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Chapter 8 Stabilisation of Cr (VI) through sintering using silica-rich clay, Part II: Electric furnace dust and filter cake

Chapter 8 Stabilisation of Cr (VI) through sintering using silica-rich clay, Part II: Electric furnace dust and filter cake

8.1 Introduction

The Estimated Environmental Concentration (EEC) and the acceptable risk level $(0.1 \times LC_{50}$[1]$)$ are often used to evaluate whether the hazardous wastes are acceptable in South Africa [15]. Therefore, bricks that are constituted from electric furnace dust and filter cake and clay can only be used in the construction industry when the EEC of Cr(VI) is lower than 0.02 ppm (acceptable risk level). The acceptable concentration of Cr(VI) in the leachates of the modified TCLP or the modified ASTM D3987-85 tests should be less than 0.013 mg/l (calculation details are given in Appendix IV). This value was used in this chapter to evaluate whether the stabilised products are environmentally acceptable.

In Chapter 7, it is proven that Cr (VI) can be stabilised through sintering using silica-rich clay. However, the optimum parameters of the sintering process and the Cr (VI) stabilisation in the wastes need to be studied when electric furnace dust and filter cake are used to substitute parts of the clay. This chapter subsequently describes (1) the optimum sinter parameters when Cr (VI) is stabilised (sinter time, temperature and the ratio of clay to dust) in stainless steel plant dust that was produced in South Africa and (2) the Cr (VI) stabilisation in the dust and filter cake using clay.

8.2 Experimental

8.2.1 Sample preparation

Approximately 125g mixtures of clay and electric furnace dust and filter cake samples were pressed into small bricks with cross sections of 28mm×100mm using a hydraulic press at 50 kN force for 5 minutes. The minimum amounts of distilled water (about 12 wt%) were added to the mixture. The green samples were then dried at 110°C for 48 hours, after which they were weighed and sintered in a tube furnace.

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[1] Acute ecotoxicity of substances in waste, which can kill 50% of the aquatic animals tested, mg/kg [15].

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8.2.2 Experimental methods

The furnace set up is similar to the one shown in Figure 7.1. In this set of experiments, different types of clays, sinter temperatures, ratios of clay to waste and sinter times were investigated in order to find the optimum sintering parameters. The extent to which these parameters, were varied in the experiments, are listed in Table 8.1. It is shown that three clays (AS, MR and AC) were used in this study. The sinter temperatures ranged from $1000^{o}C$ to $1150^{o}C$ and the sinter time from 1 hour to 5 hours. In order to find the optimum ratio of waste to clay, different mixtures were made, ranging from 0 to 100wt%. Furthermore, lime was added to the mixture to confirm the effect of basicity (mass %CaO/mass % SiO_2) on the leachability of Cr (VI) from the stabilised wastes.

Table 8.1 The process parameters of the experiments

Waste materials	SPD	FCD1, 2 and FC
Clay type	AS, MR, AC	AS
Sinter temperature (^{o}C)	1000, 1050, 1100, 1150	1000
Sinter time (hours)	1, 3, 5	5
Amount of waste materials (wt%)	0, 40, 50, 60, 70, 100	50
Spiked agent (50%AS+50%SPD)	CrO_3, $K_2Cr_2O_7$, K_2CrO_4, $CaCrO_4$ and K_2O	-

Since the Cr (VI) concentration in the sintered brick is very low (possibly in the ppb range), it is impossible to directly determine the stabilisation behaviour of Cr (VI) using the available analytical methods such as SEM-EDS and XRD. Therefore, large amounts of Cr (VI) were spiked into the mixture in order to identify where Cr (VI) is and how it is stabilised in the sintering process. In these experiments, reagent grade CrO_3 (1 wt% and 10 wt%), $K_2Cr_2O_7$, K_2CrO_4 as well as synthetic $CaCrO_4$[2] (the same amount of Cr (VI) as in 1 wt%CrO_3), were spiked into the mixture of 50 wt% AS and 50 wt% waste to study the stabilisation of Cr (VI). K_2O (2.07 wt% and 4.07 wt%) was also spiked into the

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[2] The process whereby $CaCrO_4$ was prepared is given in Appendix V.

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50%AS-50%SPD mixtures (added as K_2CO_3) to study the influence of alkaline metals on the leachability of Cr (VI).

Dry air was purged through the furnace in the experiments. Both heating and cooling rates of the furnace were ~1.5^{o}C/min.

8.2.3 Analytical methods

The modified TCLP and modified ASTM D 3987-85 tests were used to evaluate the leachability of Cr (VI) from the sintered product. Two TCLP solutions were prepared for the modified TCLP tests: TCLP solution 1 had a pH of approximately 4.93, and was prepared by diluting a mixture of 11.4ml analytical reagent glacial acetic acid and 128.6 ml 1 M NaOH solution in 2 l with distilled water. TCLP solution 2 was prepared by diluting 11.4ml analytical reagent glacial acetic acid in 2 l solution with distilled water. TCLP solution 2 was only used for the sintered pure SPD brick and the lime spiked brick. TCLP solution 1 was used for the remainder of sintered samples. The modified ASTM D 3987-85 leaching solution consists of distilled water with a pH of approximately 6.

The Cr (VI) concentration in the leachate was determined photometrically using a UV-Vis spectrophotometer. Due to the fact that the concentrations of toxic substances [except Cr (VI)] which leached from the sintered bricks in the modified TCLP test are higher than that in the modified ASTM D 3987-85 test, the leachable toxic substances [except Cr (VI)] in the modified TCLP leachate from the selected samples were measured using an ICP-OES. The redox potential of the leachate was determined using a Thermo Model 97-78-00 Platinum Redox Electrode. XRD, SEM-EDS and XRF were used to analyse the sintered bricks with respect to the crystalline phases present, microstructure and chemical composition.

8.3 Results and discussion

8.3.1 Effect of clay type on the leachability of Cr (VI)

The effect of different types of clays on the leachability of Cr (VI) from the sintered brick is shown in Figure 8.1. The results indicate that the Cr (VI) concentration in the leachate

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of the modified TCLP tests are below the detection limit of the spectrophotometer, while the Cr (VI) concentrations from the modified ASTM D 3987-85 test are significantly higher and can therefore be determined.
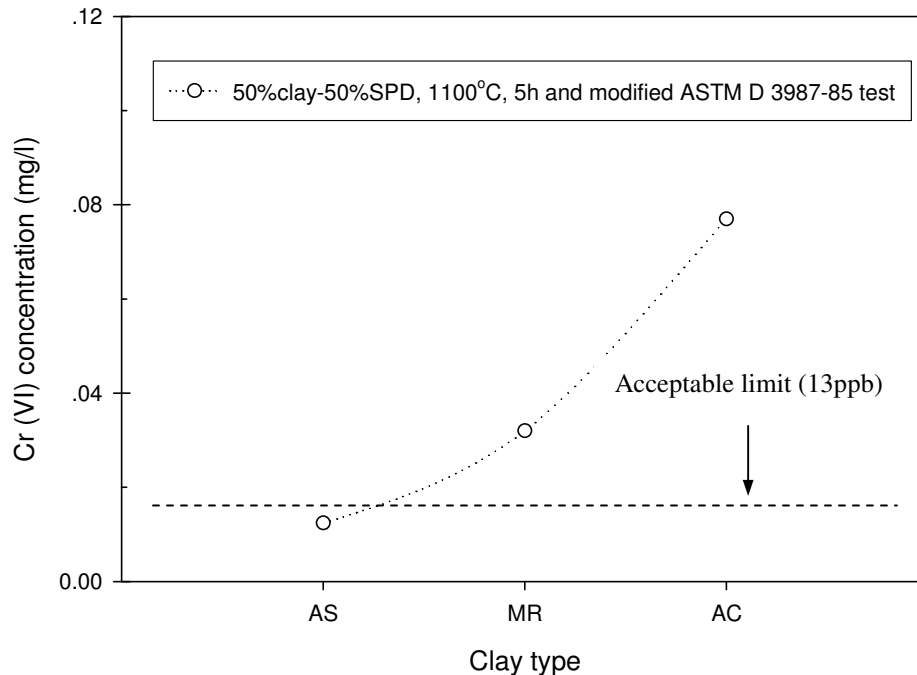

Figure 8.1 The influence of different types of clays on the leachability of Cr (VI)

This is due to the fact that in the modified TCLP tests, the leaching buffer solution has a pH of approximately 4.93, while the modified ASTM D 3987-85 leaching solution has a pH of approximately 6. When the sintered product is added to the leachant, it can change the redox potential of the leachate and therefore possibly transform extracted Cr (III) species into Cr (VI) species. On the other hand, the extraction of other species, such as Fe^{2+} and organic components, can potentially reduce Cr (VI) species into Cr (III) species [178-180], thereby changing the Cr (VI) concentration in the leachate.

Figure 8.1 also shows that clay AS has the best stabilisation capacity of Cr (VI), while clay AC has the worst. It could be due to the different mass % CaO/mass %SiO_2 ratios in the sintered bricks (0.15, 0.18, 0.21 for AS, MR and AC containing bricks, respectively). In order to examine this hypothesis, synthetic sample with a mass %CaO/mass %SiO_2

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ratio of 0.5 was prepared by adding CaO to the 50wt% SPD-50wt% AS mixture. The sample was also sintered at 1100°C for 5 hours in the tube furnace. The results from the modified TCLP and modified ASTM D 3987-85 tests are plotted in Figure 8.2. It is important to note that the Cr (VI) concentrations from the leachates of the modified TCLP and the modified ASTM D 3987-85 tests increased to more than 7.6 mg/l when the mass %CaO/mass %SiO$_2$ ratio increased from 0.15 to 0.5. It shows that the mass %CaO/mass %SiO$_2$ ratio has a significant influence on the leachability of Cr (VI), and confirms that an increase in the basicity of the mixture increases the leachability of Cr (VI). This is similar to what was reported for the refractories industry [160].
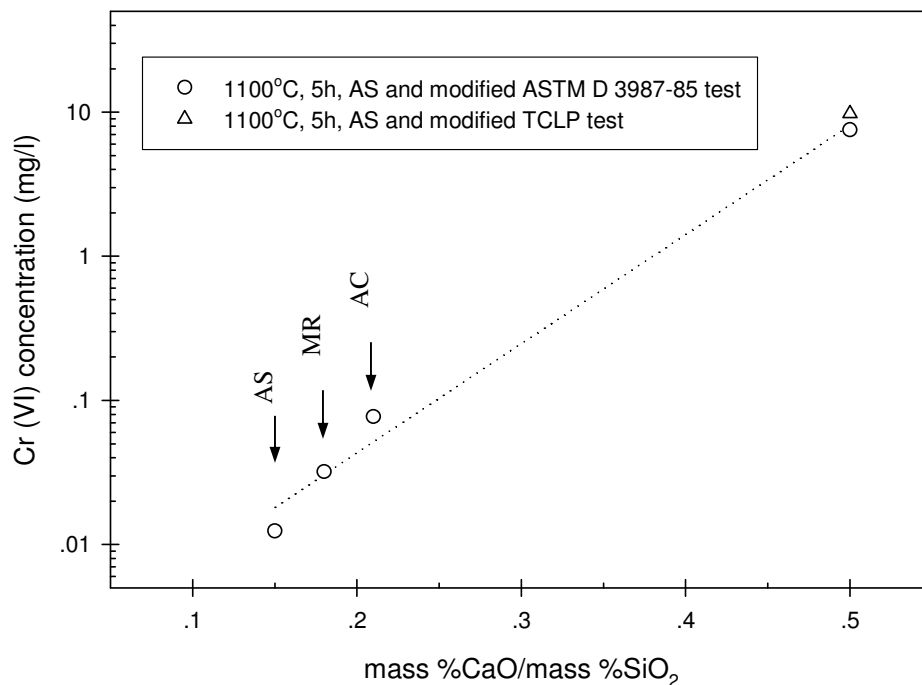

