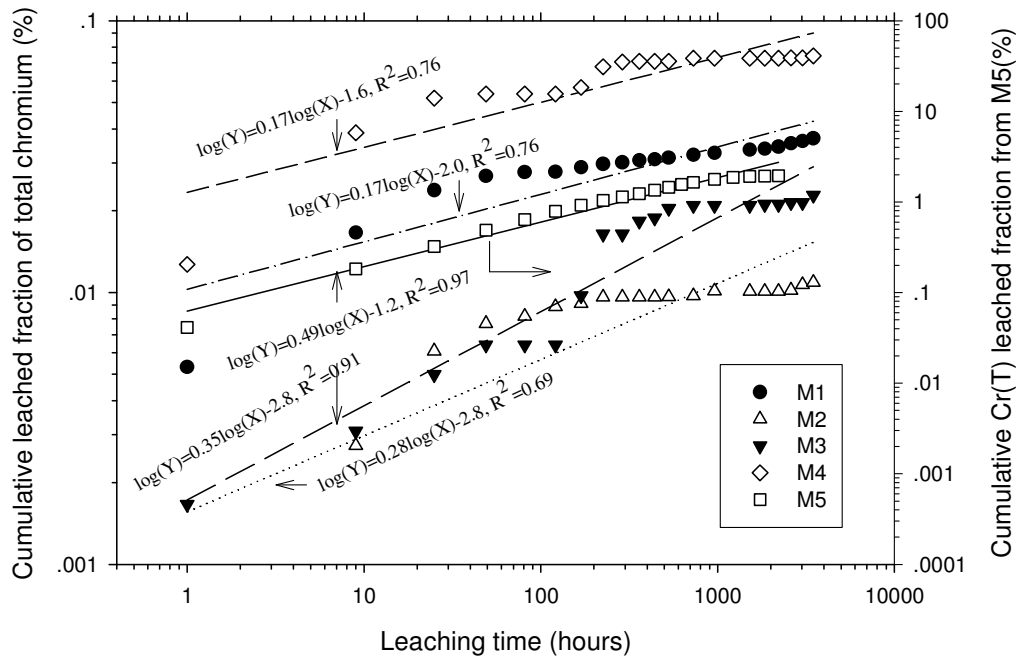


Figure 9.5 Logarithm of cumulative Cr (T) release vs. logarithm of leaching time

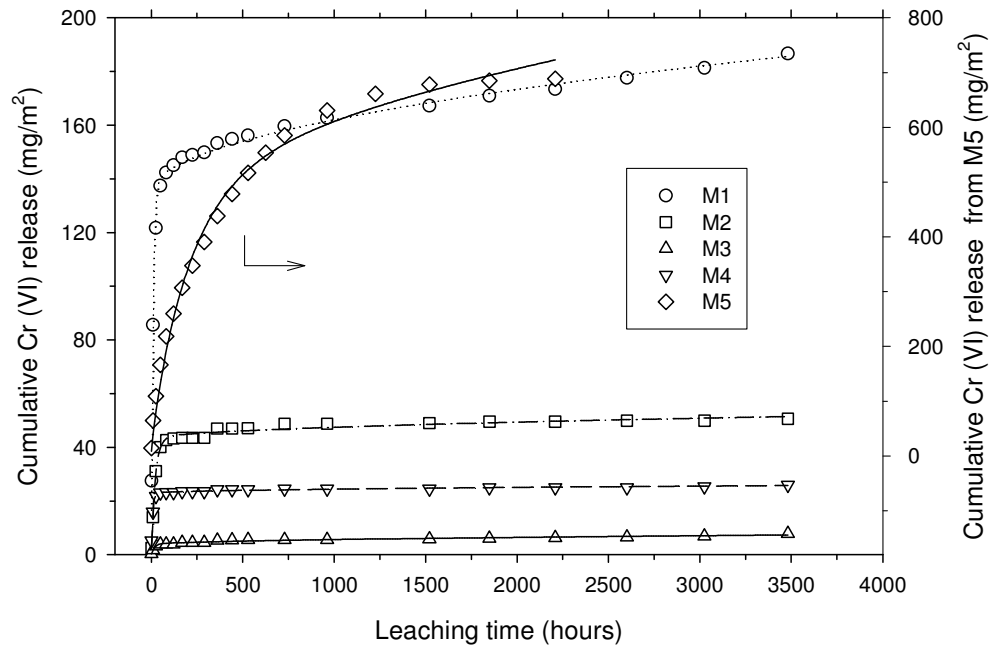


Figure 9.6 Cumulative Cr (VI) release from the solidified wastes (M1-50%SPD+50%AS; M2-50%SPD+50%MR; M3-20%FCD1+80%AS; M4-20%FCD2+80%AS and M5-20%FC+80%AS)

(the data are shown in Appendix VI). Coefficients  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  of this model are given in Table 9.3. It can be seen from Table 9.3 that the  $k_4$  values are at least 7 orders of magnitude smaller than the values for  $k_1$ ,  $k_2$  and  $k_3$ . Cr (VI) therefore leaches from the stabilised wastes through initial wash-off and matrix diffusion. The large amounts of Cr (VI), which leached during the initial stage, are due to wash-off from the surface of the stabilised waste samples. The leaching of Cr (VI) slows down after approximately 81h, 121h, 81h and 49h for samples M1, M2, M3 and M4, respectively. The controlling leaching mechanism of Cr (VI) therefore changes to matrix diffusion. The correlation coefficients ( $R^2$ ) of the cumulative release fraction between model predicted and experimental values for all the leaching experiments are more than 0.97.

