

Chapter 6 The aging behaviour of Cr (VI)-containing Electric furnace dust and filter cake from a stainless steel waste treatment plant

6.1 Introduction

Chromium exists in various oxidation states, the most stable ones being Cr (III) and Cr (VI). In soil and aqueous solutions, numerous authors reported that Cr (VI) can easily be reduced into Cr (III) by Fe (II) via reaction 6.1, S²⁻ or organic components at room temperature [151,152].



Peterson et al. reported that Cr (VI) in the contaminated soil samples can be reduced into Cr (III) by Fe²⁺-bearing slag or minerals, such as magnetite (Fe₃O₄), ferrous containing goethite [FeO(OH)], biotite [K(Mg,Fe²⁺)₃(Al,Fe³⁺)Si₃O₁₀(OH,F)₂] and pyrite (FeS₂) [153-156].

On the other hand, Cr (III) can also be oxidised into Cr (VI) by either MnO₂, or in the presence of lime and oxygen either at ambient or high temperatures according to reaction (6.2) [38,157,158].



The oxidation mechanism of Cr₂O₃ by lime particles is schematically shown in Figure 6.1 [158]. It shows that the oxidation reaction occurs on the boundary between Cr₂O₃ and lime particles. The Cr (III) oxidation reaction can be restricted by minimising the total exposure grain area and oxygen diffusion [158].

As discussed in the previous chapter, the electric furnace dust and filter cake are classified as hazardous wastes based on the significant Cr (VI) in the leachates from the TCLP and ASTM D3987-85 tests. However, these Cr (VI)-containing wastes contain free lime particles as well as Fe²⁺-bearing components. Since the leachability of Cr (VI) from these wastes influences its treatment policy, it is very important to study the aging behaviour of Cr (VI) in these wastes. Moreover, the experimental results can also serve as

guidelines on the management of other Cr-containing pyrometallurgical wastes, such as ferrous slag and waste refractories.

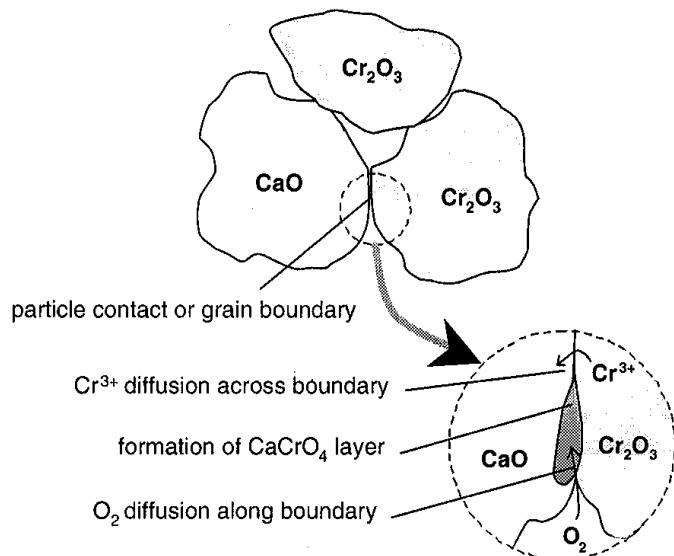


Figure 6.1 Oxidation mechanism of Cr_2O_3 by CaO in air [158]

In this chapter, the leaching behaviour of Cr (VI) from the electric furnace dust and filter cake over 4 months is discussed. The synthetic mixtures of Cr_2O_3 and CaO were also prepared to confirm the oxidation of Cr (III) into Cr (VI) in the presence of lime at ambient atmosphere and temperature.

6.2 Experimental

6.2.1 Sample preparation

Two pyrometallurgical wastes were used in this study, i.e., stainless steel plant dust (SPD) and filter cake (FC). The original filter cake contains significant moisture (typically 50%). It was dried at 110°C, crushed and ground. Representative waste powder samples were taken using a splitter. Approximately 25 g sub-samples were then taken and contained in a plastic boat. These samples were then stored in a room with a controlled temperature of 20 ± 2 °C. The influence of several parameters on the oxidation or reduction of chromium were examined: (1) pellets vs. powdered samples, (2) temperature, (3) particle size of the wastes, and (4) atmosphere (the contents of water vapour and oxygen).

