Chapter 7 Stabilisation of Cr (VI) through sintering using silica-rich clay, Part I: Synthetic samples

7.1 Introduction

Cr (VI) is toxic, carcinogenic, highly soluble and strongly oxidizing [13]. The Cr (VI)-containing wastes can be treated by different methods, such as high temperature recovery processes, conventional chemical precipitation processes [161], carbon absorption processes [161] and stabilisation/solidification processes [5,44,56,157,162]. Stabilisation/solidification processes are effective technologies whereby Cr (VI)-containing pyrometallurgical wastes can be treated. The wastes can be cemented, glassified and sintered into value added products such as bricks, cement and glass during the processes. Furthermore, it requires low investment costs and is easy to operate. Only small amounts of secondary waste residues emit from these processes.

Recently, Hattori et al. reported that Cr (VI)-containing sludge wastes can be immobilised by silica-rich clay at 1000^oC [157]. Thermodynamic calculations and experimental work revealed that chromium (VI) species react with silica to form the less soluble chromic oxide (Cr_2O_3) and uvarovite ($Ca_3Cr_2Si_3O_{12}$) at high temperatures and therefore reduce the leachability of Cr (VI) [157]. Huang et al. studied the incorporation of Cr (III) and Cr (VI) in a simulated basaltic industrial waste ($40.5\%SiO_2$-$11.5Al_2O_3$-$23\%Fe_2O_3$-$11.5\%CaO$-$10.0\%MgO$-$3.5\%Na_2O$) [162]. It was found that chromium is stabilised by being crystallised as Cr-rich primary spinel phases at high temperatures and secondary spinel during cooling [162]. Furthermore, the stabilised waste product can be used as a medium-grade abrasive, whereby the wastes are transformed into commercial products. Maine et al. proposed that chromium in fired mixtures of 50% clay-50% ferrochrome dust is stabilised in the amorphous glassy phase (Mg-Al-Fe-Si rich) [17].

More recently, several workers have used sinter operations to stabilise Cr (VI) and soluble salts in the stainless steel plant dust and ferrochrome dust [5,16,44,58]. However, the mechanisms whereby Cr (VI) in these wastes are stabilised and the leaching

mechanisms of chromium species from the stabilised wastes forms using clay are not clear. In addition, identifying the optimum sinter parameters remain a challenge due to the variation of the characteristics of the stainless steel plant dust, ferrochrome dusts and filter cake from the waste acid treatment plant.

This chapter investigates the effects of sinter temperature, sinter time, clay type, CaO content and sinter atmosphere on the leachability of Cr (VI) from synthetic CrO_3-clay mixtures, the possible mechanisms whereby Cr (VI) is stabilised using silica-rich clay, were also studied.
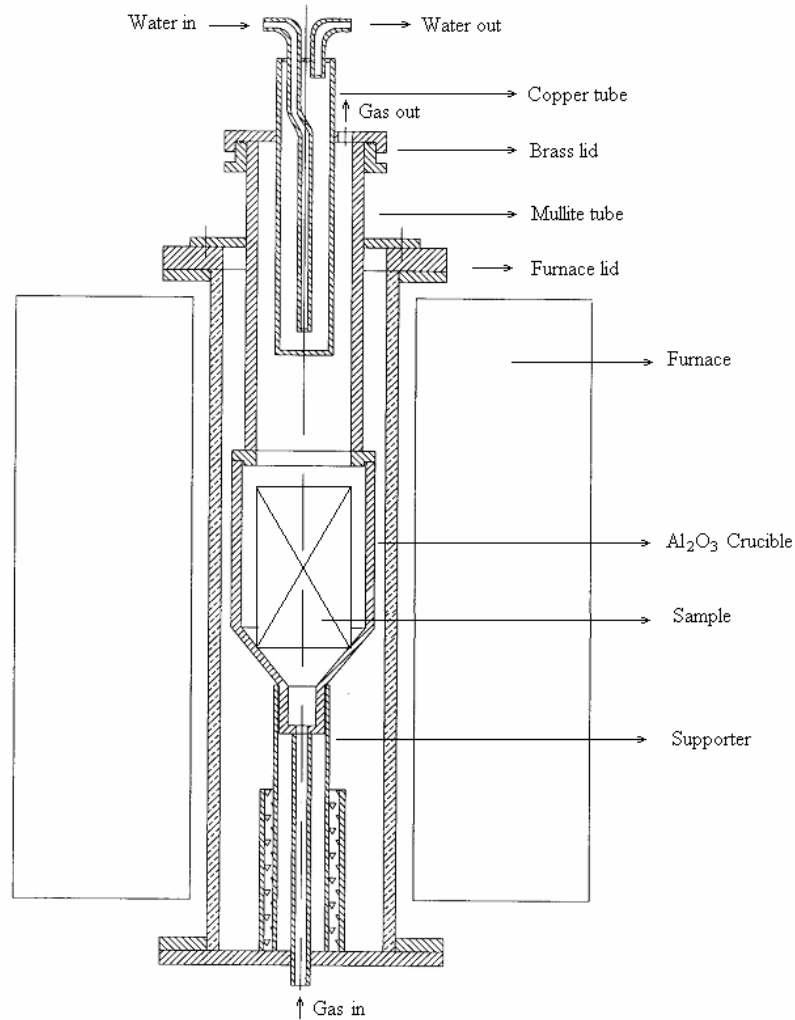
7.2 Experimental

7.2.1 Materials

Three clay samples (AS, AC and MR) were collected from a local brick plant. The as-received clays were sieved manually using a screen with a pore size of 1mm. The particle size distributions of the clays of the –1mm fraction were determined with a Malvern Mastersizer 2000. The thermal characteristics of the clays were examined by the same TG/DTA instrument as described in Chapter 3. Approximately 30mg ground clay samples were heated in dry air at a flow rate of 50ml/min at 20°C/min from room temperature up to 1300°C.