**Table 9.3** Controlling leaching mechanisms of Cr (VI) from the stabilised wastes

Sample	$k_1$	$k_2$	$k_3$	$k_4$	Controlling leaching mechanisms
M1	1.35E+02	1.05E-01	8.62E-01	5.13E-11	Wash-off and diffusion
M2	4.28E+01	4.71E-02	1.46E-01	2.38E-11	Wash-off and diffusion
M3	3.67E+00	6.26E-02	6.15E-02	1.09E-12	Wash-off and diffusion
M4	2.28E+01	1.42E-01	5.02E-02	7.25E-12	Wash-off and diffusion
M5	3.88E+02	4.84E-03	7.12E+00	2.52E-09	Wash-off and diffusion

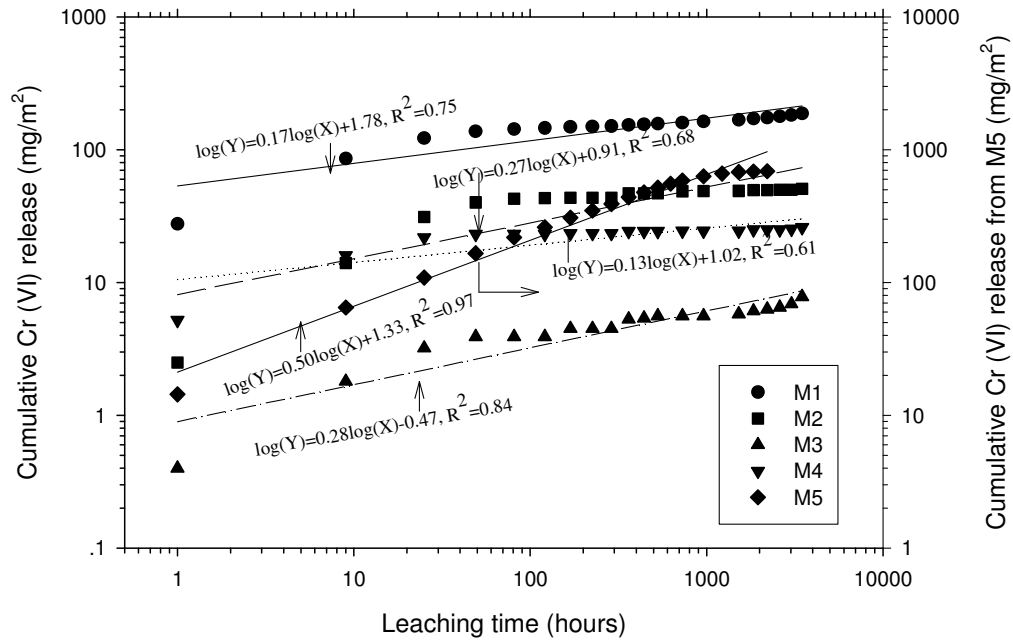
The cumulative leached concentration of Cr (VI) from the stabilised wastes (samples M1, M2, M3, M4 and M5) are 1.87, 0.50, 0.08, 0.26 and 6.80 mg/l, respectively (Table VI.1). According to Kim et al., the solubility of the leaching components influences the cumulative release of the toxic substances [195]. By comparing the cumulative total chromium that leached from the stabilised wastes with the amount of Cr (VI) that leached, it is clear that more than 97.9%, 86%, 80%, 81% and 98.5% of the leachable chromium is in the oxidation state of Cr (VI) for M1, M2, M3, M4 and M5 respectively. This is due to the lower solubility of Cr (III)-containing species (below 0.0026g/l [192,193]), while the Cr (VI)-containing components, such as  $K_2CrO_4$  (629g/l),  $K_2Cr_2O_7$  (49g/l),  $Na_2CrO_4$  (873g/l) and  $CaCrO_4$  (163g/l) [197], are highly soluble.