The pellets were prepared from the powdered wastes using a stainless steel die with a diameter of 40 mm at 5 kN force using a hydraulic press for 5 minutes.

Two temperatures were examined in this study, i.e. $20\pm2^{\circ}\text{C}$ and $30\pm1^{\circ}\text{C}$. For the aging experiment at $30\pm1^{\circ}\text{C}$, the powdered samples were contained in plastic boats. They were then put on a water bath which was controlled at $30\pm1^{\circ}\text{C}$ during the aging experiment.

To study the effect of particle size on the leaching behaviour of Cr (VI), three ranges of particles sizes were selected, i.e., -53um, +53um-106um and +106um. The powdered waste samples were sieved and splitted into small batches which served as representative samples for the aging experiments.

The effect of atmospheric conditions on the leaching behaviour of Cr (VI) at $20\pm2^{\circ}\text{C}$ was also examined. This was done by storing several sets of samples under dry air, water-saturated air, dry Ar gas and water-saturated Ar gas. Under conditions of a “dry air atmosphere”, the waste samples were stored inside desiccators that contained silica gel at the bottom of the desiccators. If distilled water was contained at the bottom of the desiccators, the condition of so-called water-saturated air was created. For the dry Ar gas environment, silica gel was put into the bottom of the desiccators, after which they were sealed with high vacuum grease and dry argon gas with a purity of 99.999% purged through the desiccators. If distilled water was contained at the bottom of the desiccators, the environment was the so-called water-saturated argon gas.

In order to better understand the effect of lime on the oxidation behaviour of Cr (III) in the wastes, the synthetic powder mixtures of Cr_2O_3 and CaO were prepared. The Cr_2O_3 was first washed with a 1 mol/l NaOH solution for 4 hours and twice filtered by distilled water in order to reduce the residual Cr (VI) in the Cr_2O_3 powder. The molar ratios of Cr_2O_3 to CaO were chosen to be the same as the ratio in the filter cake and steel plant dust.

6.2.2 Leaching experiment and analysis methods

All the waste samples were analysed, using a modified TCLP test. This “modified” TCLP test differs from the standard TCLP test in that approximately 25 g samples were used, instead of 100 g samples. Some of the analyses were duplicated. Cr (VI) in the waste samples were extracted with glacial acetic acid solution (TCLP solution 2) using a 1:20 ratio of solid to leachant, and an end-over-end rotator at 30 rpm (Figure 6.2) at 20 ± 2 °C. The leachants were subsequently sampled and filtered using a Millipore membrane filter with a pore size of 0.22um.



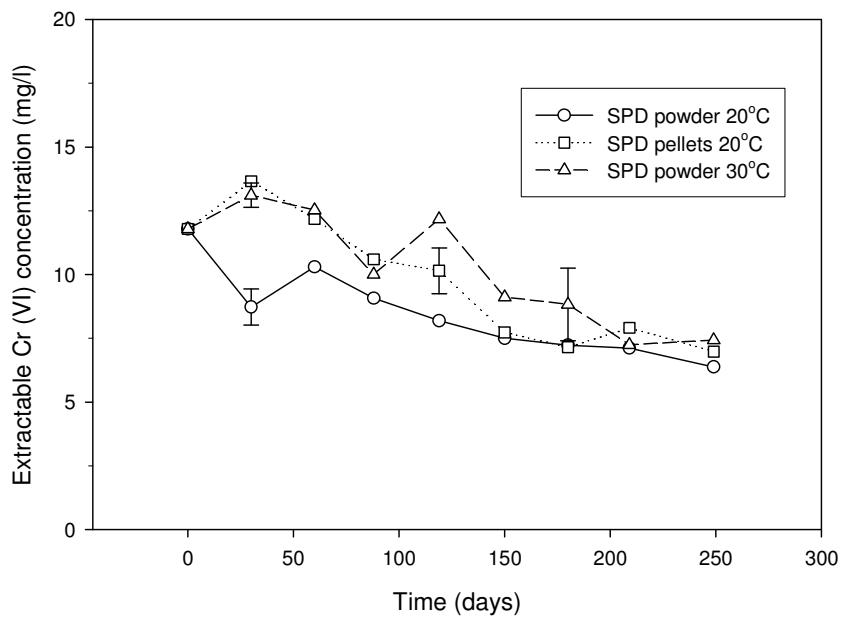
Figure 6.2 Experimental setup of the modified TCLP test

The extractable Cr (VI) was determined with a Perkin Elmer Lambda 25 UV/Vis Spectrometer at a wavelength of 542nm (The analytical method is given in Appendix I). Calcium containing phases in samples of different particles size fractions were semi-quantitatively determined using a Siemens D-501 XRD.