Figure 8.2 The influence of mass %CaO/mass %SiO$_2$ ratio on the leachability of Cr (VI) from the stabilised wastes (SPD, 1100°C and 5 hours)

8.3.2 Effect of leach time on the leachability of Cr (VI) in the modified TCLP test
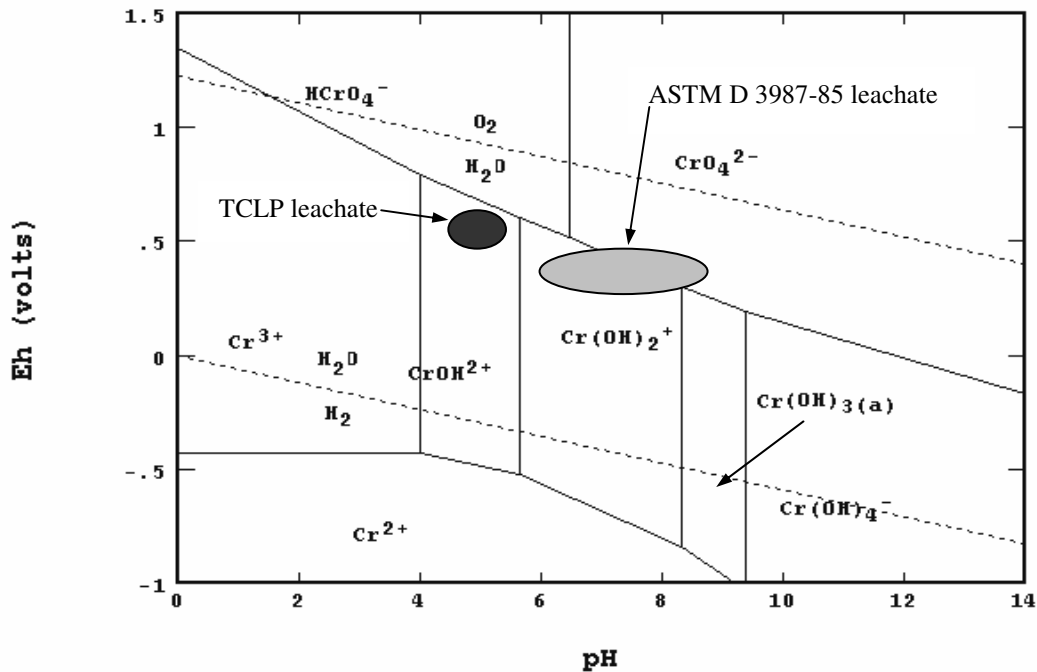
The effect of leach time on the leachability of Cr (VI) in the modified TCLP test after spiking 2mg/l Cr (VI) into the TCLP leachate of sample 40%AS-60%SPD that was sintered at 1100°C for 5h is shown in Figure 8.3. It is clearly shown that Cr (VI) recovery

decreases with increasing leaching time, which means that the spiked Cr (VI) was reduced or transformed into Cr (III) during the leaching period. This ties up with reports from the literature which indicate that the extracted Cr (VI) is influenced by the potential of the leaching solution, pH and/or the reductant in the solution [170-172].
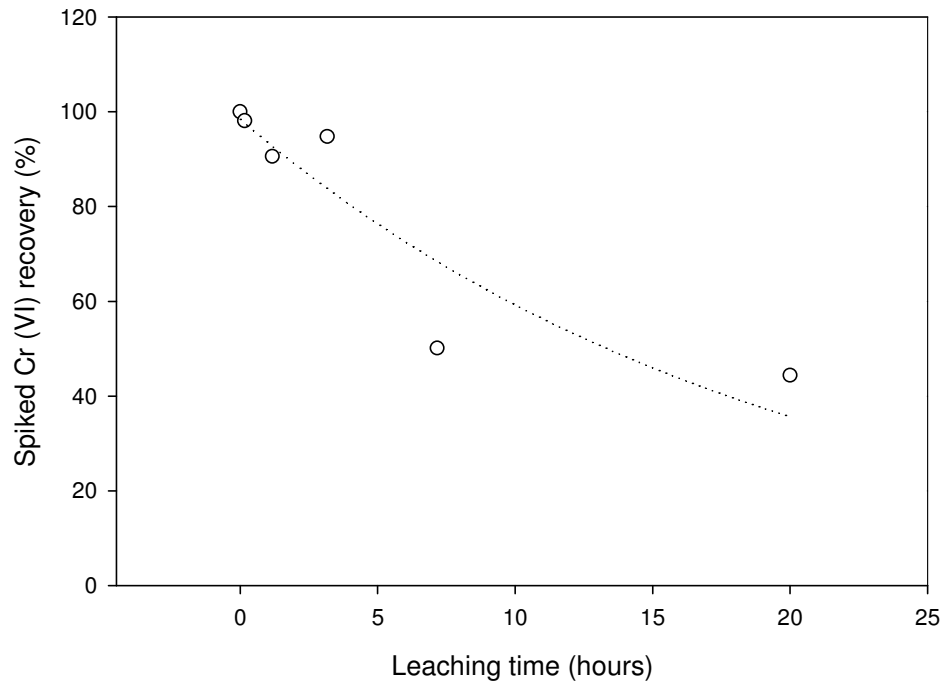
Figure 8.3 The Cr (VI) concentration in the modified TCLP leachate as a function of time (spiked with 2mg/l Cr (VI) in leachate from 40%AS-60%SPD sample @ 1100°C for 5h)
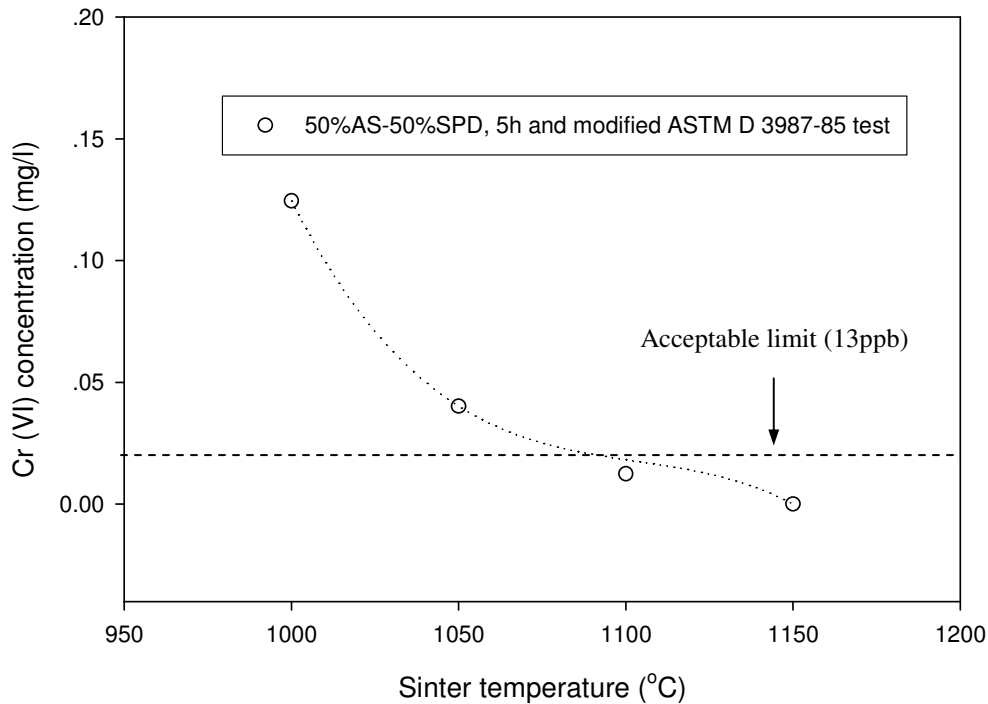
The Eh-pH diagram for chromium species is shown in Figure 8.4. It indicates that the stable Cr-containing ion is Cr (III) during the TCLP leaching period (in the pH range of 4.66-5.36 and Eh range of 0.425-0.537 V), while Cr (III) can transform into Cr (VI) species with an increase in pH as is associated with the ASTM D 3987-85 leachate (in the pH range of 6.08-8.66 and Eh range of 0.311-0.412 V). It possibly contributes some Cr (VI) to the final leachate. In addition, organic compounds and iron (II) in the leachate can potentially reduce Cr (VI) components to Cr (III) [151].

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Figure 8.4 The Eh-pH diagram for Cr species calculated using STABCAL with 10^{-6}mol/l chromium concentration at 25°C [181]

8.3.3 Influence of sinter temperature on the leachability of Cr (VI)

The effect of sinter temperature on the leachability of Cr (VI) from 50%AS-50%SPD mixtures that were reacted for 5 hours is shown in Figure 8.5. It shows that increasing sinter temperature promotes the stabilisation of Cr (VI). The modified TCLP test indicated that the Cr (VI) concentration in the leachate is under the detection limit of the spectrophotometer when the brick was sintered at temperatures of 1050°C and higher for 5 hours. However, the Cr (VI) concentration was detectable in the leachate from the modified ASTM D 3987-85 test. Cr (VI) concentrations in the leachates of the modified ASTM D 3987-85 test from the bricks, which were sintered at 1000°C and 1050°C, are higher than the acceptable limit, while when the brick was sintered at 1100°C for 5 hours, Cr (VI) was stabilised according to both the modified TCLP test and the modified ASTM D 3987-85 test [Cr (VI) concentration < 13 ppb].