It is noted that the leachable Cr (VI) concentrations from the stabilised wastes which were sintered in a Muffle furnace are higher than the Cr(VI) that leached from the sintered waste that were sintered in the tube furnace. The leachable Cr (VI) from the stabilised mixture of 50%AS-50%SPD is higher than that from the stabilised mixture of 50%MR-50%SPD. It is also found that the leachable Cr (VI) concentrations from the stabilised wastes exceed the acceptable limits. These are not fully in agreement with the results in Chapter 8. This is possibly due to the variations of the experimental conditions, such as the usage of the purge gas, different heating and cooling rates, leaching time and kinetics conditions.

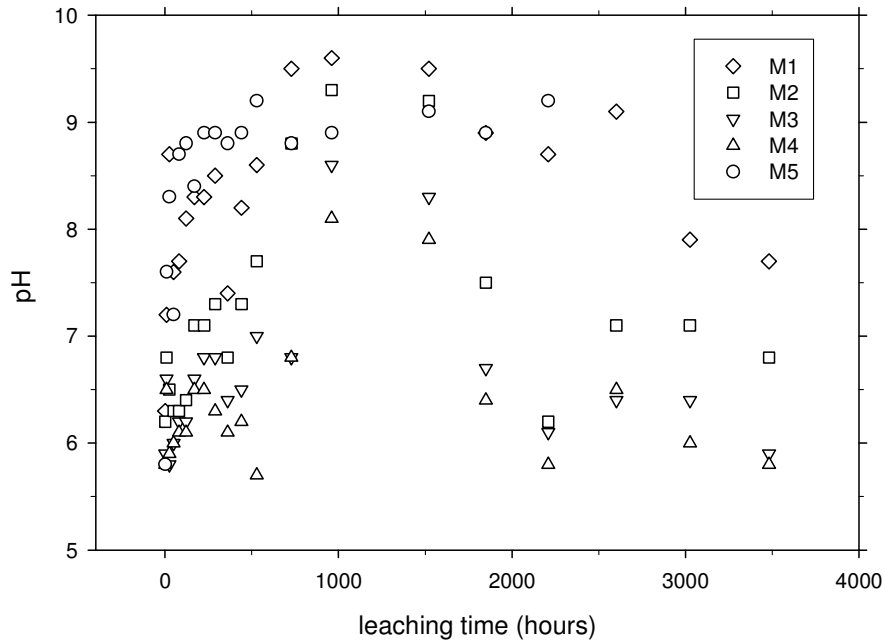
Figure 9.7 shows the logarithm of cumulative Cr (VI) release versus the logarithm of leaching time of the stabilised wastes. The slopes from linear regressions for samples M1, M2, M3, M4 and M5 are 0.17, 0.27, 0.28, 0.13 and 0.50, respectively. It means that leaching of Cr (VI) from samples M1, M2, M3 and M4 is controlled by initial wash-off, while in sample M5 it is controlled by matrix diffusion. It can also be seen from Figure 9.7 that the leachable Cr (VI) from sample M5 is substantially higher than that from the other stabilised wastes. This might be due to the reformation of Cr (VI) during the sinter process since the filter cake contains significant concentrations of calcium oxide, which can react with Cr(III) under oxidizing conditions to form  $\text{CaCrO}_4$  [182].