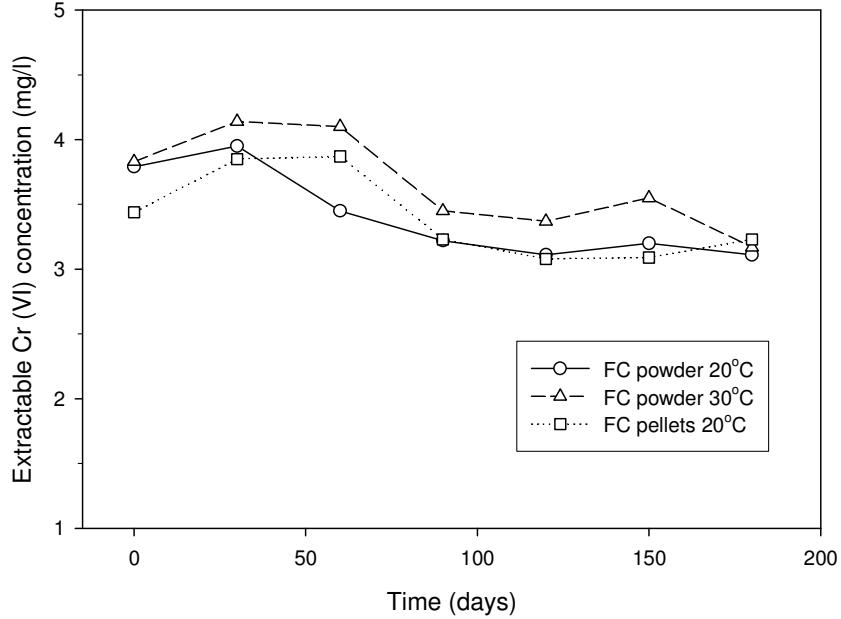
6.3 Results

6.3.1 Effects of temperature and time on the aging behaviour of Cr (VI)

Increasing temperature promotes the extraction of Cr (VI) (Figure 6.3a and 6.3b). This agrees with data from the literature [38,159]. The amount of extractable Cr (VI) is higher when the SPD is pelletised, than when it remains in powder form. The same trend was



(a) SPD



(b) FC

Figure 6.3 Effects of temperature and aging time on the leaching behaviour of Cr (VI)

not observed for the FC. It is also noted that the extractable Cr (VI) in the wastes decreases with increasing aging time, possibly due to the reducing reaction 6.1.

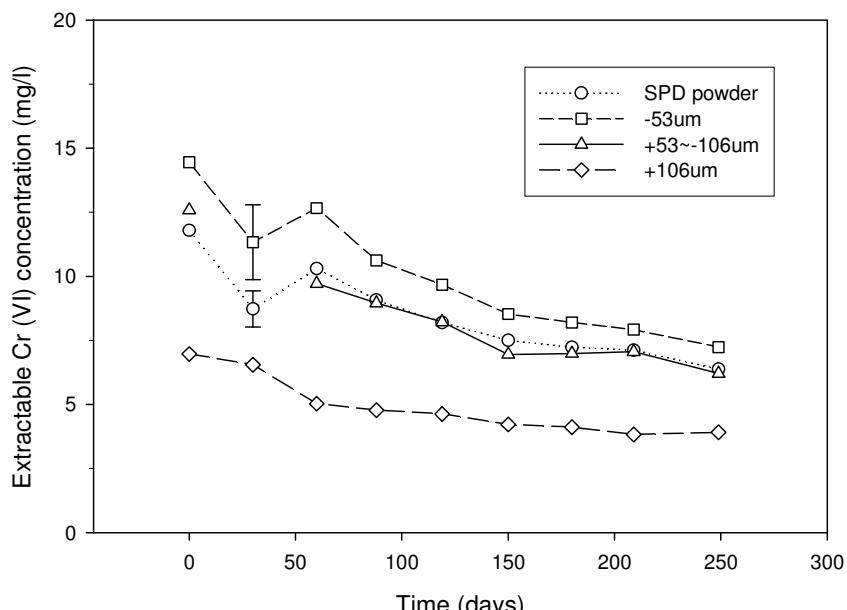
6.3.2 Effect of particle size of the wastes on the aging behaviour of Cr (VI)