Representative clay samples of approximately 135g were mixed with analytical reagent grade CrO_3 to attain the same Cr (VI) concentration as is found in the stainless steel plant dust (245mg/kg). The minimum amount of distilled water (approximately 15ml) was added to each sample. The mixture was pressed in a mould (28mm×20mm×100mm) using a hydraulic press at 50 kN force. The samples were then dried at 110^oC for 48 hours after which they were reacted in a tube furnace. Figure 7.1 schematically shows a cross section of the furnace. In this set of experiments, the sinter temperature, sinter time, sinter atmosphere, initial Cr (VI) concentration and the influence of lime addition were investigated. The experimental parameters are shown in Table 7.1. The sinter temperatures ranged from 1150^oC to 1250^oC. The sinter time ranged from 3 to 7 hours. Reagent grade CaO was added to the clays in order to obtain mass %CaO/mass %SiO_2

(in the clay) ratios of 0.05, 0.1 and 0.2. Different initial amounts of CrO_3 and different atmospheres (air and argon) in the brick were also considered (Table 7.1). The samples that were spiked with 245 mg/kg CrO_3 and sintered at 1200^oC for 5 h were duplicated.

Figure 7.1 The furnace set-up

Table 7.1 Experimental conditions

Clay	AS, MR, AC
Sinter temperature (^oC)	1150, 1200, 1250
Sinter time (hours)	3, 5, 7
CaO/SiO$_2$ mass ratio	0, 0.05, 0.1, 0.2
Initial Cr (VI) concentration (mg/kg)	0, 245, 2450
Atmosphere	Dry air and argon

The heating and cooling rates during the experiments were ~1.5^{o}C/min. The temperature profile of the tube furnace was measured with a calibrated type-B thermocouple with an error of ±1°C.

In order to examine chromium losses during the sintering process, and therefore potential secondary pollution, a water-cooled copper finger was set inside the tube furnace to condense any volatile Cr-containing species. The condensate was dissolved in 50ml nitric acid solution (1mol/l). The total chromium concentration was determined using a UV/Vis spectrophotometer.

7.2.2 Analytical techniques

X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM-EDS) were used to examine the phase compositions, chemical compositions and microstructures of the sintered samples (described in Chapter 3). Cr (VI) in the sintered brick was digested in a sodium carbonate/sodium hydroxide solution and photometrically determined using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

The sintered clay products were ground and the leachability of Cr (VI) was evaluated with the modified TCLP and modified ASTM D 3987-85 tests. The Cr (VI) concentration in the leachate was determined (see Appendix I). The detection limit of Cr (VI) using this method is approximately 0.004 mg/l, while it is reliable when Cr (VI) concentrations are higher than 0.01 mg/l [163,164].

7.3 Results and discussion

7.3.1 Characteristics of the clays

7.3.1.1 Particle size distribution, chemical composition, phase composition and microstructure

Clays AS and AC are grayish in colour, while MR is brownish. The particle size distributions of the sieved clays are shown in Figure 7.2. It shows that the mean size of

clays AS, MR and AC are approximately 52, 34 and 22 μm, respectively. The chemical compositions of the clay samples are shown in Table 7.2. Approximately 93 wt% of clay AS consists of SiO_2 and Al_2O_3, while clay MR contains less silica but more iron oxide, alumina and alkali metal oxides than clay AS. Clay AC has the highest Al_2O_3 and TiO_2 contents and loss on ignition (LOI) at 1000^oC.
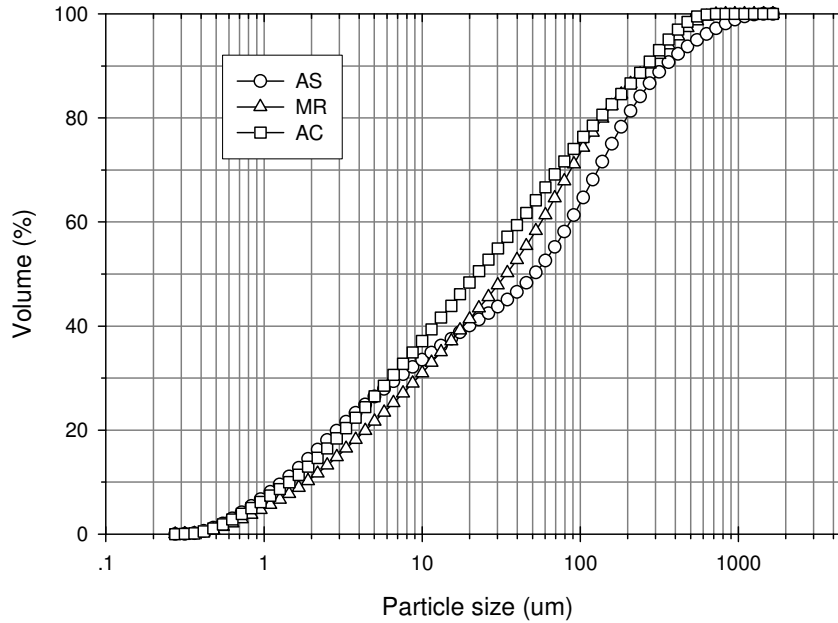

Figure 7.2 The particle size distribution of the clays

Table 7.2 The chemical compositions of the clays (wt.%)

Clay	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	Cr$_2$O$_3$	LOI	Total
AS	80.68	0.78	12.20	0.99	0.02	0.06	0.00	0.06	0.87	0.02	3.84	99.45
MR	67.33	0.82	16.06	6.49	0.18	0.86	0.04	0.16	4.18	0.03	3.45	99.60
AC	57.03	1.40	27.18	3.04	0.02	0.19	0.07	0.05	0.53	0.03	9.46	99.00

The XRD patterns of the clays are shown in Figure 7.3. Clay AS contains the crystalline phases quartz (SiO_2), kaolinite ($Al_2Si_2O_5(OH)_4$), microcline ($KAlSi_3O_8$) and small amounts of rutile (TiO_2) and $(Al,Fe,Ti)_3O_5$. Clays MR and AC contain muscovite $((K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2)$ besides the above phases. Iron is incorporated in