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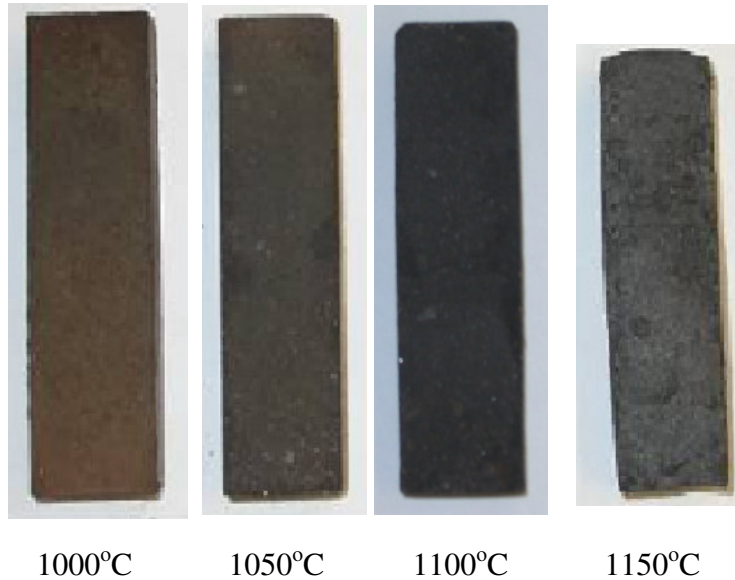
Figure 8.5 The influence of sinter temperature on the leachability of Cr (VI)

In South Africa, the TCLP test is generally used to evaluate whether hazardous wastes are environmentally acceptable. In this study, the Cr (VI) concentrations in the leachate when the sintered bricks were examined with the modified TCLP test are below 10 ppb, which is environmentally acceptable in South Africa. However, the leachable Cr (VI) in certain of the leachates of the modified ASTM D 3987-85 test is above 13 ppb and is still considered to be a potential threat to the environment and human health. It is therefore recommended that the modified ASTM D 3987-85 test is used to evaluate the degree of toxicity of the sintered bricks.

The physical appearance of the bricks (50%AS-50%SPD), which were sintered at different temperatures are shown in Figure 8.6. It shows that the brick that was sintered at 1000°C remained brown (the original colour of the stainless steel plant dust), while it changed into dark grey with an increase in sinter temperature. The brick shrank

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significantly at sintering temperatures above 1100°C for 5 hours. For a 50%AS-50%SPD mixture, the optimum sintering temperature is therefore 1100°C.


| 1000°C | 1050°C | 1100°C | 1150°C |

Figure 8.6 Bricks (constituted of 50%clay/50%dust) sintered at different temperatures

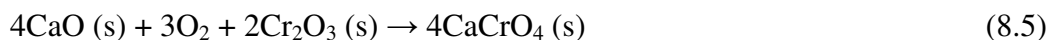### *8.3.4 Influence of the SPD content of the brick on the leachability of Cr (VI)*

The influence of the SPD content of the brick on the leachability of Cr (VI) is shown in Figure 8.7. These bricks contain clay AS and were sintered at 1100°C for 5 hours. It can be seen that the leachability of Cr (VI) increases with increasing stainless steel plant dust content of the sintered brick. Increasing SPD ratio increases the initial Cr (VI) concentration in the mixture, which can potentially increase the leachable Cr (VI). In addition, the silica content of the brick decrease with a reduction in the clay content of the mixture, and therefore increases the mass %CaO/mass %SiO$_2$ ratio in the mixture.

Two reference samples, i.e., pure AS clay and pure stainless steel plant dust samples, were also sintered under the same conditions (Figure 8.7). It was found that 4×10^3 mg Cr (VI) per kg SPD leached from the pure sintered stainless steel plant dust, which is considerably more than the amount that leached from the original stainless steel plant dust (approximately 2.5×10^2 mg Cr (VI) /kg stainless steel plant dust). This indicates that
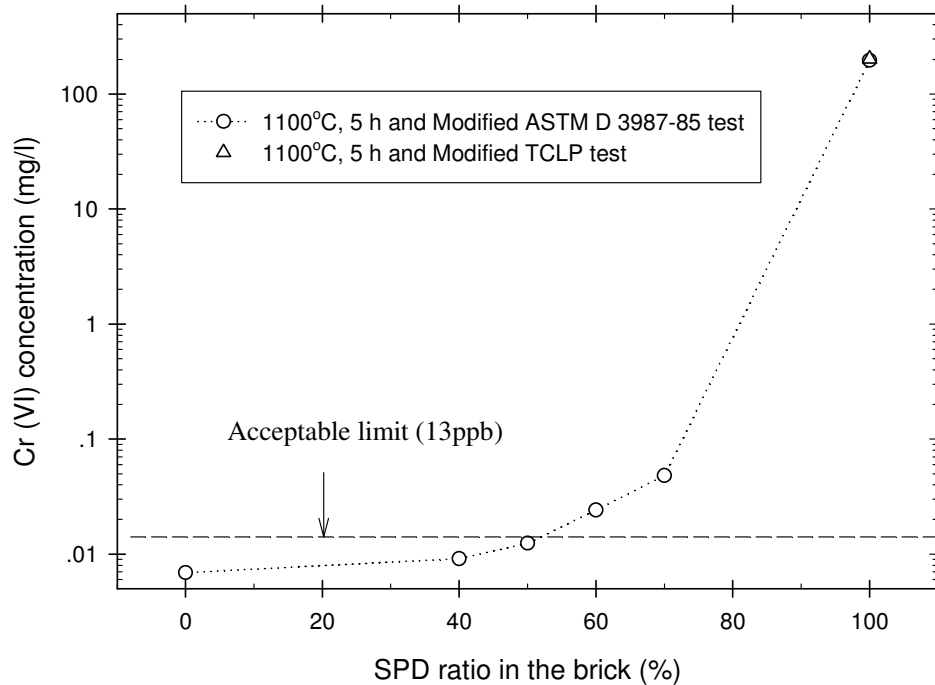
Figure 8.7 The influence of the ratio of SPD in the brick on the leachability of Cr (VI)

Cr (VI) must have formed during the sinter process either by oxidisation or through both oxidation and reaction with CaO or alkali oxides to form Cr (VI)-containing components via the following reactions [174,182,183]:

$$2Cr_2O_3 \text{ (s)} + 3O_2 \rightarrow 4CrO_3 \text{ (s)} \tag{8.4}$$

$$4CaO \text{ (s)} + 3O_2 + 2Cr_2O_3 \text{ (s)} \rightarrow 4CaCrO_4 \text{ (s)} \tag{8.5}$$

$$1/2FeCr_2O_4 + Na_2CO_3/K_2CO_3 + 7/8O_2 \rightarrow Na_2CrO_4/K_2CrO_4 + 1/4Fe_2O_3 + CO_2 \tag{8.6}$$
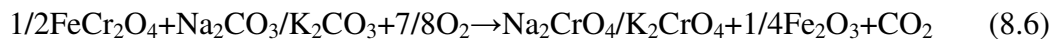
For the AS-SPD mixture, the leachability of Cr (VI) from the bricks, which were sintered at $1100^{\circ}C$ for 5 hours, are below the acceptable limit of South Africa (13 ppb in this study) when it contained 50 wt% SPD or less. Judging from both the regulatory limits on Cr (VI) and using as much stainless steel plant dust as possible in the sinter process, the optimum stainless steel plant dust content in the brick is 50 mass %.

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8.3.5 Influence of sinter time on the leachability of Cr (VI)

The effect of sinter time on the leachability of Cr (VI) was studied by sintering 50%AS-50%SPD mixtures at 1100^oC for 1, 3 and 5 hours. The results are shown in Figure 8.8. It shows that increasing sinter time increases the stabilisation of Cr (VI). The leachability of Cr (VI) from the bricks, which were sintered at 1100^oC for 5 hours, is below the acceptable limit of 13 ppb. A 50%AS-50%SPD mixture that is sintered at 1100^oC, should therefore at least be reacted for 5 hours in order to sufficiently stabilise the Cr (VI).
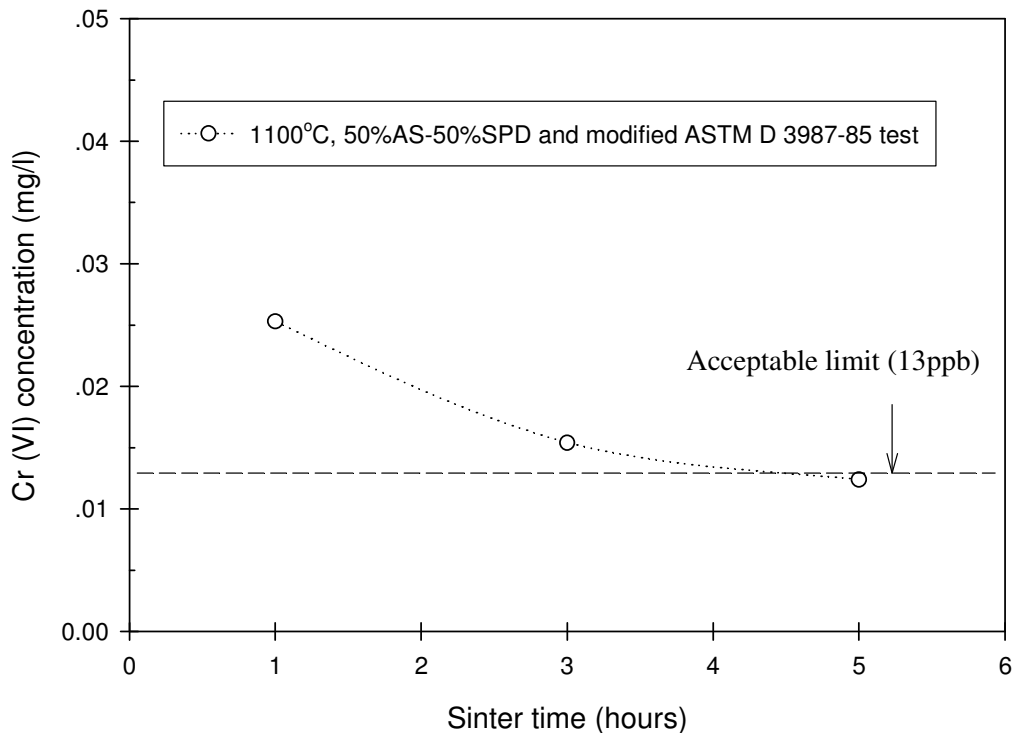
Figure 8.8 The influence of sinter time on the leachability of Cr (VI)

8.3.6 The leachability of other toxic substances from the stabilised wastes

The leachability of selected toxic substances from the stabilised SPD (sintered with 50% clay AS at 1100^oC for 5 hours) is shown in Table 8.2. It shows that the concentrations of all of these leachable toxic substances are below the acceptable risk levels of South Africa, except for possibly cadmium. It confirms that when Cr (VI) is stabilised with clay in a sinter process, other toxic substances such as arsenic, zinc and lead are also

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stabilised. Sintering is therefore considered to be an effective process to stabilise stainless steel plant dust.