As discussed in Chapters 7 and 8, the Cr (VI)-containing species can possibly form during the sinter process via oxidation by air or reaction with lime, alkali oxides and oxygen. Cr (III)-containing species, which are close to the surface of the sample, can readily react with oxygen and reform Cr (VI). These Cr (VI)-containing species can easily leach out when they come in contact with the leachant (distilled water). This explains why surface wash-off is the controlling leaching mechanism during the initial leaching period from the stabilised wastes.

The cumulative releases of species, such as chromium, might also be influenced by the pH of the leaching solution [193]. The average pH values of the leachate during the leaching experiments on the stabilised wastes are shown in Figure 9.8. The pH values



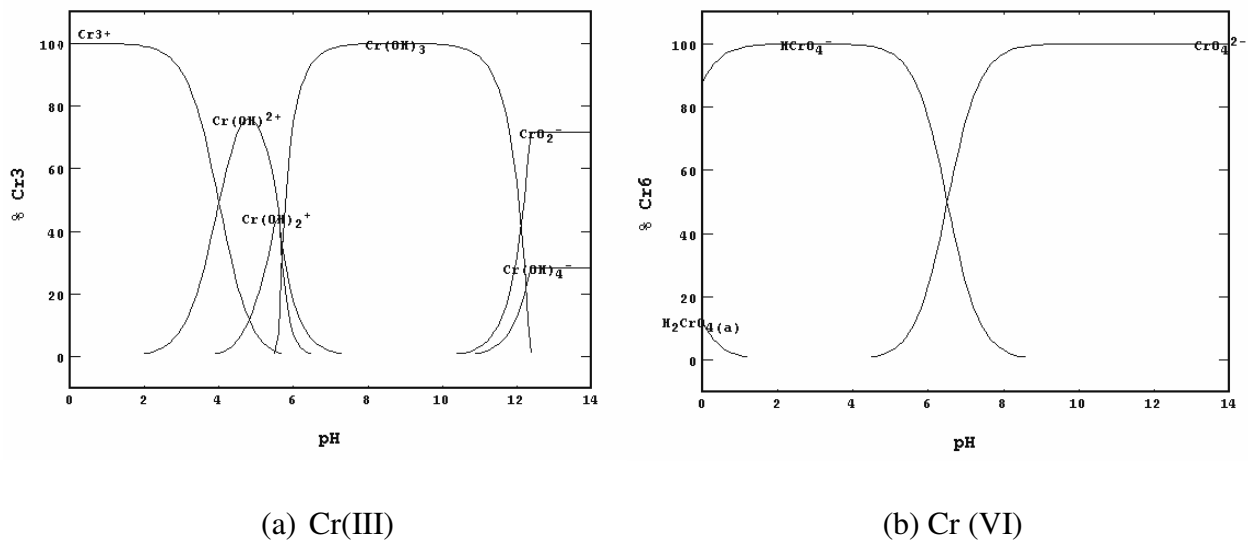
**Figure 9.7** The logarithm of cumulative Cr (VI) release versus logarithm of leaching time of the stabilised wastes



**Figure 9.8** The pH profile of the leachant vs. time during the leaching process

range from 5.8 to 9.6. The pH values of the leachates of samples M1, M2, M3 and M4 initially increased, after which it decreased as the leaching process proceeded. The pH of the sample M5 remained constant after approximately 81 h of leaching.