Chapter 7 Stabilisation of Cr (VI) through sintering using silica-rich clay, Part I: Synthetic samples

the muscovite phase structure and exists in $(Al,Fe,Ti)_3O_5$. Trace amounts of $ZrSiO_4$ particles also exist in clay AS.
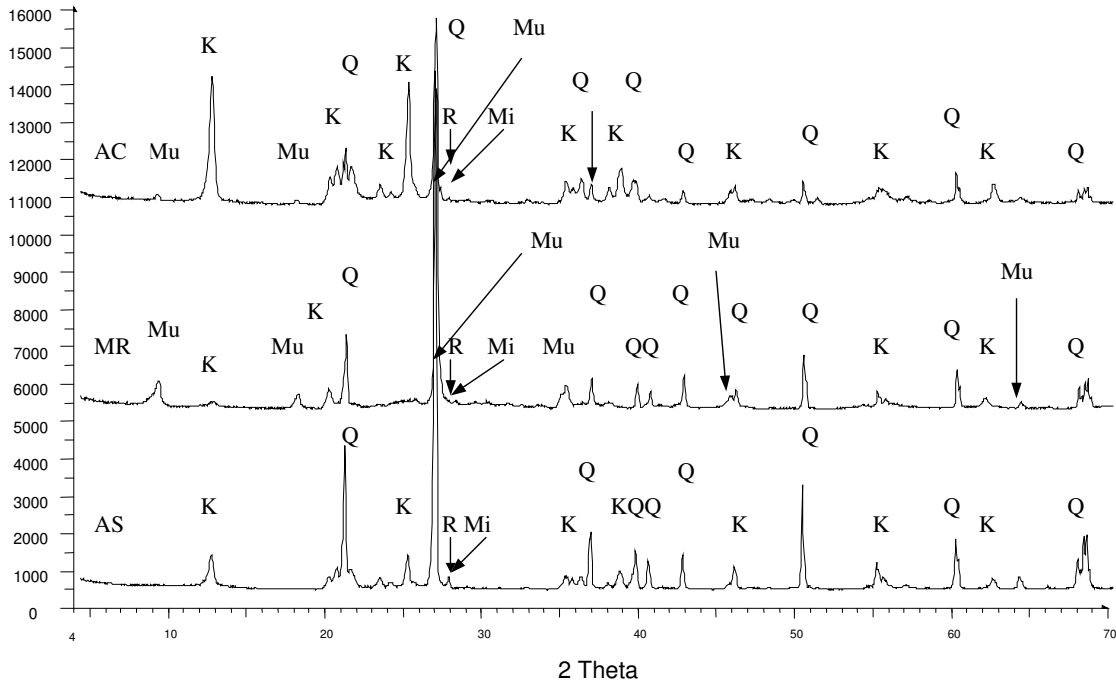
Figure 7.3 The crystalline phases present in the clays (Q-quartz, K-kaolinite, Mi-Microcline, Mu-Muscovite, R-Rutile)

The semi-quantitative XRD analysis of the clays is shown in Table 7.3. It indicates that quartz and kaolinite are the major phases in clay AS. Clay MR contains large portions of quartz and muscovite (about 92 wt%), while quartz, kaolinite and muscovite comprises about 95 wt% of the crystalline phases in clay AC. It further confirms that clay AC should have the highest loss on ignition due to the high content of kaolinite and muscovite (approximately 72 wt% in clay AC vs. 31 wt% and 46 wt% for clays AS and MR, respectively). Most of the potassium in clay MR is in muscovite.

Table 7.3 Semi-quantitative XRD analysis

Clay	Q	K	Mi	Mu	R
AS	64.5	31.4	2.4	nd*	1.7
MR	50.5	4.7	1.4	41.3	2.1
AC	22.4	62.3	2.4	10.1	2.8

Note: Q-quartz, K-kaolinite, Mi-Microcline, Mu-Muscovite, R-Rutile.   *nd-not determined

Chapter 7 Stabilisation of Cr (VI) through sintering using silica-rich clay, Part I: Synthetic samples

---

The thermal characteristics of clays have extensively been investigated [165-169]. It was also examined in this study and is reported on in Appendix II.

7.3.2 Leaching behaviour of Cr(VI) from the sintered brick

7.3.2.1 Effect of temperature on the leachability of Cr (VI)

Cr (VI) leachability from the sintered clay which was spiked with Cr (VI), as a function of sinter temperature, is shown in Figure 7.4. Both the modified TCLP and ASTM D 3987-85 tests indicate that the Cr (VI) concentration decreases with increasing sintering temperature. The Cr (VI) concentration becomes less than 0.015 mg/l after sintering at $1200^{o}C$ and 5 hours (duplicated), which is below the acceptable environmental risk concentration of Cr (VI) of 20 ppb. Cr (VI) concentration in the leachate from the sintered brick (AS, $1250^{o}C$, 5 hours and dry air) is less than the detection limit (0.004 mg/l).
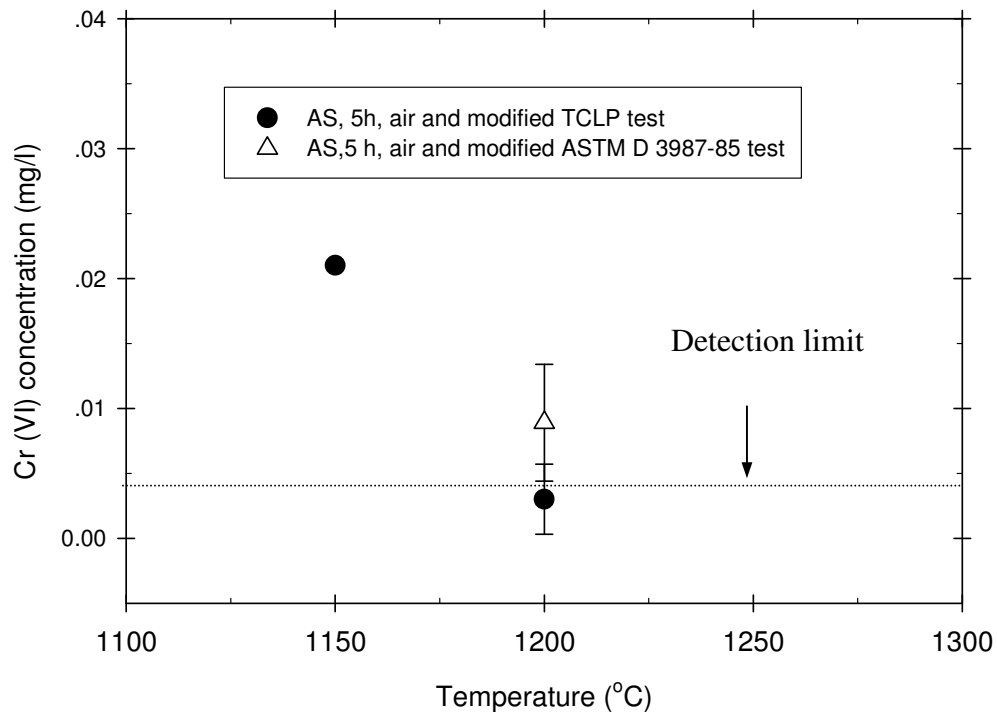
Figure 7.4 The effect of temperature on the leachability of Cr (VI)

The Cr (VI) stabilisation ratio when clay AS is used can be calculated using the following equation:

$$\text{Cr (VI) stabilisation ratio (\%)} = \frac{\text{Cr (VI)}_{\text{spiked}} - \text{Cr (VI)}_{\text{in the sintered brick}}}{\text{Cr (VI)}_{\text{spiked}}} * 100 \qquad (7.1)$$

Where Cr (VI) $_{\text{spiked}}$ is the total amount of Cr (VI) which was spiked into the clay brick, and Cr (VI) $_{\text{in the sintered brick}}$ is the Cr (VI) content of the sintered brick.