Table 8.2 Concentrations of toxic substances in the modified TCLP leachates from the stabilised 50%AS-50%SPD mixture that was sintered at 1100^oC for 5 hours.
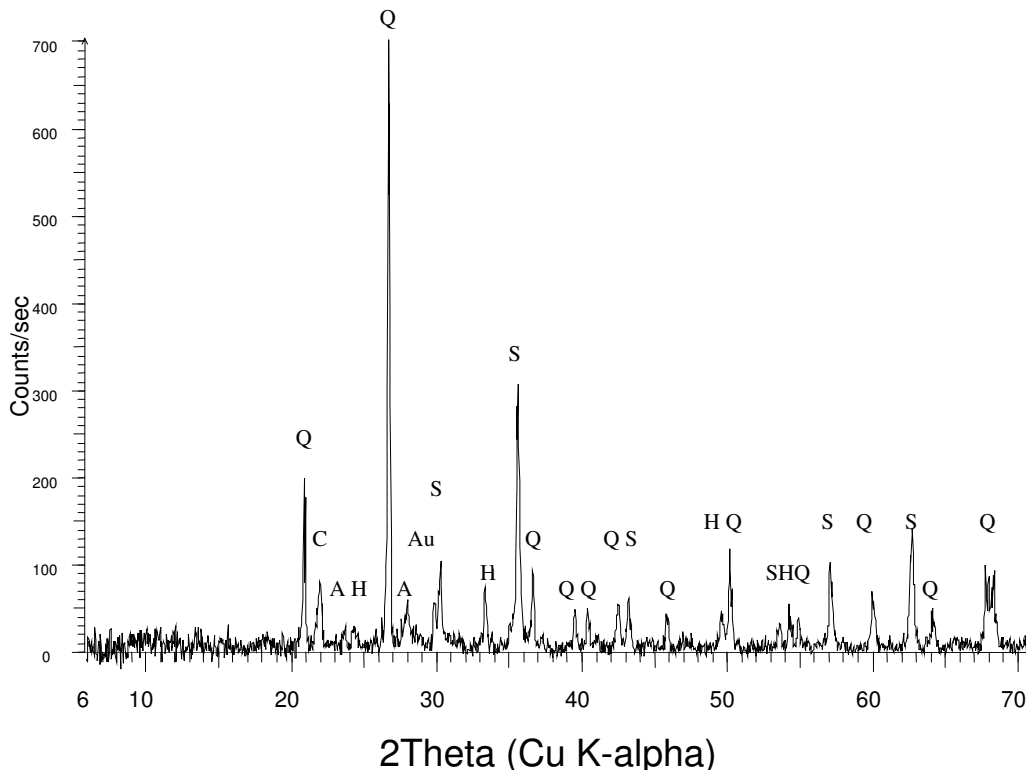
Elements	As	Al	Ca	Cd	Cr	Fe	Mg	Mn	Ni	Pb	Si	V	Zn
Conc. (ppm)	<0.1	1.3	5.56	<0.05	0.16	5.27	1.60	0.29	0.38	<0.05	2.24	<0.05	0.21
ARL *[15]	0.43	na	na	0.031	4.7**	na	na	0.3	1.14	0.1	na	1.3	0.7

Note: *: Acceptable Risk Level; **: ARL of Cr (III); na-not available.

8.3.7 Crystalline phases present in and microstructure of the sintered brick

The XRD pattern of the brick which was sintered at 1100^oC for 5 hours indicates the brick consist of quartz, cristobalite, anorthite ($CaAl_2Si_2O_8$), hematite (Fe_2O_3), augite [$Ca(Mg,Fe,Al)(Si,Al)_2O_6$] and spinel phase [$(Fe,Zn,Ni,Mg,Mn)(Fe,Cr,Al)_2O_4$] (Figure 8.9). The peaks of hematite have slightly shifted, presumably due to Cr_2O_3, Al_2O_3 and Mn_2O_3 being taken into solid solution with Fe_2O_3. SEM-EDS results confirmed the existence of these phases.
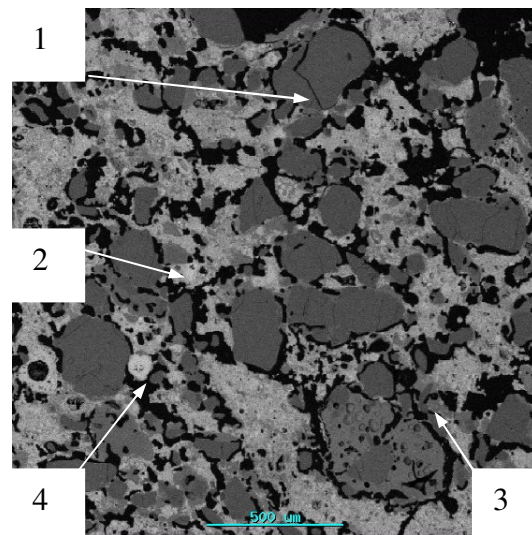
The microstructures of selected sintered brick samples are shown in Figures 8.10-8.13. It indicates that the sintered bricks, which were made at 1050, 1100 and 1150^oC, consist of un-reacted big quartz particles, crystals (spinel and hematite), silicate phases (anorthite and augite), pores and un-reacted metal particles (Figure 8.10). The spinel phases are either dendritic or cubic (Figure 8.11). Large amounts of small pores remain in the sintered wastes. Columnar hematite crystals, which contain small amounts of Cr, Mn and Al in solid solution were found in the sintered brick (Figure 8.12). Precipitated augite crystals were dendritic or needle-like in shape (Figure 8.13), while anorthite crystals were very fine and very difficult to identify. It was also found that larger quantities of augite and a glassy phase were formed during the sintering process of mixtures 50%AS-50%SPD and 50%MR-50%SPD than in mixture of 50%AC-50%SPD, while less anorthite were found.

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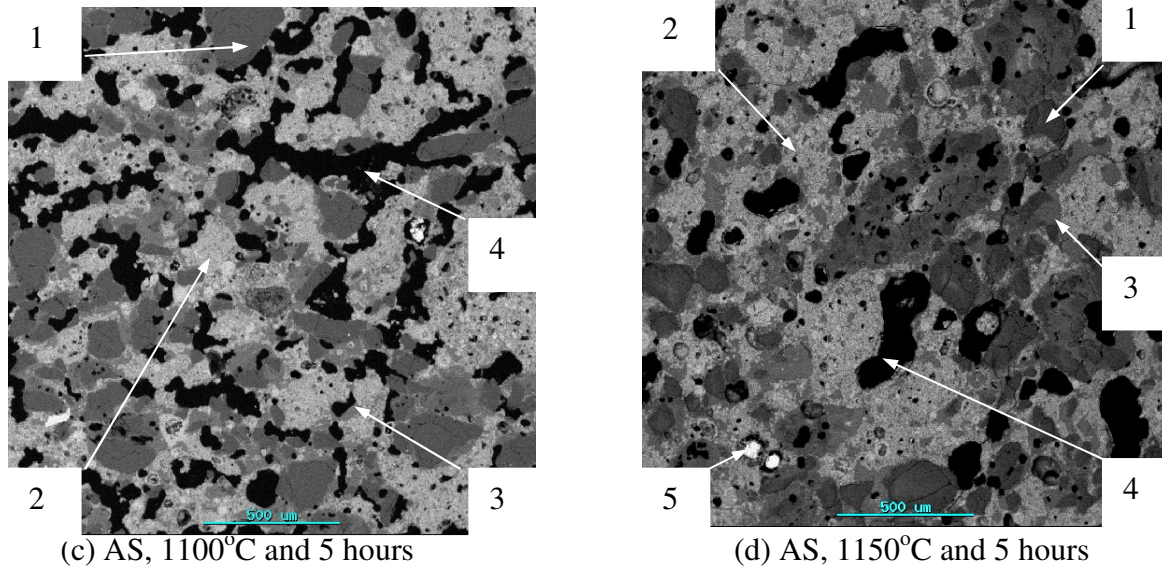
Figure 8.9 The XRD pattern of the sintered brick 50%AS-50% SPD at 1100°C for 5h (Q-quartz; C-cristobalite; A-anorthite; H-hematite; Au-augite and S-spinel)
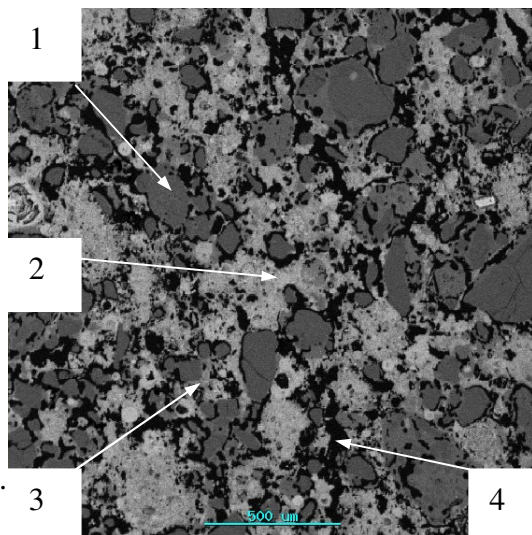

(a) AS, 1100°C and 1 hour   (b) AS, 1100°C and 3 hours

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(c) AS, 1100°C and 5 hours

(d) AS, 1150°C and 5 hours

Figure 8.10 Microstructure of the 50%AS-50%SPD sintered brick (1-unmelted quartz; 2-hematite and spinels; 3-anorthite and augite; 4-pores; 5-unreacted metal particles)
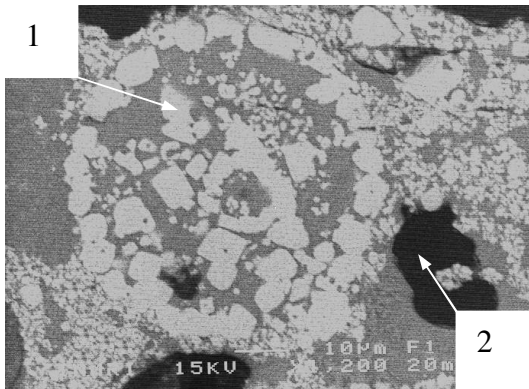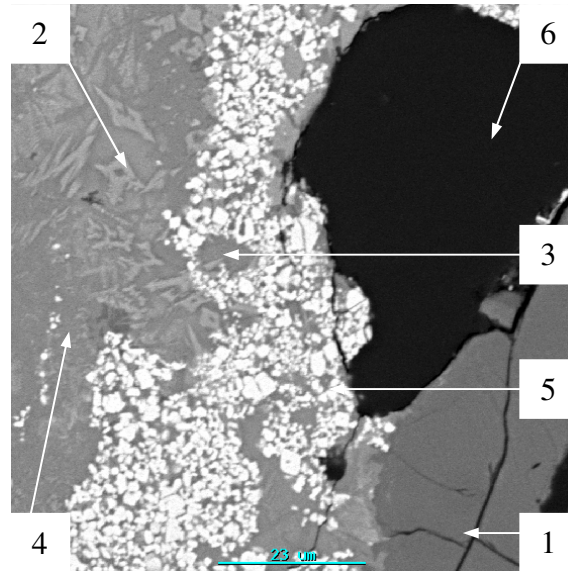