Figure 9.9 shows the solubility diagrams of chromium species calculated using STABCAL-W32 [181]. It shows that Cr (III) precipitates in the pH range of approximately 5.5 to 12.5, while Cr (VI) would not precipitate in the whole pH range and only change from  $\text{HCrO}_4^-$  and  $\text{H}_2\text{CrO}_4$  to  $\text{CrO}_4^{2-}$ . The pH of the leachate during the semi-dynamic leaching test was in the precipitation range of Cr(III) (Figure 9.8). It therefore indicates that it can influence the leachable total chromium concentration in the leachate, but not the leaching mechanisms of total chromium. It can also explain that more than 80% of chromium in the experiment is Cr(VI).



**Figure 9.9** The solubility diagrams of chromium species calculated using STABCAL-W32 at 25°C with a concentration of  $10^{-6}$  M [181].

## 9.5 Conclusions

Semi-dynamic leaching tests were conducted in order to understand the leaching mechanisms of the chromium species from the stabilised waste forms. Semi-empirical

models from the literature were used to evaluate the dominant leaching mechanisms of the chromium species.

- 1) It shows that the predominant leaching mechanisms of chromium species are initial surface wash-off followed by matrix diffusion.
- 2) Only very small amounts of chromium leaches out from the solidified products. The cumulative release fractions of chromium from the solidified wastes are lower than 2% over a period of approximately 5 months.
- 3) The cumulative leached concentrations of total chromium from stabilised wastes M1, M2, M3 and M4 are less than the acceptable limits for chromium, while the leachable chromium from sample M5 exceeds the acceptable risk level of chromium.
- 4) More than 80% of the leachable chromium from the stabilised products is Cr (VI) species due to the high solubility of Cr (VI) in distilled water.
- 5) The leachable Cr (VI) concentrations from the stabilised wastes which were sintered in a Muffle furnace exceed the acceptable limits, and are higher than from the stabilised wastes that were sintered in a tube furnace. This is possibly due to the variations of the experimental conditions, such as purge gas, heating and cooling rates, leaching time and leaching solution.



## Chapter 10 Summary and Conclusions

The Cr (VI)-containing pyrometallurgical wastes (stainless steel plant dust, ferrochrome dust and filter cake from the waste acid treatment plant) potentially pose a threat to the environment and human health. In South Africa, the ferrochromium industry and the stainless steel industry produces approximately 100,000 t and 24,000 t of Cr (VI)-containing dust per year, respectively [17,39]. It is therefore of great importance to investigate the problem comprehensively and develop an appropriate treatment process.

A number of problems currently hamper the treatment of these wastes, such as the variation in composition of the stainless steel plant dust, significant contents of volatile substances in the ferrochrome dust and sulphur content in the filter cake.

The characteristics and microstructures of these wastes were therefore first investigated in order to fully understand the behaviour of these wastes, and to postulate the formation mechanisms of them. Suggestions are also given on how to reduce the amounts of wastes. The leachability and the aging behaviour of these wastes were then studied in order to further understand the toxic properties of these wastes.

It has been proven that stabilisation/solidification processes are effective technologies, whereby electric furnace dusts can be cemented, glassified and sintered into value added products. In the present thesis, the stabilisation of Cr (VI) in these wastes with silica-rich clay was studied, as well as the leaching behaviour of chromium species from the stabilised wastes. A summary of the results are given and the following conclusions can be drawn:

## 10.1 Summary

### 10.1.1 Stainless steel plant dust (SPD)

The stainless steel plant dust is chocolate-brown in colour, and consists of very fine particles. It has a bulk density of  $1.39\text{gcm}^{-3}$  and low moisture content (0.40%). On leaching in water the examined stainless steel plant dust produces alkaline solutions.