The mass of the green brick, which was spiked with CrO_3 and sintered at 1250°C for 5 hours using clay AS, is 133.6g, while the mass of the brick after being sintered is 127.9 g. The Cr (VI) concentration in the sintered brick is 1.15 ppm (as determined by ICP-OES). Hence, the stabilisation ratio can be calculated as:
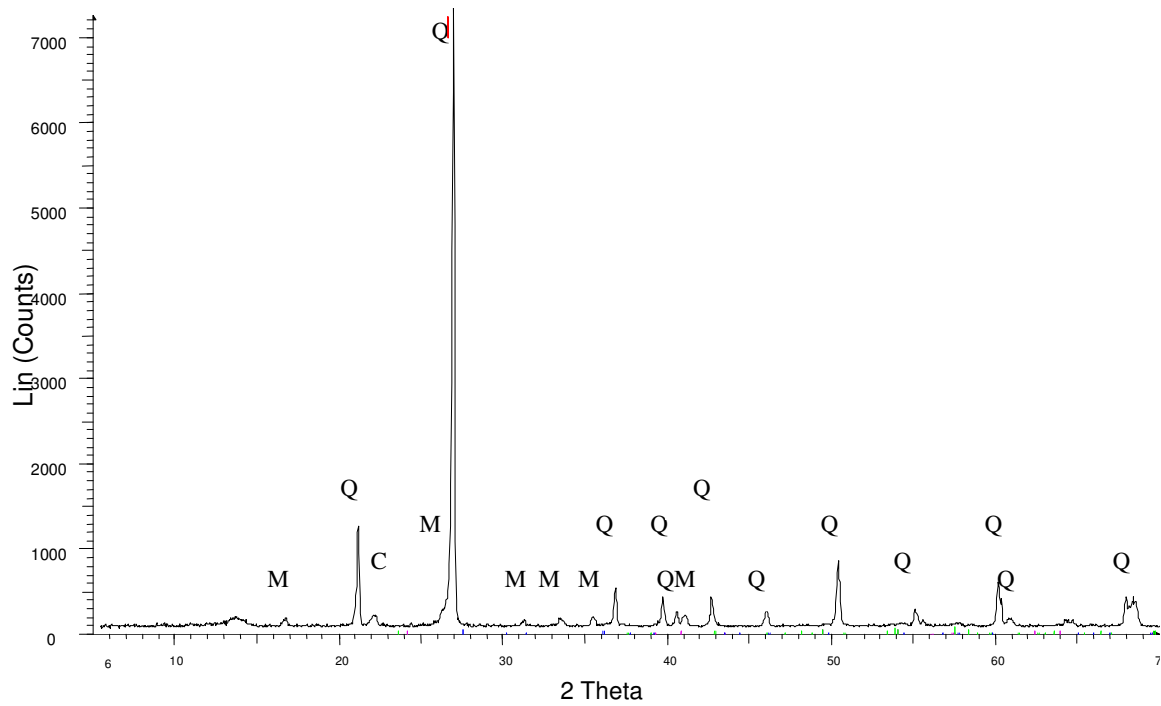
$$\text{Cr (VI) stabilisation ratio (\%)} = \frac{245 mg/kg * 0.1336 kg - 1.15 mg/kg * 0.1279 kg}{245 mg/kg * 0.1336 kg} * 100$$

$$= 99.6$$

This indicates that sintering is an effective method whereby Cr (VI)-containing wastes can be treated.

The XRD results show that the major phases present in the sintered brick are quartz, mullite ($3Al_2O_3 \cdot 2SiO_2$) and cristobalite (Figure 7.5). The microstructure of the brick after it has been sintered at 1200°C for 5 hours is shown in Figures 7.6 and 7.7. It indicates that a glassy phase, small quartz particles and rutile or $(Al,Fe,Ti)_3O_5$ are sintered together to form the major matrix of the brick (Figure 7.6). In addition, the glassy phases (Al-Si-K-Fe based) exist between the quartz particles. The typical EDS analysis of the different phases is shown in Table 7.4 (average value obtained from 5 analyses at different positions in the brick). Mullite crystals are too fine, and could not be analysed without picking up from the surroundings.