Figure 8.11 Microstructure of the 50%AS-50%SPD brick that was sintered at 1100°C for 5 h (1-spinel; 2-pore)
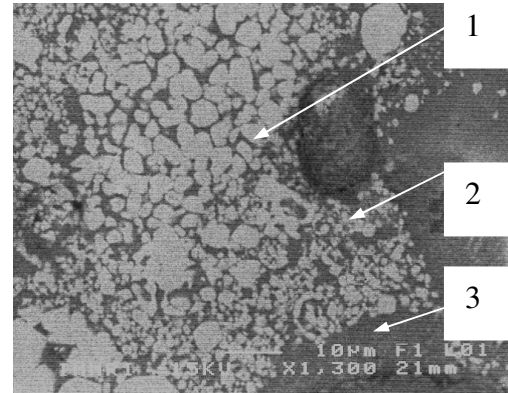
Figure 8.12 Columnar hematite crystals (1), spinels (2) and anorthite (3) in the 50%AS-50%SPD brick sintered at 1100°C for 5 h

The elemental X-ray maps indicate that the spinels mainly contain iron and chromium but also small amounts of Al, Mg, Mn, Zn and Ni. It includes larger Cr-rich spinel crystals and very fine Fe-rich spinel crystals.
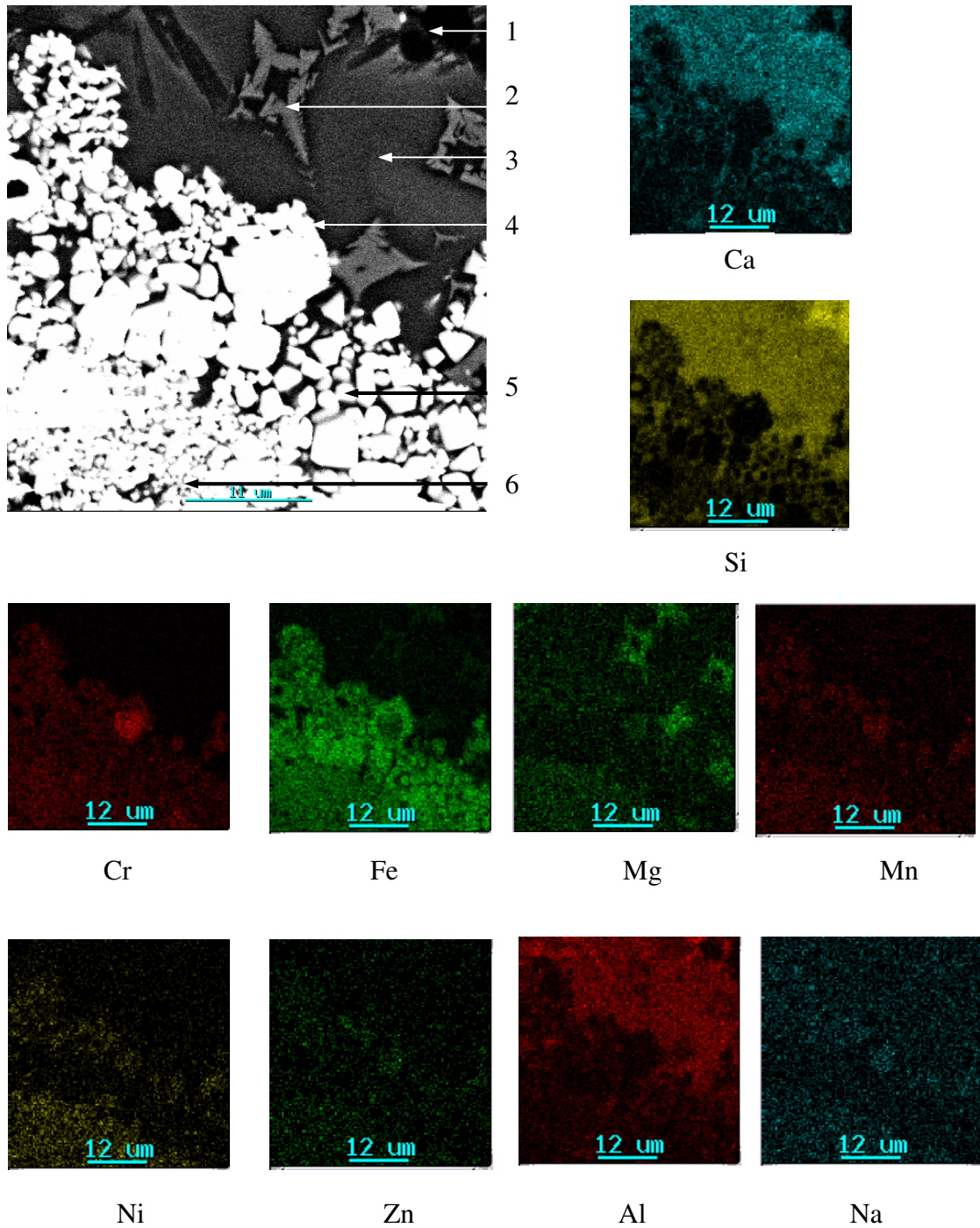
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Figure 8.13 The X-ray map of the sintered brick (1100°C, 5h and 50%AS-50% SPD) (1-Quartz; 2-Augite; 3- Glassy phase; 4- Anorthite; 5- Spinel; 6-Pore)

Hematite contains Fe, Cr, Al and Mn. Augite contains calcium, silicon, aluminium, iron and magnesium, while anorthite is Ca-Al-Si-Fe-O based (Figure 8.14). Typical EDS analyses of these phases indicated that the spinel and hematite phases contain chromium (average of 8 different analyses) (Table 8.3). The Cr_2O_3 content in the spinel and hematite ranged from approximately 8 to 54wt%. It is assumed that hematite crystals formed due to the oxidation of spinel particles. In addition, augite crystals also contain small amounts of chromium. Calcium is present in the augite, anorthite and glassy phases.

Table 8.3 Typical EDS analyses of the phases present in the brick (50%AS-50%SPD, sintered at 1100°C for 5h) (mass%)

Phases	Fe_2O_3	Cr_2O_3	CaO	Al_2O_3	SiO_2	MgO	MnO	ZnO	NiO	K_2O
Cr-rich spinel	17.5	53.4	0	2.3	0	5.7	8.7	10.9	1.5	0
Fe-rich spinel	45.2	29.1	0	2.5	0	3.5	8.5	5.2	6.0	0
Hematite	88.1	8.1	0	1.6	0	0	2.2	0	0	0
Augite	15.5	1.4	23.2	7.6	44.0	7.6	2.5	0	0	0
Anorthite	3.3	0	19.3	29.0	48.4	0	0	0	0	0
Quartz	0	0	0	0	100	0	0	0	0	0
Glassy phase	5.0	0	18.3	12.2	62.3	0	0	0	0	2.2

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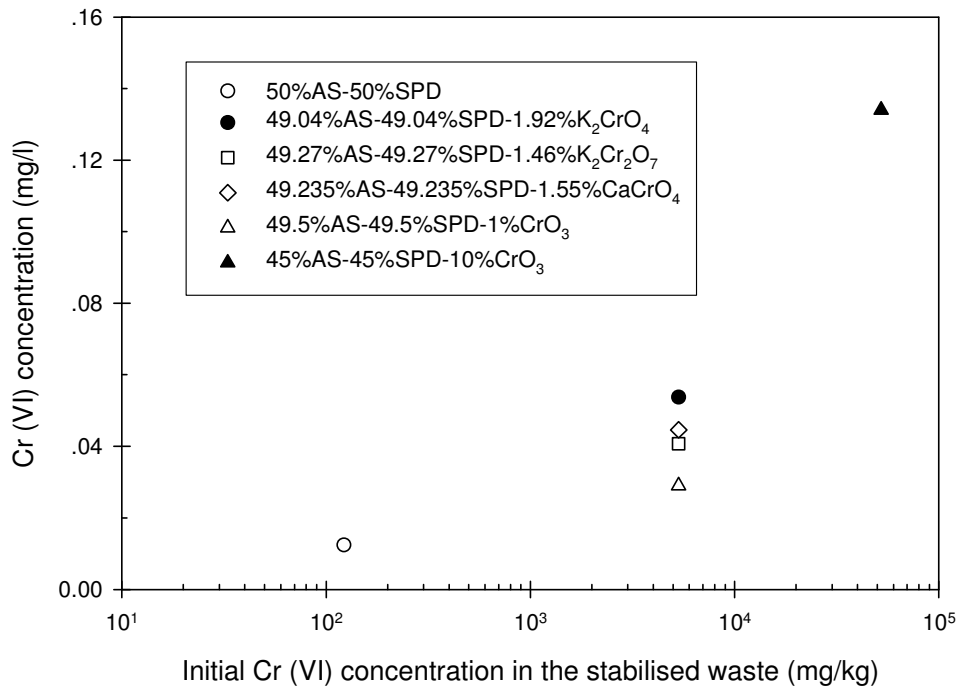
Figure 8.14 The microstructure of the sintered brick (1100°C, 5h and 50%AS-50% SPD) (1-Quartz; 2-Augite; 3- Glassy phase; 4- Cr-rich spinel; 5-Anorthite; 5-Hematite; 6-Fe-rich spinel)

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8.3.8 Cr (VI) stabilisation in the sintered brick

Cr (VI) species can potentially exist in the forms of chromium trioxide, chromates and dichromates in the wastes. For this reason, CrO_3, $K_2Cr_2O_7$ and K_2CrO_4 were spiked into the mixture of 50%AS-50%SPD to investigate the Cr (VI) stabilisation. In addition, calcium chromate ($CaO \cdot CrO_3$), which can potentially be formed in the electric furnace dust during the sintering process due to the significant concentrations of free $Ca(OH)_2/CaCO_3$ in the stainless steel plant dust [182], was also spiked into the mixture of 50%AS-50%SPD. These mixtures were sintered in the tube furnace at 1100^oC for 5 hours. The modified TCLP and modified ASTM D 3987-85 tests were used to evaluate the leachability of Cr (VI) in the sintered bricks.

Figure 8.15 shows the effect of the initial Cr (VI) concentration on the leachability of Cr (VI). It indicates that the Cr (VI) leachability only slightly increases when Cr (VI) is spiked into the 50%AS-50%SPD mixture. The amount of leachable Cr (VI) is 0.134 mg/l even though the brick was spiked with 10 wt% CrO_3.