The SPD is iron oxide, chromium oxide and CaO rich, but also contains some MgO, MnO, SiO<sub>2</sub>, ZnO and nickel. The main phases that are present in the SPD are the (Mg,Fe,Mn,Cr)<sub>3</sub>O<sub>4</sub> spinel phase, quartz, Ca(OH)<sub>2</sub> and nickel. TG/DTA analysis in air indicated that mass losses and gains occur during heating of SPD due to reactions in which H<sub>2</sub>O and CO<sub>2</sub> are driven off, and metallic particles oxidize.

A microstructural examination of the SPD showed that the stainless steel plant dust contains particles that are irregular in shape, spherical or near spherical particles and particles coated with slag or oxides.

TCLP and ASTM 3987-85 tests show that stainless steel plant dust is a hazardous material due to the fact that the leachable Cr(VI) from SPD exceeds the limit of South Africa on Cr(VI). It is therefore pose a potential threat to the environment. Distilled water leaching experiments on the stainless steel plant dust showed that approximately 65% of the Cr (VI) leaches out within 5 min, but that the Cr (VI) leaches out more easily in acidic and basic solutions than in distilled water. Furthermore, 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 reactions whereby Cr (III) is transformed into Cr (VI).

Aging experiments on the SPD show that the extractable amount of Cr (VI) from the SPD decreases with increasing aging time, possibly due to the reduction reaction of Cr (VI) into Cr (III) by Fe (II)-containing phases. The extractable amount of Cr (VI) from the SPD increases with decreasing particle size. Higher water vapour content in the atmosphere tends to increase the extractable amounts of Cr (VI) from the SPD.

Cr (VI) in the stainless steel plant dust can be stabilised by mixing stainless steel plant dust with clay, and sintering it at 1100°C for 5 hours. Decreasing sinter temperature, increasing waste content in the brick and reducing sinter time increase the leachability of Cr (VI) from the stabilised stainless steel plant dust. Increasing mass %CaO/mass %SiO<sub>2</sub> ratios and alkali oxides contents in the SPD-clay mixtures significantly increase the leachable Cr(VI) from the brick due to the formation of Cr (VI)-containing phases, such as CaCrO<sub>4</sub> and alkali chromates. The spiked Cr (VI) recovery decreases with increasing leaching time in the modified TCLP test, probably due to the fact that Cr (VI) is reduced into Cr (III) by Fe<sup>2+</sup> and organic components.

In South Africa, the TCLP test is generally used to evaluate whether hazardous wastes are environmentally acceptable. The Cr (VI) concentrations in the leachate when the sintered bricks were examined with the modified TCLP test are below 10 ppb in this study, which is environmentally acceptable in South Africa. However, the leachable Cr (VI) in the leachates of the modified ASTM D 3987-85 test is higher than that in the modified TCLP test and still considered to be a potential threat to the environment and human health. This is due to the effects of redox potential and pH of the leachates, Fe<sup>2+</sup> and organic components.

When Cr (VI) in the stainless steel plant dust is stabilised with clay in a sinter process, other toxic substances such as As, Zn and Pb are also stabilised. The emission factor from the stabilised SPD mixtures is similar to that of the cement industry.

The semi-static leaching experiment showed that the predominant leaching mechanisms of chromium species from the stabilised SPD are initial surface wash-off followed by matrix diffusion. Only very small amounts of chromium leaches out from the solidified SPD, and it is less than the acceptable limits for chromium. Approximately 98% of the leachable chromium from the stabilised SPD is Cr (VI). However, the leachable Cr (VI) concentrations from the stabilised SPD which was sintered in a Muffle furnace exceed the acceptable limits. This must be due to variations in the experimental conditions, such

as type of purging gas, heating and cooling rates, leaching time and type of leaching solution.

### ***10.1.2 Ferrochrome plant dust (FCD1, FCD2 and FCD3)***

The ferrochrome dusts are fine particles, have bulk densities that vary between 0.49 and 2.42gcm<sup>-3</sup>, and have low moisture contents. Ferrochrome fine dusts (FCD1 and 2) generate slightly basic solutions (pH≈8), while ferrochrome coarse dust (FCD3) produces strong basic solutions (pH≈11).