The mass balance of the sample which was spiked with CrO_3 and sintered at 1200°C for 5 hours are attached in Appendix III. It shows that chromium is stabilised in the brick, probably in the mullite phase and glassy phases.
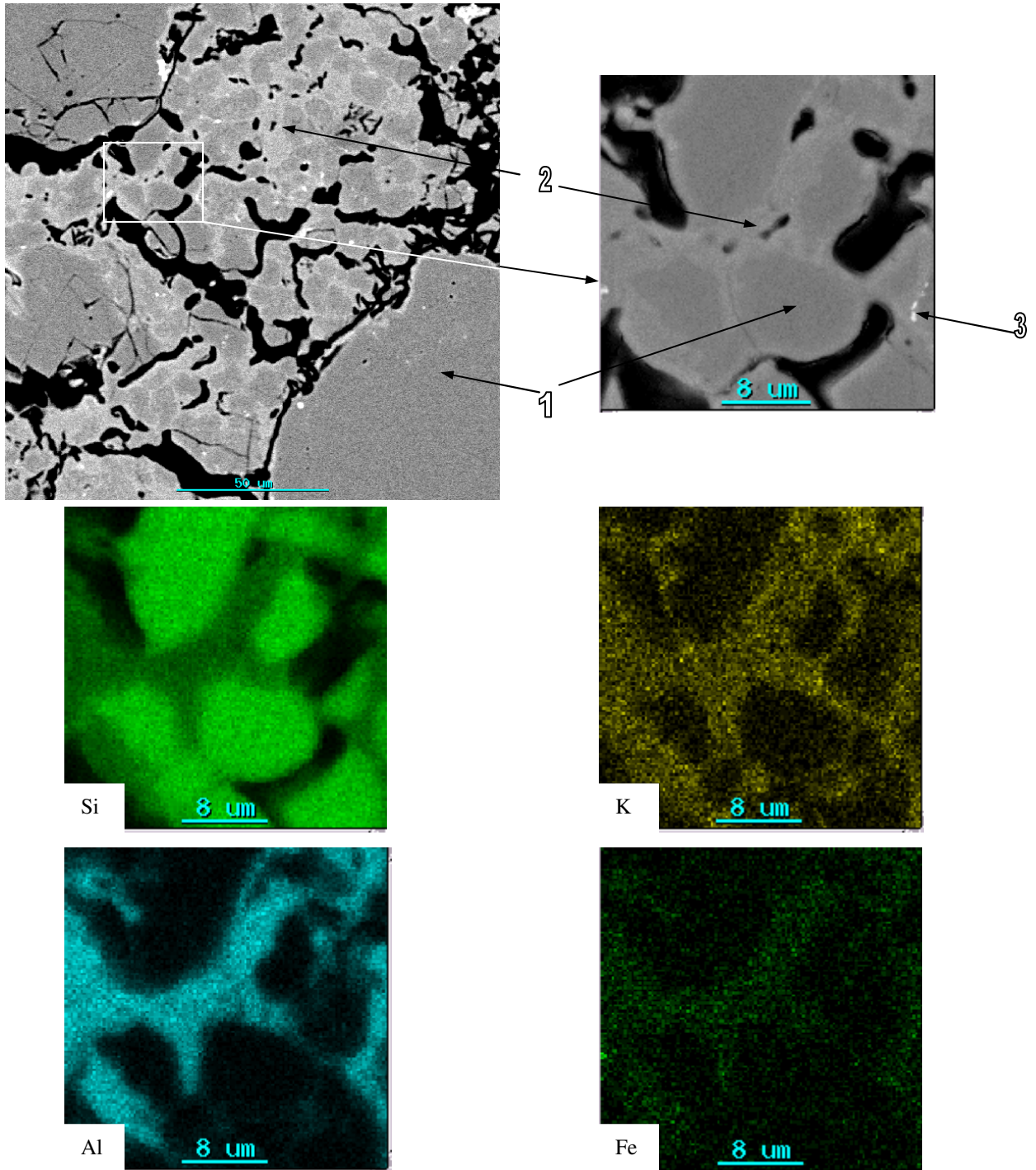
Chapter 7 Stabilisation of Cr (VI) through sintering using silica-rich clay, Part I: Synthetic samples

Figure 7.5 XRD Pattern of the sintered brick (1200°C, 5h, AS+CrO$_3$) (Q-quartz, M-Mullite, C-Cristobalite, R-Rutile)

Table 7.4 Typical EDS analysis of different phases (wt%)

Phases	SiO$_2$	Al$_2$O$_3$	K$_2$O	TiO$_2$	Fe$_2$O$_3$
Silica	100	0	0	0	0
Mullite+ silica	60.9	35.9	0	0	3.2
Rutile	0	0	0	100	0
(Al,Fe,Ti)$_3$O$_5$	0	11.2	0	48.8	40.0
Glassy phase	53.7	39.8	1.5	0	5.0

7.3.2.2 Effect of sintering time on the leachability of Cr (VI)

Chapter 7 Stabilisation of Cr (VI) through sintering using silica-rich clay, Part I: Synthetic samples

Figure 7.6 Typical microstructure and X-ray map of the sintered clay brick (1200°C and

5h) (1-Quartz, 2-Glassy phase (Si-Al-K-Fe), 3-Rutile)
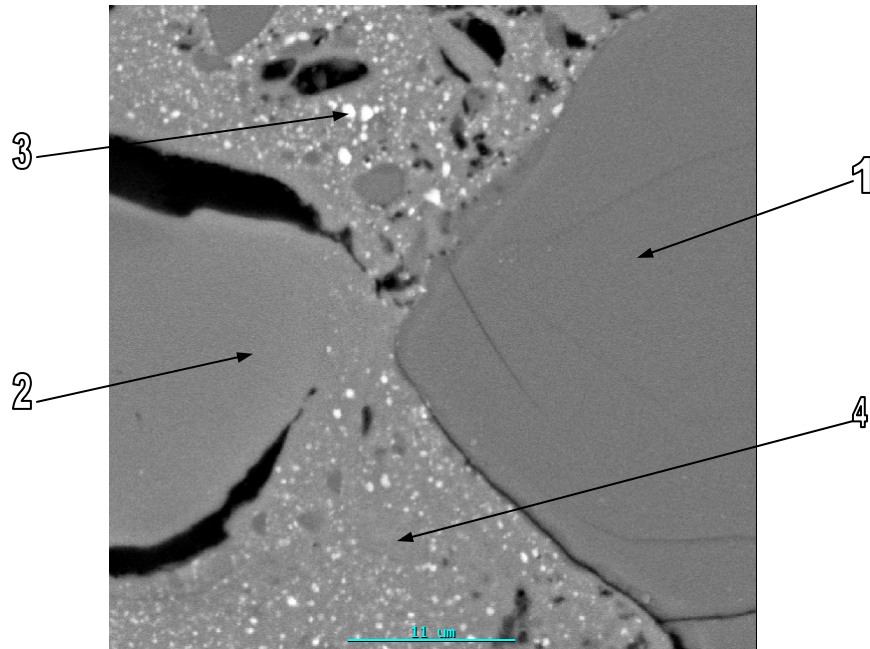
Figure 7.7 Typical microstructure of the sintered clay brick (1200°C and 5h)(1-Quartz, 2-Mullite+ silica, 3-(Al,Fe,Ti)$_3$O$_5$, 4-Glassy phase (Si-Al-K-Fe based))

The effect of sintering time on the leachability of Cr (VI) is shown in Figure 7.8. According to the modified TCLP test, the leachability of Cr (VI) decreases with increasing of sintering time, while the modified ASTM D 3987-85 test indicated that the leachable Cr (VI) remains constant. The leachable Cr (VI) concentrations are in both instances however, in compliance with the regulatory limits of South Africa (the acceptable environmental risk concentration of Cr (VI) is 20 ppb). The difference in leachability of Cr (VI) between these two leaching tests is due to the fact that leach solutions of different pH were used [170-172]. Figure 7.8 also indicates that Cr (VI) can be stabilised with clay AS by sintering it at 1200°C over 3 hours.