Figure 8.15 The influence of the initial Cr (VI) content on the leachability of Cr (VI)

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The Cr (VI) leached ratio when the 50%AS-50%SPD mixtures were spiked with Cr (VI) species was calculated using the following equation:

$$\text{Cr (VI) leached ratio (\%)} = \frac{\text{Cr(VI)}_{\text{sintered brick}}}{\text{Cr (VI)}_{\text{green mixture}}} * 100$$

Where Cr (VI) $_{\text{green mixture}}$ is the total leachable Cr (VI) which was present in the mixture that was spiked with Cr (VI), i.e., the sum of the Cr (VI) present in the spiked Cr (VI) containing species and leachable Cr (VI) in the SPD, and Cr (VI) $_{\text{sintered brick}}$ is the leachable Cr (VI) from the sintered brick.

The results are shown in Table 8.4. It indicates that Cr (VI) in the sintered bricks are significantly stabilised (the leached ratios of Cr (VI) < 0.2%). This indicates that sintering the mixture of SPD and clay is an effective method whereby Cr (VI)-containing electric furnace dust can be treated.

Table 8.4 Calculated Cr (VI) leached ratios in the 50%AS-50%SPD mixture which were sintered at 1100°C for 5 hours and spiked with Cr (VI) species (%)

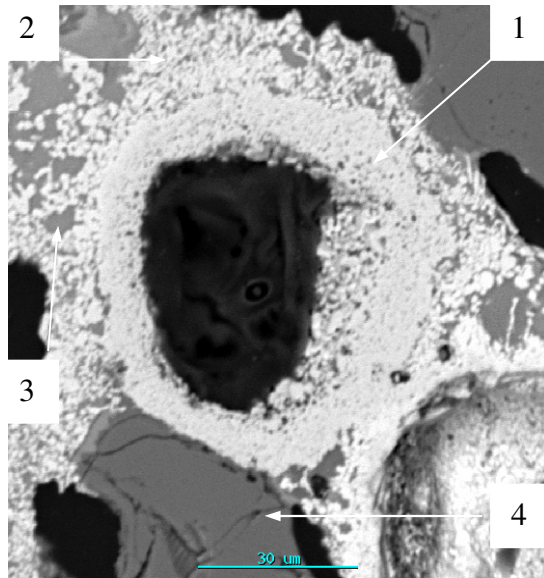| Mixtures	Initial Cr (VI) conc. (mg/kg)	Cr (VI) leached ratio (%)
50%AS-50%SPD	122.3	0.20
49.04%AS-49.04%SPD-1.92% K_2CrO_4	5321	0.02
49.27%AS-49.27%SPD-1.46%$K_2Cr_2O_7$	5321	0.02
49.235%AS-49.235%SPD-1.55%$CaCrO_4$	5321	0.02
49.5%AS-49.5%SPD-1%CrO_3	5321	0.01
45%AS-45%SPD-10%CrO_3	52110	0.005

XRD patterns of the stabilised SPD that was spiked with Cr (VI) species and sintered at 1100°C for 5 hours are shown in Figure 8.16. It was found that the major phases that were present in these samples were quartz, cristobalite, anorthite, hematite, augite and spinel. No Cr (VI) containing phases could be detected by XRD, even though one of the mixtures was spiked with 10 wt% CrO_3. It also shows that the hematite and spinel

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contents of the sintered brick that was spiked with $10\%CrO_3$ is higher than in any of the other samples which were spiked with Cr(VI).
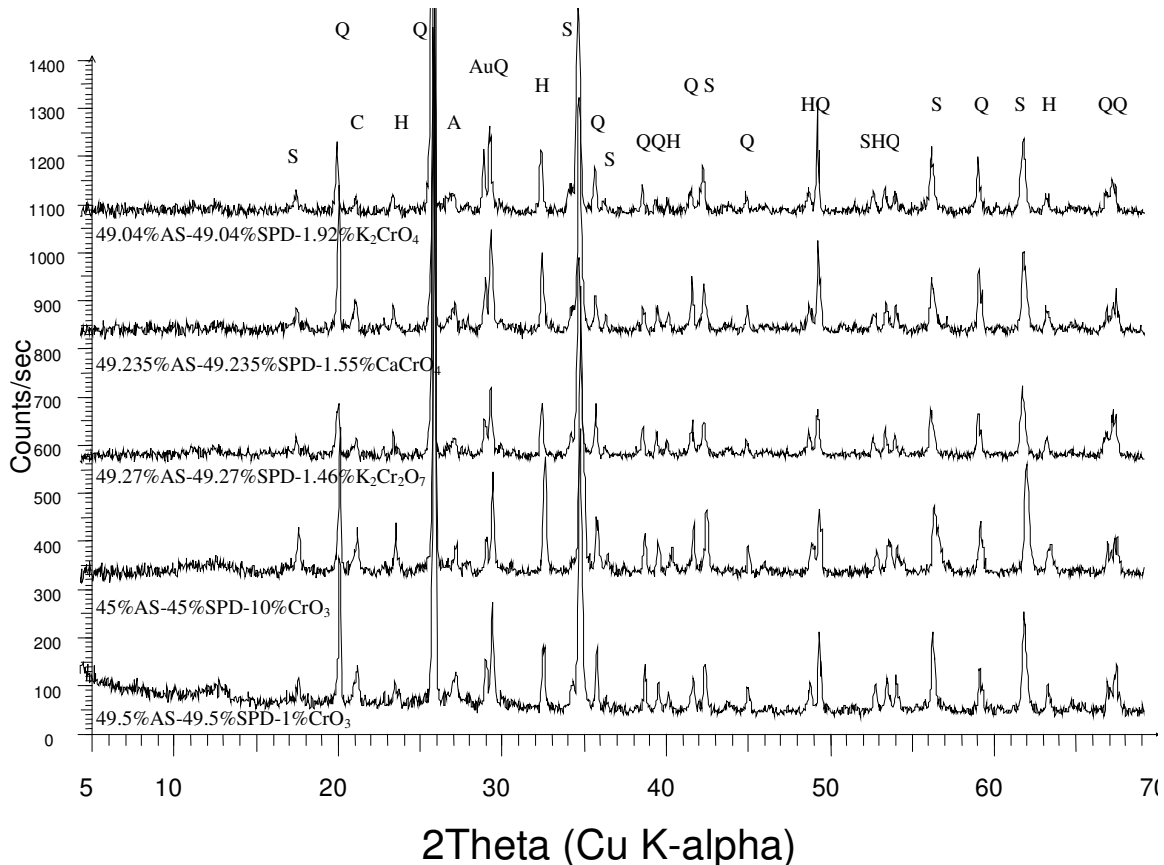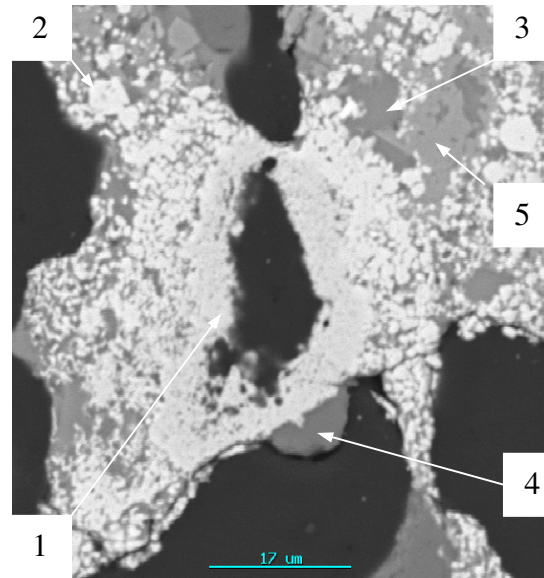

Figure 8.16 XRD patterns of the stabilised SPD that was spiked with Cr(VI) and sintered at 1100^oC for 5h(Q-quartz; C-cristobalite; A-anorthite; H-hematite; Au-augite and S-spinel)
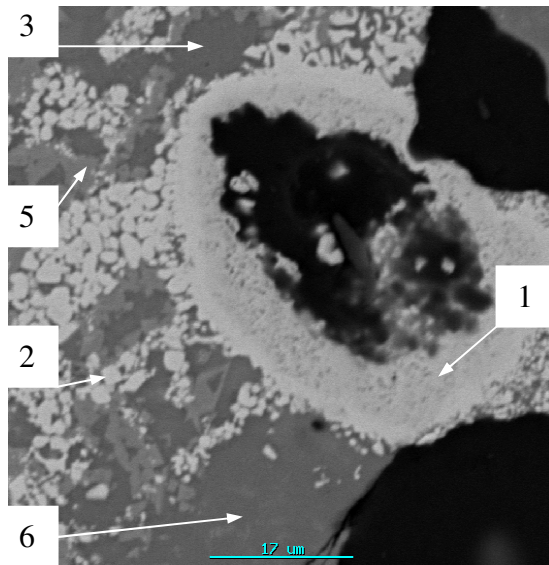
The typical microstructures of the stabilised wastes that were spiked with Cr (VI) and were sintered at 1100^oC for 5h are shown in Figure 8.17. It shows that most of the chromium exists in the hematite $[(Fe,Cr,Al,Mn)_2O_3]$ and spinel phases $[(Fe,Mn,Mg,Ni,Zn,Cr,Al)_3O_4]$. It was also found that large Cr_2O_3 particles were present in the 50%AS-50%SPD mixtures which were spiked with CrO_3, K_2CrO_4 and $K_2Cr_2O_7$ (Figure 8.17). It is possibly due to the decomposition of the spiked Cr (VI) species [184-186]. Cr_2O_3 particles could not be found in the sintered brick which was spiked with $CaCrO_4$ (Figure 8.18).
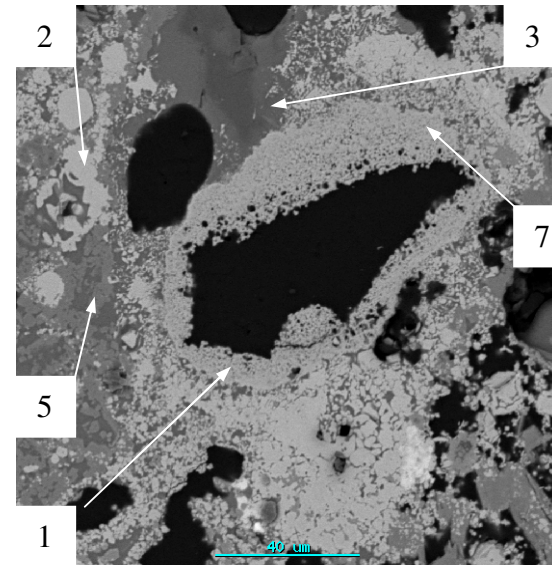
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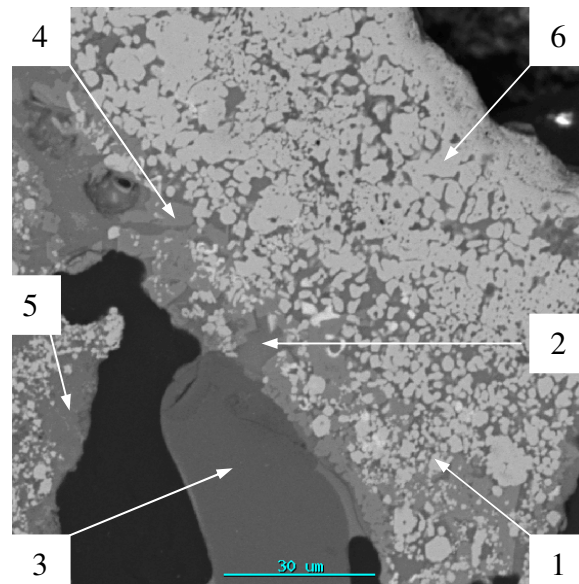(a) Spiked with 10%CrO$_3$