The effect of particle size of the waste on the extractable Cr (VI) concentration is shown in Figure 6.4. It shows that the extractable Cr (VI) content increases with decreasing particle size in the SPD, while it increases with increasing particles size of the FC. The Cr (VI) which is extractable from the stainless steel plant dust and filter cake seems to remain constant after 5 months (150 days) and 3 months (90 days), respectively.

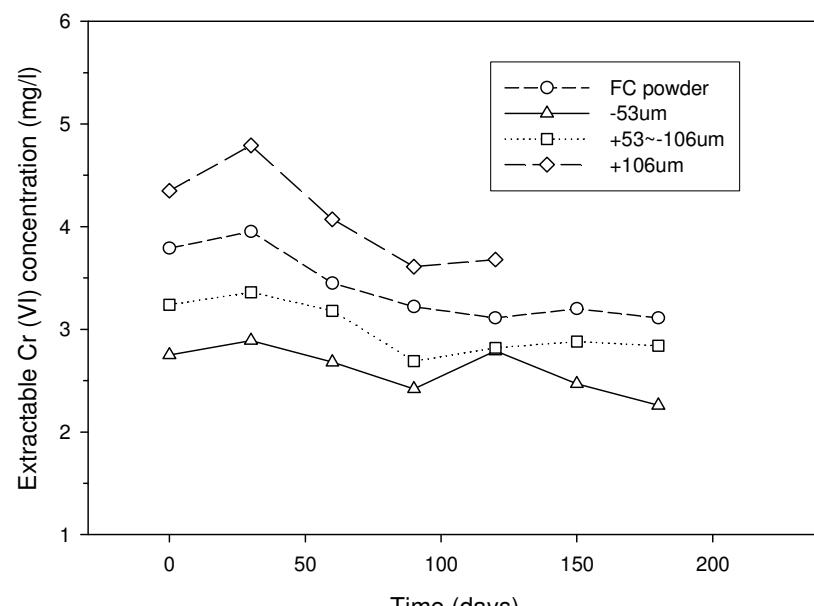
Figure 6.4 also shows that most of the extractable Cr (VI) comes from particles smaller than 53 µm in the SPD, while particles larger than 106 µm in the FC shares about 66 wt% of the leachable Cr (VI) in FC. It is also found that the extractable Cr (VI) in the wastes decreases with increasing aging time. After 8 months (approximately 240 days), approximately 44 %, 51% and 51 % of the extractable Cr (VI) in the SPD were decreased in the particles larger than 106 µm, the particles between 53 µm and 106 µm and the particles smaller than 53 µm, respectively. However, the reduction in the amount of extractable Cr (VI) in the FC was less (approximately 20%), presumably due to the relative low concentrations of Fe (II) in the FC.

6.3.3 Effect of atmosphere on the aging behaviour of Cr (VI)

The results are shown in Figure 6.5. The error bars are due to the increasing of the samples mass which absorbed water vapour during the aging experiment. It indicates that the extractable Cr (VI) from the SPD samples that were stored under the water-saturated conditions is higher than that of the samples that were stored under dry conditions, whereas the extractable Cr (VI) from the SPD samples that were stored in dry air is lower than that of the samples that were stored in dry Ar (Figure 6.5a). The extractable Cr (VI) from the SPD samples that were stored in water-saturated air is similar to that of the samples that were stored in water-saturated Ar (Figure 6.5a). Furthermore, it seems that there is no significant difference for the FC samples under different partial pressure and different water vapour content during the aging experiment (Figure 6.5b). The influence