7.3.2.3 Effect of clay on the leachablity of Cr (VI)
The effect of different clays on the leachability of Cr (VI) from the sintered bricks is shown in Figure 7.9. It shows that there is no significant difference between the amounts of Cr (VI) that leached when the three different types of clay were used. In addition,
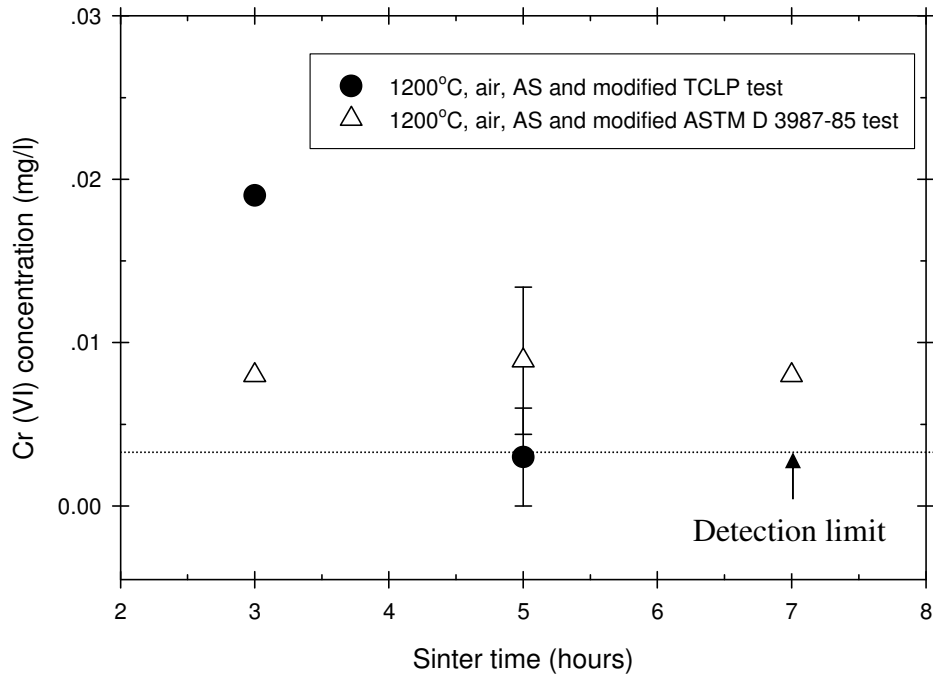
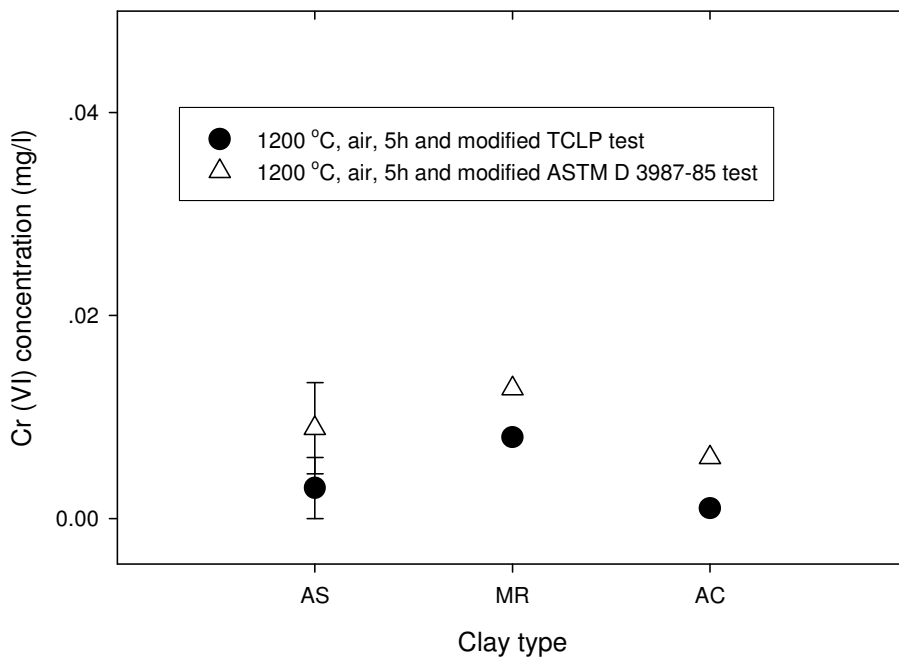**Figure 7.8** The effect of sintering time on the leachability of Cr (VI)

Figure 7.9 The effect of clays on the leachability of Cr (VI)

Figure 7.9 indicates that all the clays have enough capacity to stabilise such lower amounts of Cr (VI) in the clay (approximately 245 mg/kg).

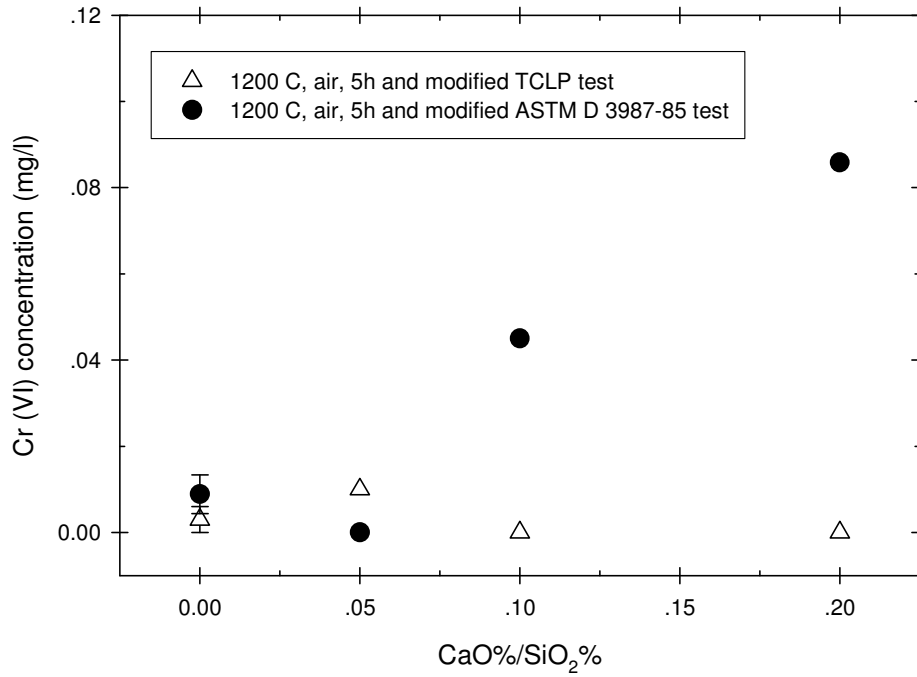*7.3.2.4 Effect of CaO content on the leachability of Cr (VI)*