(b) Spiked with 1%CrO$_3$

(c) Spiked with 1.46% K$_2$Cr$_2$O$_7$
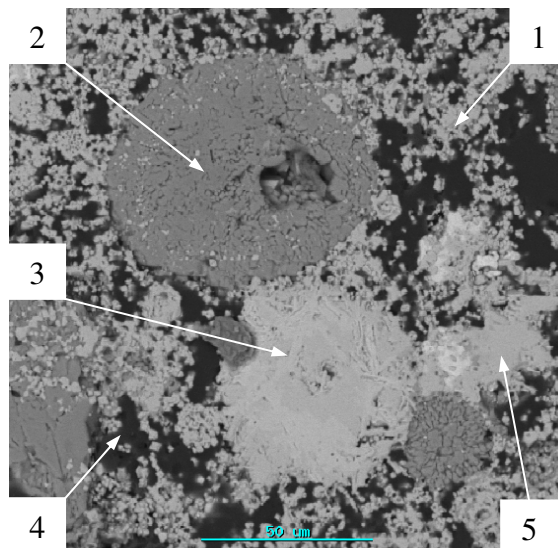
(d) Spiked with 1.92% K$_2$CrO$_4$

Figure 8.17 The typical microstructure of the stabilized SPD that was spiked with Cr (VI) and sintered at 1100°C for 5h [1-Cr$_2$O$_3$; 2-spinel (Fe,Mn,Mg,Ni,Zn,Cr,Al)$_3$O$_4$; 3-glassy phase; 4-unreacted quartz; 5-Augite Ca(Mg,Fe)(Si,Al)$_2$O$_6$; 6-Anorthite Ca(Al,Fe)$_2$Si$_2$O$_8$; 7-Hematite (Fe,Cr,Mn)$_2$O$_3$]

Figure 8.18 The typical microstructure of the stabilized SPD that was spiked with 1.55%$CaCrO_4$ and sintered at 1100^oC for 5h [1-spinel $(Fe,Mn,Mg,Ni,Zn,Cr,Al)_3O_4$; 2-glassy phase; 3-unreacted quartz; 4-Augite $Ca(Mg,Fe)(Si,Al)_2O_6$; 5-Anorthite $Ca(Al,Fe)_2Si_2O_8$; 6-Hematite $(Fe,Cr,Mn)_2O_3$]

In order to verify the association between the formation of Cr (VI) and the presence of lime and/or alkali oxides, the sintered pure stainless steel plant dust (~4,000 mgCr(VI)/kg sintered waste) was also examined phase chemically (Figure 8.19). It indicates that the main crystalline phases are dicalcium silicate, spinel, hematite and a glassy phase (Table 8.5). Small amounts of calcium and alkali oxides were found to be present in the spinel and glassy phases of this sample, which was not the case in the samples to which clay was added. It is presumed that CaO and alkali oxides can form Cr (VI) species in the sintered wastes via reactions 8.5 and 8.6. This increases the extractable Cr (VI) from the sintered SPD.

Figures 8.20 and 8.21 summarises the influences of the mass %CaO/mass %SiO_2 ratio and the mass % K_2O in the mixtures on the leachability of Cr (VI) under different initial Cr (VI) concentrations [5321 mg Cr(VI)/kg mixture added as 1 wt% CrO_3, 1.46 wt% K_2CrO_4, 1.92 wt% $K_2Cr_2O_7$ and 1.55%$CaCrO_4$, and 245.6mg Cr(VI)/kg mixture added as

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Figure 8.19 The microstructure of the sintered SPD (1100°C, 5h and 100% SPD) (1- Spinel; 2-Dicalcium silicate (2CaO·SiO$_2$); 3- Hematite; 4- Pore; 5-glassy phase)
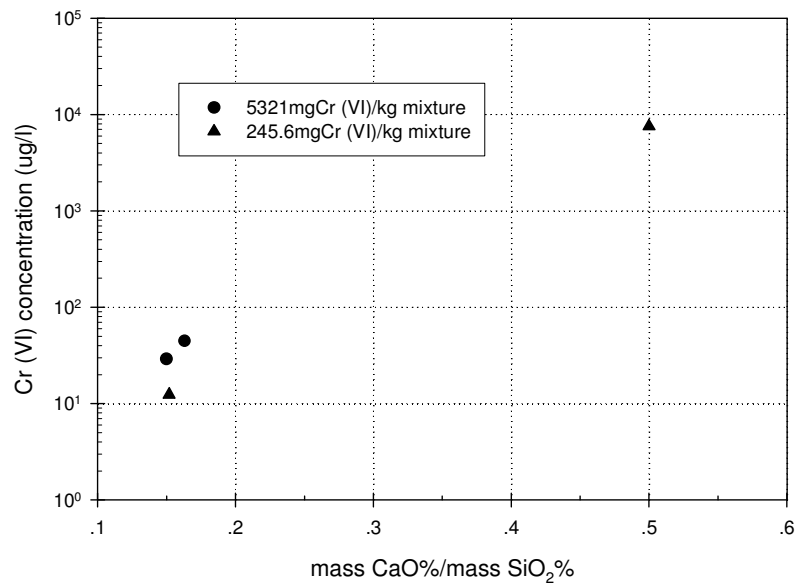
Table 8.5 Typical EDS analyses of the phases present in the brick (100%SPD, sintered at 1100°C for 5h) (mass%)

| Phases	Fe$_2$O$_3$	Cr$_2$O$_3$	CaO	Al$_2$O$_3$	SiO$_2$	MgO	MnO	NiO	Na$_2$O
Spinel	55.3	21.2	2.5	0	0	5.7	7.0	5.2	3.1
Hematite	88.1	8.1	0	1.6	0	0	2.2	0	0
Dicalcium silicate	1.1	0.9	66.2	0	31.8	0	0	0	0
Glassy	33.1	9.5	28.8	0	23.3	1.0	1.0	0.8	1.0

K$_2$CO$_3$ (2.07wt% and 4.07wt%), CaO]. It indicates that the leachability of Cr (VI) increases with increasing mass %CaO/mass % SiO$_2$ ratio and the mass % K$_2$O in the mixtures. It implies that the contents of lime and alkali metal oxide content play important roles in the leachability of Cr (VI), due to the formation of Cr (VI)-containing phases, such as CaCrO$_4$ and alkali chromates [182,183]. Figures 8.20 and 8.21 also indicate that increasing initial Cr (VI) contents increase the leachability of Cr (VI).

8.3.9 Stabilisation of Cr (VI) in ferrochrome fine dust and filter cake by sintering

The mixtures that consist of 50wt% AS-50wt% waste (ferrochrome fine dust or filter cake) were sintered in a tube furnace at 1000°C for 5 hours. The leachability of Cr (VI)

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Figure 8.20 The influence of mass %CaO/mass %SiO$_2$ ratio on the leachability of Cr(VI) [5321mg Cr(VI)/kg mixture - 1 wt% CrO$_3$ and 1.55%CaCrO$_4$, and 245.6mg/kg –50%AS-50%SPD and CaO spiked 50%AS-50%SPD, 1100°C and 5 hours]
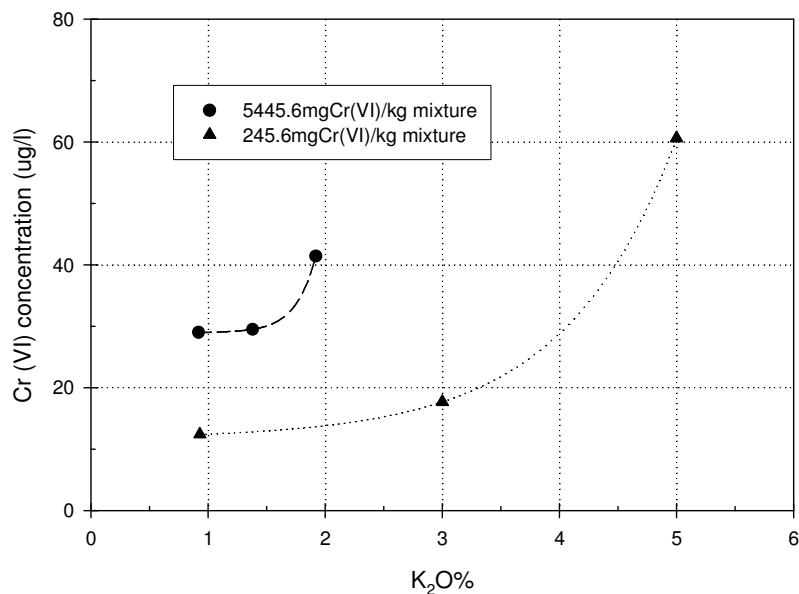
Figure 8.21 The influence of mass % K$_2$O in the mixture on the leachability of Cr(VI) [5321 mg Cr(VI)/kg mixture-1 wt% CrO$_3$, 1.46 wt% K$_2$CrO$_4$ and 1.92 wt% K$_2$Cr$_2$O$_7$, and 245.6mg/kg–50%AS-50%SPD and 2.07wt%, 4.07wt% K$_2$CO$_3$ spiked, 1100°C and 5 h]