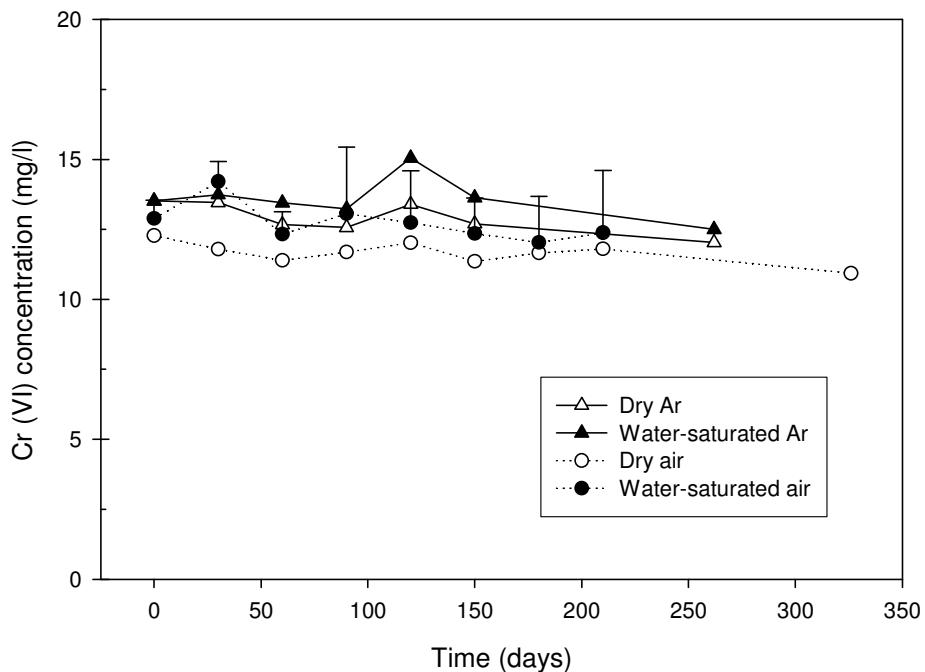


(a) SPD

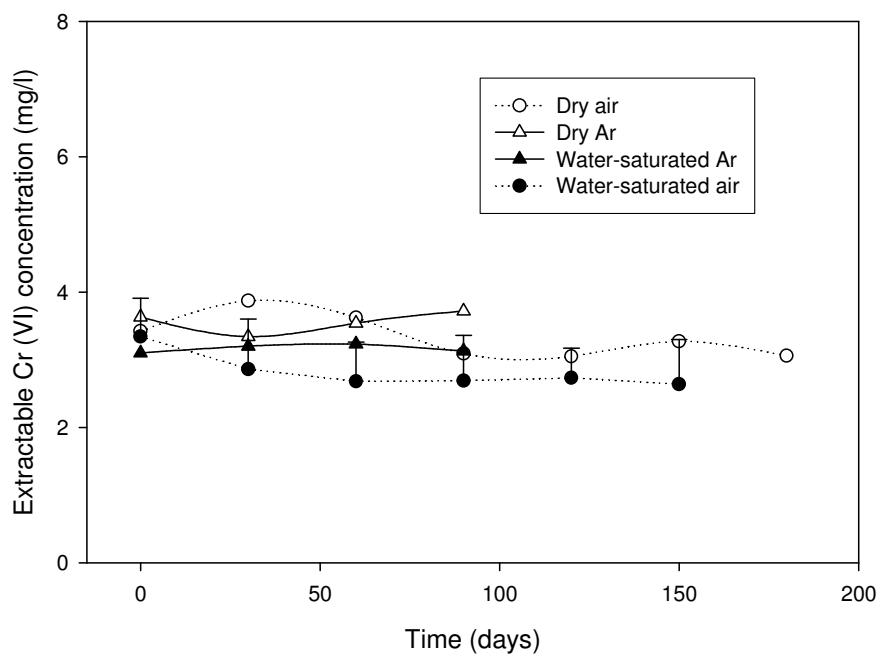


(b) FC

Figure 6.4 Effect of particle size of the wastes on the Cr (VI) aging behaviour



(a) SPD



(b) FC

Figure 6.5 Effect of atmosphere on the Cr (VI) aging behaviour

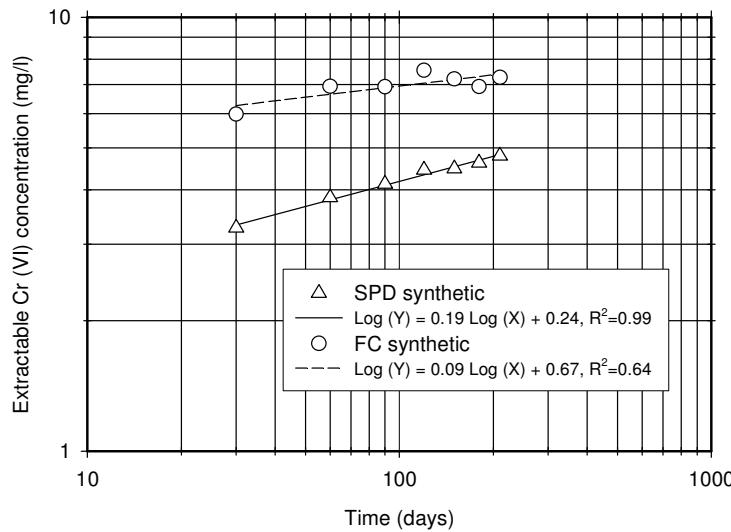
of partial oxygen pressure and water vapour content on the extractable amount of Cr(VI) from the FC could not unequivocally be determined, presumably due to the low concentrations of chromium in the FC.

6.4 Discussion

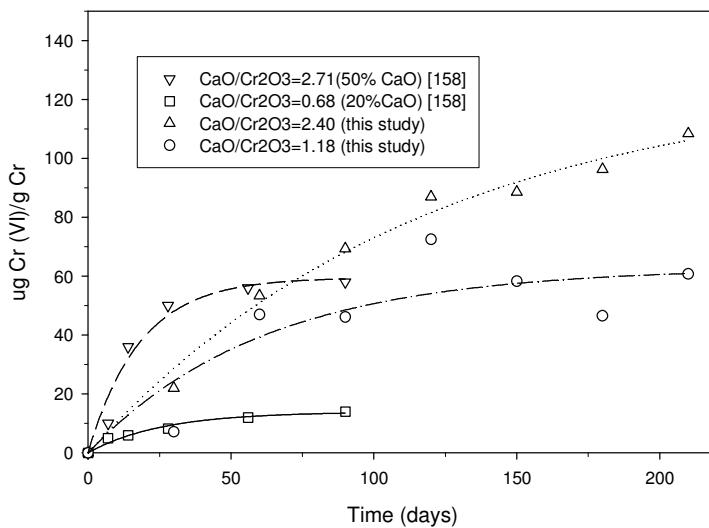
Both reactions 6.1 and 6.2 can possibly happen during the aging period since both SPD and FC contain Fe^{2+} and calcium bearing phases (calcium hydroxide and calcium fluorite in the case of SPD and free lime particles and calcium fluorite in the case of FC, Chapter 3). Chemical analysis also showed that 5.49 wt% Fe(II) is present in the SPD, possibly in the spinel phases $[(\text{Fe},\text{Mg},\text{Mn})(\text{Fe},\text{Cr})_2\text{O}_4]$. It is also believed that trace amounts of Fe (II) (below 0.01%) are present in the FC. In this study, calcium containing phases, such as CaO , CaCO_3 , CaF_2 and $\text{Ca}(\text{OH})_2$, and Fe^{2+} bearing components are considered to play significant roles in the aging behaviour of Cr (VI). However, the reported rates of these two reactions are significantly different. Cr (III) can slowly be oxidised into Cr (VI) in the presence of lime at ambient conditions [38], while it is fast for Fe (II) to reduce Cr (VI) at room temperature to Cr (III), especially in aqueous solution [152].

In order to confirm the conversion of Cr (III) by lime in the wastes under oxidising atmospheres, two synthetic mixtures of Cr_2O_3 and CaO were prepared, one with a CaO mol%/ Cr_2O_3 mol% ratio of 2.40 (similar to the SPD) and one with a CaO mol%/ Cr_2O_3 mol% ratio of 1.18 (similar to the FC). Figure 6.6a shows the results of the aging experiment for the synthetic samples. It clearly shows that the extractable Cr (VI) concentration increases with time. It is further confirmed that Cr (III) can be oxidised into Cr (VI) in the presence of lime. The linear regression analysis of the experimental data shows that the slope of the extractable Cr (VI) versus time curve for the synthetic SPD is higher than that of the synthetic FC. It therefore indicates that Cr (III) is more easily oxidised in the samples with the higher molar ratio of CaO to Cr_2O_3 , for the same oxidation period. It means that the $\text{CaO}/\text{Cr}_2\text{O}_3$ molar ratio has a significant influence on the oxidation of Cr (III) to Cr (VI) in the presence of lime. The results are very similar to

the results of Pillay et al. who respectively used mixtures of 50 wt% CaO and 20wt% CaO and Cr₂O₃ in air (Figure 6.4b) [158].