The effect of the basicity ratio of the clay-CrO_3 samples (expressed as mass %CaO/mass %SiO_2) on the leachability of Cr (VI) is shown in Figure 7.10. The modified ASTM D 3987-85 test indicates that the addition of lime increases the leachability of Cr (VI), while the modified TCLP tests indicates that the leachability of Cr (VI) is not affected by the basicity ratio. The Cr (VI) concentration in the leachate from the modified ASTM D 3987-85 test on the brick with a mass %CaO/mass %SiO_2 ratio of 0.05 and the modified TCLP test on the bricks with a mass %CaO/mass %SiO_2 ratio of 0.1 and 0.2, is below the detection limit. It is, therefore, very important to keep the CaO content in the sintered brick as low as possible (0.05 under current experimental conditions) when Cr (VI) in the wastes is stabilised using clay. By only considering the effect of CaO, it can therefore be expected that the extractable Cr(VI) content from the mixture of AC-CrO_3 is higher than that from the mixtures of clays MR/AS-CrO_3, since it has the highest mass %CaO/mass %SiO_2 ratio in the mixture.

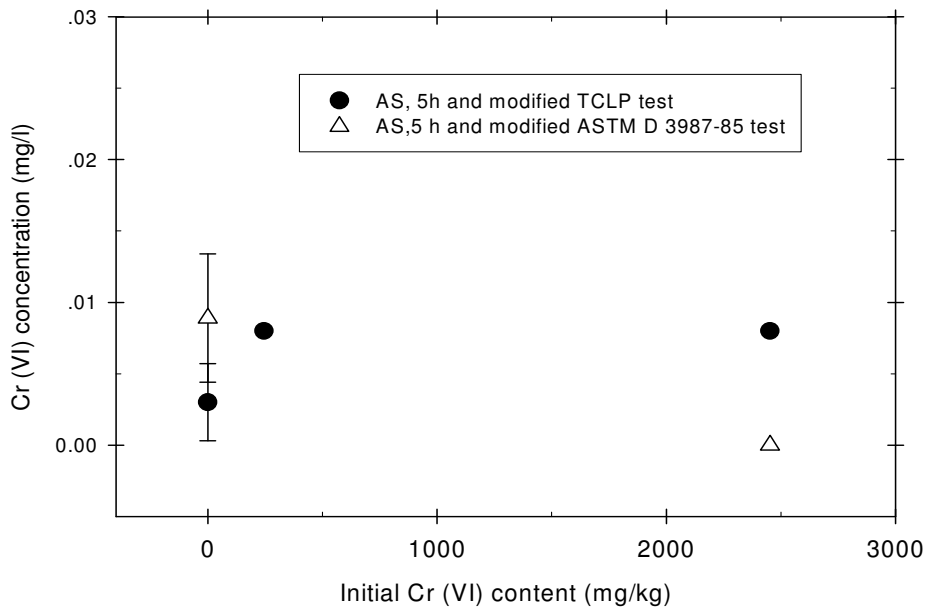*7.3.2.5 Effect of initial Cr (VI) content on the leachability of Cr (VI)*

The effect of initial Cr (VI) content on the leachability of the Cr (VI) is shown in Figure 7.11. It shows that the leachability of Cr (VI) remains below 0.01 mg/l although the initial Cr (VI) content in the green brick can be as high as approximately 2450 mg/kg. Cr (VI) can therefore be effectively stabilised by clay.

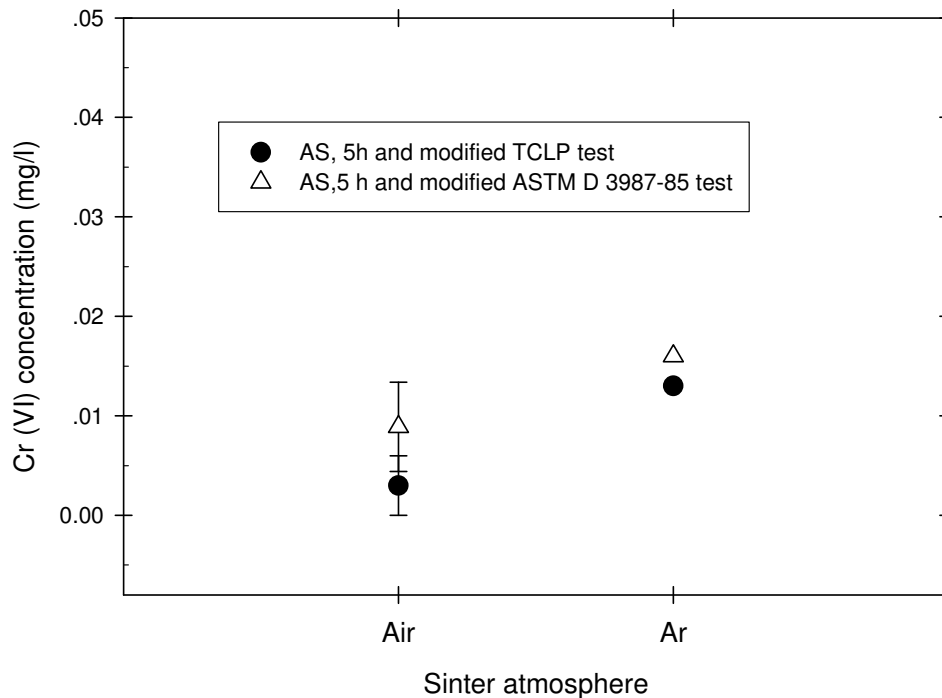*7.3.2.6 Effect of sinter atmosphere on the leachability of Cr (VI)*

The effect of sinter atmosphere on the leachability of Cr (VI) from the sintered bricks is shown in Figure 7.12. It indicates that sinter atmosphere has no significant influence on the leachability of Cr (VI).