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from the different types of stabilised wastes is shown in Figure 8.22. It indicates that the stabilised FCD1 can meet the regulation limits for Cr (VI), while Cr (VI) concentrations in the leachate from the stabilised FCD2 and FC exceed the regulation limits on Cr (VI). The significant levels of Cr(VI) from the stabilised filter cake is presumably due to high concentrations of $CaO/CaCO_3$ and CaF_2 in the mixture.
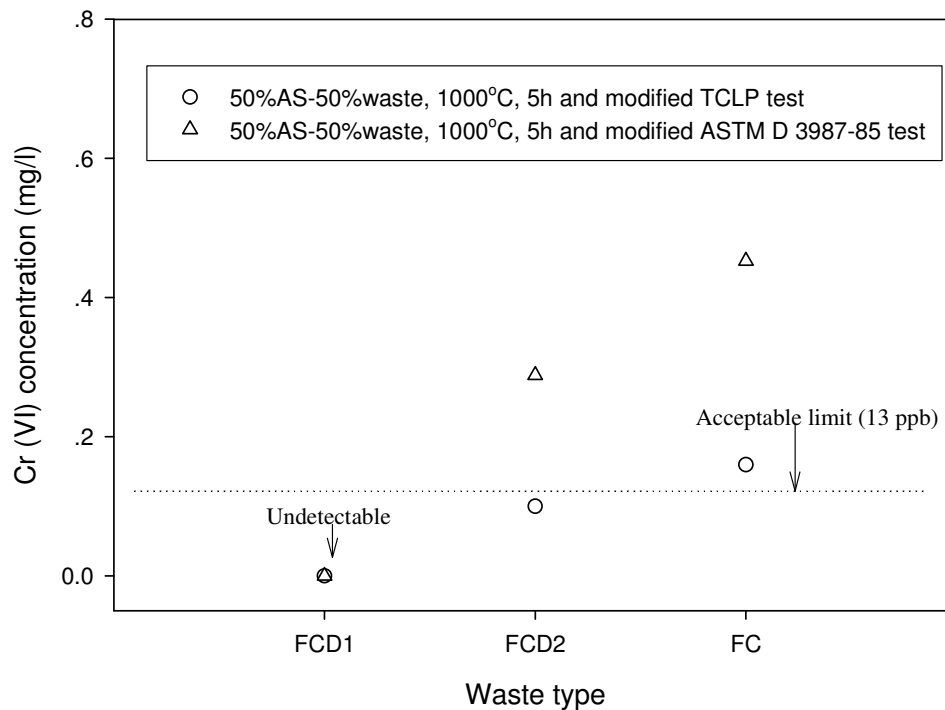
Figure 8.22 The leachability of Cr (VI) from the stabilised wastes (50%AS-50%FCD1, FCD2 or FC) that were sintered at 1000^oC for 5 hours

The leachability of selected toxic substances from the leachates of the modified TCLP test is reported in Table 8.6. It indicates that zinc concentrations in the leachate of the modified TCLP test exceed the acceptable risk level. This is due to the significant contents of zinc oxide in the original ferrochrome dust, which can be extracted under the slightly acidic conditions associated with TCLP solution 1. The concentration of calcium in the leachate from the stabilised FC is 938 mg/l, which is presumably due to the significant contents of calcium in the filter cake. The concentrations of arsenic, chromium

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Table 8.6 Concentrations of selected elements in the leachates of the modified TCLP tests from the stabilised FCD1, FCD2 and FC (ppm)

| Elements	As	Al	Ca	Cd	Cr	Fe	Mg	Ni	Pb	Si	V	Zn
FCD1	<0.1	2.29	60.3	<0.05	0.09	1.22	29.4	<0.05	<0.05	33.5	<0.05	95.3
FCD2	<0.1	1.10	25.6	<0.05	0.34	0.14	40	<0.05	<0.05	23.1	<0.05	9.34
FC	<0.1	1.10	938	<0.05	0.33	0.23	5.04	0.13	<0.05	234	1.01	0.56
ARL *[15]	0.43	na	na	0.031	4.7**	na	na	1.14	0.1	na	1.3	0.7

Note: *: Acceptable Risk Level; **: ARL of Cr (III); na-not available.

and nickel are lower than the acceptable risk level, while the cadmium content is possibly above the acceptable risk level.
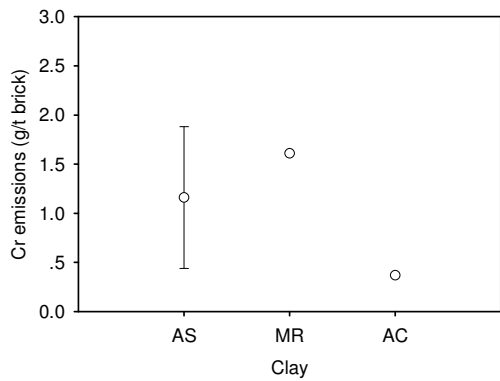
The stablisation of ferrochrome dust and filter cake in a sinter process at 1000°C for 5 hours using 50% clay AS is therefore not successful, as the acceptable risk levels of Cr(VI) (20ppb) or zinc (0.7ppm) for South Africa cannot be met.

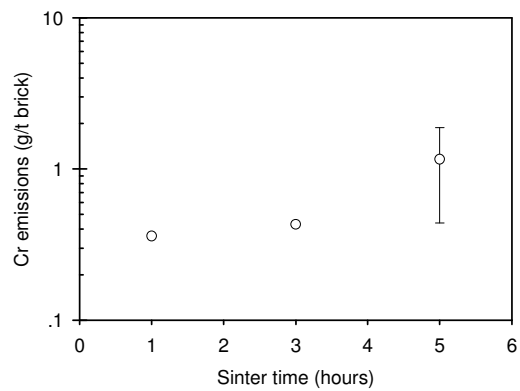### 8.3.10 Chromium emission during the sinter process

Chromium can be vaporised at high temperatures mostly through the formation of Cr (VI) species via the following reaction [173-175]:

$$1/2Cr_2O_3 \text{ (s)} + 3/4 \text{ } O_2 \text{ (g)} \leftrightarrow CrO_3 \text{ (g)}$$
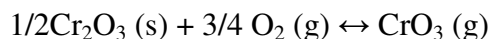
The effects of different parameters on chromium emission are shown in Figure 8.23. It shows that chromium emission from the mixture of 50%AC-50%SPD is lower than that from the mixtures of 50%MR-50%SPD and 50%AC-50%SPD (Figure 8.23a). The total chromium emission factors from the stabilised waste during the sinter process is approximately 0.5 to 1.8 g/ton brick produced at 1100°C for 5 hours. It is lower than the emission factors from steel plants (4.0-36.1 g/t steel) and sewage sludge incineration (10g/t) [177], while it is similar to the cement industry (approximately 1.6g/t cement produced [176]). It indicates that under current experimental conditions the sinter process

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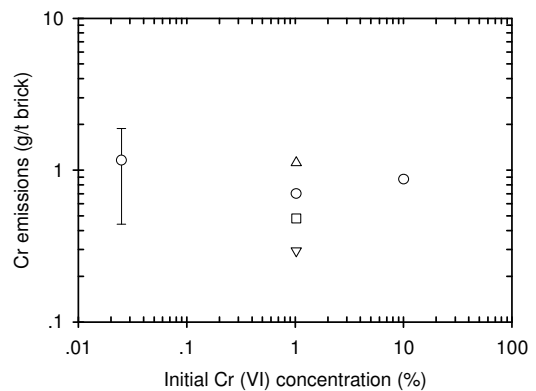
(a) Effect of clay type on Cr emission
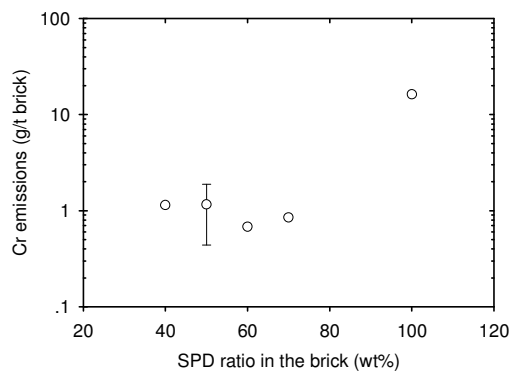
(1100°C, 50wt%SPD and 5 h)

(d) Effect of sinter time on Cr emission
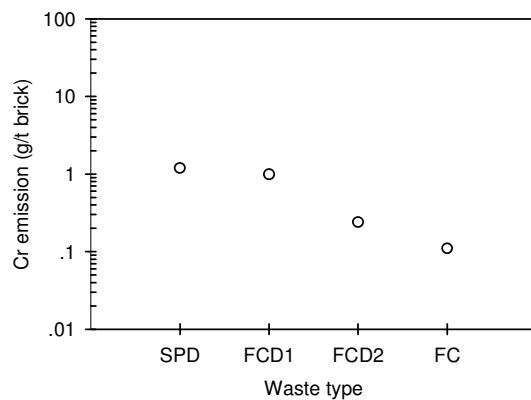
(AS, 50wt% and 1100°C)
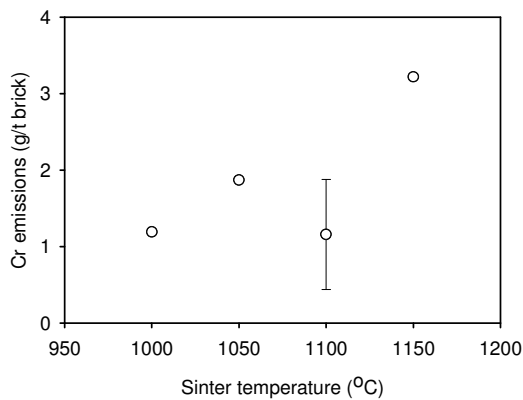
(b) Effect of sinter temperature on Cr

emission (AS, 50wt%SPD and 5h)

(e) Effect of initial Cr (VI) concentration

on Cr emission (AS, 1100°C and 5h)

(c) Effect of wastes content on Cr

emission (AS, 1100°C and 5 h)

(f) Chromium emission of different

wastes (1000°C and 5h)

Figure 8.23 Chromium emission during the sinter process

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can be considered a safe process to treat SPD. In addition, increasing sinter temperature, waste ratio in the brick and sinter time increase the chromium emissions. However, increasing initial Cr (VI) concentration has no significant influence on chromium emission. A mass balance on the waste mixture (50%AS-50%SPD) which was sintered at 1100°C for 5 hours confirmed that chromium was stabilised in the brick (see Appendix III).

Chromium emission from stabilised ferrochrome fine dust 2 and filter cake that was sintered at 1000°C is lower than the emission factor of the stabilised stainless steel plant dust and stabilised ferrochrome fine dust 1 (Figure 8.23 f).

8.4 Conclusions

Bricks were produced by mixing wastes (stainless steel plant dust, ferrochrome dust and filter cake) and clay. The leachability of Cr (VI) from the stabilised wastes were investigated. The following conclusions can be drawn:

(1) When the bricks were sintered at 1100°C for 5 hours with a 50 wt% SPD content in the brick, Cr (VI) in the stainless steel plant dust can be significantly stabilised.

(2) 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.

(3) Clay AS has the best stabilisation capacity of Cr (VI) in stainless steel plant dust, while clay AC has the worst. This is presumably due to the higher mass %CaO/mass %SiO_2 ratio in the AC-SPD mixtures.

(4) 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. A sinter process whereby SPD is mixed with clay is therefore considered to be an effective process to stabilise toxic substances in stainless steel plant dust.

(5) Cr (VI) recovery decreases with increasing leaching time. This is due to the fact that the spiked Cr (VI) was reduced or transformed into Cr (III) during the leaching period.

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(6) The leachability of Cr(VI) is influenced by the mass%CaO/mass%SiO$_2$ ratio and alkali metal oxides content in the raw materials.

(7) Ferrochrome dust and filter cake 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.

(8) The emission factors from the stabilised wastes (SPD, FCD1, FCD2 and FC) are similar to those reported for the cement industry.