(a) The oxidation of Cr₂O₃ by CaO in air at 20°C (synthetic samples)



(b) Effects of CaO/Cr₂O₃ mole ratio on the oxidation of Cr₂O₃

Figure 6.6 The oxidation of Cr₂O₃ by CaO particles in air at 20°C (synthetic samples)

(a) and effects of CaO/Cr₂O₃ mole ratio on the oxidation of Cr₂O₃ (b)

If it is assumed that the reaction between CaO and Cr₂O₃ particles proceed as is shown in Figure 6.1 [158], it can be expected that this reaction would slow down as time

progresses. This can explain why the extractable Cr (VI) from SPD and FC remain constant after 5 months (150 days) and 3 months (90 days), respectively. Moreover, larger reaction surfaces are present in the pellets and therefore, more extractable Cr (VI) should exist. Increasing temperature promotes the diffusion of the reactants and the rates of the chemical reactions, and should therefore increase the formation of Cr (VI). This is in agreement with the experimental results (Figure 6.3).

The synthetic experiments suggest that Cr (III) species in the SPD and FC would be oxidised into Cr (VI), since they contain CaO/CaCO₃ or Ca(OH)₂. In addition, fluorite (CaF₂) also plays a role in the formation of Cr (VI) which is similar to CaO [160]. It is therefore expected that the extractable Cr (VI) concentration should increase during the aging experiment. However, the effects of CaO/CaCO₃ or Ca(OH)₂ and CaF₂ cannot only be considered because the SPD and FC are complex systems. Figures 6.3a and 6.3b show that the extractable Cr (VI) in the SPD and FC decrease with increasing aging time. It implies that a reduction reaction occurs during the aging experiment. It is believed that Fe (II)-containing phases, such as spinel phases in the SPD and trace amounts of ferrous bearing components in the FC, play significant roles in reducing the amount of Cr (VI) from the SPD and FC during the aging experiment. However, no efforts were made to confirm this assumption.

As shown in Figure 6.4, most of the extractable Cr (VI) comes from particles smaller than 53 µm in the SPD, while particles larger than 106 µm in the FC shares about 66 wt% of the leachable Cr (VI) in FC. This is possibly due to the different distribution of Cr(VI) in these wastes. For SPD, Cr(VI) was formed due to the change of oxygen potential in the off-gas duct, flaring of the dust particles and the presence of alkali elements [65]. It is expected that more Cr(VI) can be formed in the smaller fractions of SPD due to the better kinetics conditions for the smaller particles of SPD, such as larger surface area, and higher concentrations of alkali metals than the larger fractions of SPD (7.1% in -53µm of SPD vs. 3.8% and 3.5% in 53-106µm and +106µm of SPD, respectively) (Table 6.1). Therefore, it leaches more Cr(VI) in the small fractions of SPD than the other two fractions of SPD. This is agreement with the results (Figure 6.4). However, the leachable

Cr(VI) is mainly influenced by the ratio of Ca-containing phases to Cr_2O_3 and Fe(II)-bearing species during the aging experiment. It can be expected that more Cr(VI) can be formed in the +106 μm fractions in SPD during the aging experiment due to the higher ratio of Ca-containing phases to Cr_2O_3 in the +106 μm of SPD (0.41 in +106 μm of SPD vs. 0.16 and 0.14 in +53-106 μm and -53 μm of SPD, respectively) (Table 6.2). Considering the role of Fe(II) species, it means that less decrease of the leachable Cr(VI) in +106 μm of SPD during the aging experiment (3.0mg/l in +106 μm of SPD vs. 6.4mg/l and 7.2mg/l in +53-106 μm and -53 μm of SPD, respectively).