The FCD1 and 2 contain significant concentrations of SiO<sub>2</sub>, ZnO, MgO and alkali metal oxides, but also some sulphur and chlorine, while FCD3 is SiO<sub>2</sub>-chromium oxide-iron oxide-Al<sub>2</sub>O<sub>3</sub>-MgO-C-based. The main phases present in the coarse fraction of ferrochrome dust are chromite, partly altered chromite, quartz and carbon, while the main components of the fine fractions include chromite, SiO<sub>2</sub>, ZnO, NaCl and Mg<sub>2</sub>SiO<sub>4</sub>. TG/DTA analysis in air indicated that mass losses occur during heating of ferrochrome dusts due to the combustion of carbon, loss of crystalline water and vaporisation.

Ferrochrome fine dusts consist of clusters which contain charge materials, slag droplets as well as very fine SiO<sub>2</sub>-MgO-ZnO-(Na,K)<sub>2</sub>O based particles. The coarse particles consist of reductant, slag droplets and chromite particles. It is also assumed that Cr (VI)-containing species in ferrochrome dust are generated at the top of the SAF or in the off-gas duct, as Cr (VI) is found on the surface of the dust.

TCLP and ASTM 3987-85 tests show that ferrochrome fine dusts are also hazardous materials according to South African legislation. They therefore pose a potential threat to the environment and human health. 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 of vaporisation substances such as ZnO and NaCl. Distilled water leaching experiments on ferrochrome dusts show that Cr (VI) is easily leached by distilled water.

Cr (VI) in ferrochrome fine dusts that were sintered with 50% clay AS at 1000°C for 5 hours could not be stabilised, as the concentrations of zinc and/or Cr (VI) from the stabilised wastes in the modified TCLP and ASTM D 3987-85-tests exceed the regulation limits. The emission factors from the stabilised ferrochrome fine dusts (FCD1 and FCD2) are however very low (0.2-1g/t brick), and below the chromium emission factors from the cement industry.

The predominant leaching mechanisms of chromium species from the stabilised ferrochrome fine dusts are initial surface wash-off followed by matrix diffusion. The cumulative release fraction of total chromium from the solidified products are lower than 0.1% and less than the acceptable limits for chromium.

### ***10.1.3 Filter cake (FC)***

The original filter cake consists of very fine particles, and typically has a moisture content of 50%. Filter cake produce alkaline solutions when leached in water. The concentrations of calcium, fluorine, iron and sulphur are high in the filter cake. The major phases present in the filter cake is  $\text{CaF}_2$ ,  $\text{CaSO}_4$ ,  $\text{CaCO}_3$  and a metal rich (Fe, Cr and Ni) amorphous oxide phase. TG/DTA analysis in air indicated that mass losses and gains occur during heating of these waste materials due to reactions in which  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ , fluorine, calcium and silicon are driven off.

TCLP and ASTM 3987-85 tests showed that filter cake is a hazardous material according to South African legislation. Distilled water leaching experiments on the filter cake showed that Cr (VI) is easily leached by distilled water.

By examining the aging behaviour of Cr (VI) in the filter cake it is clear that increasing temperature favours the oxidation of Cr (III) into Cr (VI). However, the extractable amount of Cr (VI) from the FC decreases with increasing aging time, possibly due to the reduction of Cr (VI) into Cr (III) by trace amounts of Fe (II)-containing phases. The extractable amount of Cr (VI) from FC increases with increasing particle size. The water

vapour and oxygen content in the atmosphere has no significant effect on the amount of extractable Cr (VI) from the filter cake.

An attempt was made to stabilise Cr(VI) in the filter cake by sintering a 50wt% AS-50wt% filter cake mixture at 1000°C for 5 hours. The modified TCLP test indicated that the FC could not be stabilised with clay, presumably due to significant levels of CaO/CaCO<sub>3</sub> and CaF<sub>2</sub> in the mixture.

A semi-dynamic leaching test on the stabilised filter cake showed that the predominant leaching mechanisms of chromium species are initial surface wash-off followed by matrix diffusion. The cumulative release fractions of total chromium and chromium (VI) exceed the acceptable limits.