Figure 7.10 The effect of mass %CaO/ mass %SiO$_2$ on the leachability of Cr (VI)
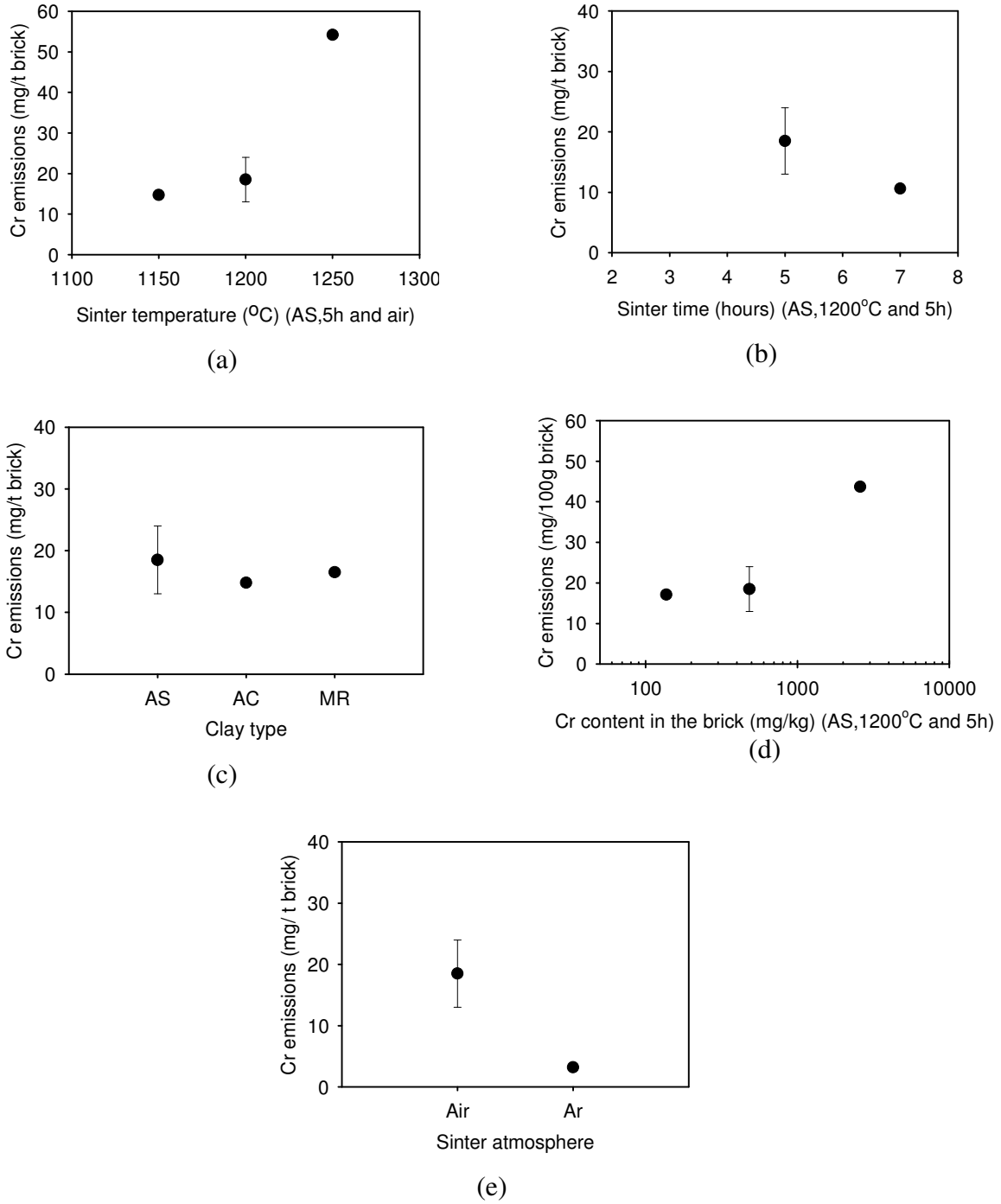

Figure 7.11 The effect of initial Cr (VI) content on the leachability of the Cr (VI)

Figure 7.12 The effect of sinter atmosphere on the leachability of the Cr (VI)

7.3.3 Chromium emissions during sintering process

Chromium emissions were very low in all the experiments although detectable (Figure 7.13). It is assumed that all the collected chromium on the copper tube is Cr (VI)-containing components due to the high vaporization tendency of Cr (VI) [173-175]. It shows that increasing sinter temperature and initial chromium content increase the chromium that is released into the atmosphere. The type of clay used has no significant influence on the chromium emission. On the other hand, the chromium emission factors during the sintering process are quite low compared to other industrial sources (Table 7.5 [176,177]). It also shows that Cr (VI) species are easier to vaporise in an atmosphere of high Po_2 (dry air) than in an atmosphere of low Po_2 (argon). The chromium emissions vary from 10.6 mg/t brick to 43.7 mg/t brick under different sinter conditions. However, chromium emissions could be potentially higher if higher concentrations of chromium are present in the wastes.

Chapter 7 Stabilisation of Cr (VI) through sintering using silica-rich clay, Part I: Synthetic samples

Figure 7.13 Chromium emissions during the sintering experiments

Table 7.5 Emission factors of chromium in various industries [177,178]

Coal-fired industrial boiler (g/t)	Oil-fired industrial boiler(g/1000l)	Steel works (g/t steel)			Municipal incinerator (g/t)	Sewage sludge incineration (g/t)	Cement Industry (g/t)
		VS	EP	BF			
1.7	2.2	9.0	13.5-36.1	4.0	1.10	10	1.6

Note: VS-Venturi Scrubber; EP-Electrostatic Precipitator; BF-Baghouse filter.

7.4 Conclusions

The stabilisation of synthetically prepared Cr (VI)-clay mixtures was investigated in this chapter. The leachability of Cr (VI) from the sintered clay bricks was evaluated through the use of the modified TCLP and ASTM D 3987-85 tests. The following conclusions can be drawn:

1) Silica-rich clay can be used to stabilise Cr (VI). The stabilisation ratio of Cr (VI) can be as high as 99.6% when the brick is sintered at 1250°C for 5 hours.

2) Increasing sintering temperature and time, and keeping the CaO/SiO_2 ratio content below 0.05 reduce the leachability of Cr (VI), while the type of clay does not seem to significantly influence the leachability of Cr (VI).

3) The leachability of Cr (VI) remains below 0.01 mg/l although the initial content of Cr (VI) in the green brick is approximately 2450 ppm. It is efficient to stabilise Cr (VI) by sintering at 1200°C over 3 hours using any of the examined clays.

4) The chromium emission during the sintering process is low and varies from 10.6 mg/t brick to 54.2 mg/t brick in this study.