Table 6.1 Chemical analysis of different size fractions of SPD and FC (wt%)

%	SPD			FC		
	+106 μm	53-106 μm	-53 μm	+106 μm	53-106 μm	-53 μm
SiO_2	4.21	4.50	3.98	1.74	1.70	1.67
TiO_2	0.11	0.07	0.07	0.05	0.03	0.04
Al_2O_3	0.26	0.28	0.31	0.40	0.42	0.44
Fe_2O_3	41.95	41.52	39.97	18.57	18.48	17.94
MnO	5.00	4.90	4.52	0.98	0.86	0.89
MgO	5.67	4.77	4.36	1.05	1.31	1.26
CaO	12.12	13.26	11.43	39.33	39.65	38.99
Na_2O	1.00	1.04	0.76	0.33	0.23	0.27
K_2O	2.46	2.79	6.31	0.05	0.05	0.05
P_2O_5	0.02	0.03	0.05	0.05	0.05	0.05
Cr_2O_3	14.92	14.48	13.78	2.84	2.93	2.91
NiO	3.16	2.96	2.53	1.39	1.53	1.41
ZnO	4.58	4.59	4.28	0.31	0.39	0.42
MoO_3	1.18	1.31	1.18	0.08	0.09	0.08
SO_3	0.45	0.39	0.62	5.03	6.11	5.76
F	nd*	nd	nd	27.72	26.05	27.70
Cl	2.04	2.33	5.13	0.03	0.05	0.05
Total	99.11	99.19	99.28	99.95	99.92	99.94

*nd-not determined

For FC, it is the precipitate from the waste solution. After it was dried, crushed and ground, the major parameter which can influence the leachability of Cr(VI) is the ratio of Ca-containing phases to Cr_2O_3 . Table 6.1 indicates that the ratio of Ca-containing phases to Cr_2O_3 in +106 μm of FC is larger than the other two fractions of FC (13.85 in +106 μm of FC vs. 13.53 and 13.40 in 53-106 μm and -53 μm of FC, respectively). Therefore, more leachable Cr(VI) would be detected. However, the reduction of the leachable Cr(VI) in different size fractions of FC has no significant change, presumably due to the low contents of chromium in FC (~3%).

Table 6.2 Semi-quantitative XRD analysis of different size fractions of SPD and FC

Samples*	SPD			FC**		
	+106 µm	53-106 µm	-53 µm	+106 µm	53-106 µm	-53 µm
CaCO₃ (%)	19.90±3.90	3.68±1.53	2.45±1.53	20.79±2.97	5.60±3.30	5.40±3.30
Ca(OH)₂ (%)	ud***	7.70±1.35	6.82±1.32	ud	ud	ud
CaF₂ (%)	3.29±1.98	1.68±0.90	2.72±1.02	78.00±3.60	88.60±4.20	87.90±3.60
Sieve analysis (%)	2.1	25.1	72.8	56.1	18.3	25.6

*: The Ca-containing crystalline phases are different to the phases which are described in Chapter 3, due to the fact that the present analysis was performed approximately 2 years later than the previous one, and some of the calcium hydroxide reacted with carbon dioxide in the air to form calcite.

**: It is only indicated that the ratio of calcite and fluorite in the crystalline phases.

***: undetectable

The extractable Cr (VI) from the SPD samples under water-saturated conditions is higher than that under dry conditions. This suggests that water vapour in the atmosphere enhances the oxidation of Cr (VI). It is expected that more leachable Cr (VI) will form in air than in argon, due to the associated higher oxygen potential. However, it was found that the amount of extractable Cr (VI) is higher in Ar than in air. The reason for this is still not clear.

6.5 Conclusions

The aging behaviour of Cr (VI) in the stainless steel plant dust and filter cake were studied and reported on in this chapter. The results show that:

- (1) The Cr (III) species can be oxidised into Cr (VI) in the presence of lime at 20°C. Increasing the molar ratio of CaO to Cr₂O₃ promote the oxidation of Cr (III).
- (2) Increasing temperature favours the oxidation of Cr(III) into Cr(VI) in the wastes.
- (3) The extractable amount of Cr (VI) from the SPD and FC decreases with increasing aging time, possibly due to the reduction reaction of Cr (VI) into Cr (III) by Fe (II)-containing phases.
- (4) The highest amount of Cr (VI) is extracted from the -53 µm size fraction of SPD, while in the case of the FC it is extracted from +106 µm size fraction.
- (5) Water vapour enhances the formation of Cr (VI) in the SPD, but not in the case of FC.