## **10.2 Conclusions**

- Stainless steel dust is postulated to form by the entrainment of charge materials, evaporation or volatilisation of elements and ejection of slag and metal by spitting or the bursting of gas bubbles.
- Ferrochrome dusts are formed by the ejection of slag and metals droplets from the electrode hole, the entrainment of charge materials, vaporisation as well as the formation and precipitation of compounds from vaporised species in the off-gas duct.
- The crystalline phases (CaF<sub>2</sub> and CaSO<sub>4</sub>) are generated in the neutralisation and reduction steps of the production process due to super saturation, while the metal rich amorphous phases are generated in the precipitation step.
- Due to the significant concentrations of Cr(VI) in 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.
- Cr (VI) in the stainless steel plant dust can be stabilised by mixing stainless steel plant dust with clay, and sintering it at 1100°C for 5 hours.

- Sintering temperature, sintering time, sinter atmosphere, initial Cr(VI) concentration, waste:clay ratio, mass %CaO/mass %SiO<sub>2</sub> ratios and alkali oxides contents in the bricks influence the Cr(VI) formation. It is postulated that Cr (VI) form when the (Mg,Fe,Mn,Cr)<sub>3</sub>O<sub>4</sub> spinel phase, alkali oxides, Ca-containing phases such as Ca(OH)<sub>2</sub>, CaO, CaCO<sub>3</sub> and CaF<sub>2</sub> react both at ambient and at high temperatures (1100°C).
- The filter cake could not be stabilised with clay at high temperature (1000°C), presumably due to significant levels of CaO/CaCO<sub>3</sub> and CaF<sub>2</sub> in the mixture.
- It is recommended that ASTM D 3987-85 test is used to evaluate the degree of toxicity of the sintered bricks.
- A semi-dynamic leaching test on the stabilised wastes showed that the predominant leaching mechanisms of chromium species are initial surface wash-off followed by matrix diffusion.

### **10.3 Recommendations for future work**

#### ***10.3.1 Modelling of the formation mechanisms of Cr (VI)***

The formation mechanisms of Cr (VI) species in the steelmaking and ferrochrome-making processes are still not completely understood as these processes are complex. Since Cr (VI) cannot form in the furnace where reducing conditions prevail, it would be meaningful to model the behaviour of the off-gases from the furnace to the baghouse filter by using thermodynamic calculation software such as FACTSage. Such a model could predict where and how Cr (VI) and other toxic substances form, but also assist in the design of the off-gas duct.

#### ***10.3.2 Simultaneous treatment of stainless steel plant dust and pickling acid***

By minimising waste generation in a steelmaking plant, one waste material is often used to treat another waste. In the present project, it was found that the pH of the stainless steel plant dust is approximately 12, while the waste pickling acid has a pH of approximately 1. In addition, the stainless steel plant dust has a reduction capacity for Cr (VI) species, and it is expected that the concentration of Fe<sup>2+</sup> would increase if the SPD is dissolved in the waste pickling acid. For the waste pickling acid, SPD might therefore be a potential

neutraliser and act as a reductant of Cr (VI). Less lime and ferrous sulphate would then be required to neutralise the acid and reduce Cr (VI) in the pickling acid. Furthermore, less sulphur would be introduced into the process due to the fact that no or less ferrous sulphate is added to reduce Cr (VI). The current filter cake production process can be used to treat the reaction product between the stainless steel plant dust and waste pickling acid. The precipitate of the process can then further be treated by either recovery or a stabilisation process. Such a simultaneous treatment process needs to be evaluated in detail.

### ***10.3.3 Properties of the bricks***

In this study, bricks were produced from mixtures of stainless steel dust and clay. These bricks can potentially be used for low cost housing, as the leachability of Cr (VI) from the bricks is under the regulatory limits. However, other properties of the bricks, such as density, apparent porosity, shrinkage during firing and cold crushing strength, need to be evaluated in order to determine whether these bricks can be used for such an application.