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Stabilisation of Cr(VI) in stainless steel plant dust through sintering using silica-rich clay

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ABSTRACT

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Keywords: Stainless steel Dust Cr(VI) Stabilisation Clay Stainless steel plant dust is considered a hazardous waste due to the fact that it contains significant levels of Cr(VI) and other heavy metals such as lead and zinc. It should therefore be treated before being stock-piled or land filled. Solidification/stabilisation processes are effective techniques for the immobilisation of heavy metals. This paper consequently describes an investigation into the stabilisation of Cr(VI) in stainless steel plant dust with silica-rich clay in a sintering process. The results indicate that Cr(VI) in the stainless steel dust can be stabilised in a 50 mass% dust:50 mass% clay mixture at an optimum sintering temperature of $1100 \,^\circ$ C, and minimum sintering time of 5 h. Chromium emission during the sintering process was found to be low, and within environmental limits.

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1. Introduction

Cr(VI)-containing solid wastes, typically dust and sludge, are generated during production processes such as the manufacture of stainless steel, chromium-containing alloys, refractory materials and chemicals. These waste materials are considered hazardous due to the toxic and carcinogenic properties of Cr(VI) compounds [1].

In a South African stainless steel plant, approximately 30 kg dust is collected by the off-gas treatment system (typically bag house filter) per ton of stainless steel produced [2]. This stainless steel dust contains significant levels of Cr(VI) (approximately 13 mg/l in TCLP leachate) [3]. However, the regulation threshold of Cr(VI) in drinking water which was specified by South Africa is 0.05 mg/l [4]. Stainless steel plant dust can therefore not simply be stockpiled or land filled, and must be treated to avoid pollution of the ground water.

The Cr(VI)-containing dust and sludge can be treated in pyrometallurgical or hydrometallurgical recovery processes [5,6] and stabilisation/solidification processes [7–10]. Stabilisation/solidification processes were found to be effective technologies whereby Cr(VI)-containing industrial wastes can be treated [7–11]. The wastes can be cemented, glassified and sintered into value added products such as cement, medium-grade abrasive, glass and bricks. In addition, only small amounts of secondary waste residues are emitted from these processes.

This paper subsequently describes the optimum sinter parameters required for stabilising Cr(VI) in stainless steel plant dust that was produced in South Africa with silica-rich clay. The possible mechanisms whereby Cr(VI) is stabilised were also studied.

2. Experimental

2.1. Raw materials and sample preparation

South African stainless steel plant dust (SPD) and clays (AS, MR and AC) were used in the stabilisation experiments (Table 1). Approximately 93 wt% of clay AS consists of SiO₂ and Al₂O₃, while clay MR contains less silica but more iron oxide, alumina and alkali metal oxides than clay AS. Clay AC has the highest Al₂O₃ and TiO₂ contents and loss on ignition (LOI) at 1000 °C. The diameters of the clay particles were below 1 mm, with mean particle sizes for clays AS, MR and AC of respectively 52, 34 and 22 μ m.

Approximately 125 g mixtures of clay and SPD samples were pressed into specimens with dimensions $28 \text{ mm} \times 20 \text{ mm} \times 100 \text{ mm}$ using a hydraulic press at 50 kN force for 5 min. Minimum amounts of distilled water (approximately 12 wt%) were added to the mixture. The green samples were dried at 110 °C for 48 h, after which they were weighed and sintered in a tube furnace.

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| Table 1 | |
|--|--|
| Chemical compositions of the dust and clays (mass%). | |

| | Dust ^a | Clay AS | Clay MR | Clay AC |
|--------------------------------|-------------------|---------|---------|---------|
| SiO ₂ | 4.81 | 80.68 | 67.33 | 57.03 |
| TiO ₂ | 0.08 | 0.78 | 0.82 | 1.4 |
| Al_2O_3 | 0.40 | 12.2 | 16.06 | 27.18 |
| Fe ₂ O ₃ | 43.4 | 0.99 | 6.49 | 3.04 |
| MnO | 5.08 | 0.02 | 0.18 | 0.02 |
| MgO | 5.44 | 0.06 | 0.86 | 0.19 |
| CaO | 12.9 | 0 | 0.04 | 0.07 |
| Na ₂ O | 0.60 | 0.06 | 0.16 | 0.05 |
| K ₂ O | 0.97 | 0.87 | 4.18 | 0.53 |
| P_2O_5 | 0.04 | | | |
| Cr_2O_3 | 14.6 | 0.02 | 0.03 | 0.03 |
| NiO | 2.79 | | | |
| V_2O_5 | 0.09 | | | |
| ZnO | 4.49 | | | |
| MoO ₃ | 1.35 | | | |
| Ga ₂ O ₃ | n.d. | | | |
| PbO | 0.39 | | | |
| SO₃ | 0.47 | | | |
| F | nd | | | |
| Cl | 0.86 | | | |
| LOI | -0.21 | 3.84 | 3.45 | 9.46 |
| Total | 98.55 | 99.45 | 99.6 | 99 |
| С | 0.68 | | | |
| Fe (T) | 31.6 | | | |
| Fe (0) | 1.13 | | | |
| Fe (II) | 5.49 | | | |
| Fe (III) | 24.98 | | | |

n.d. = not determined.

^a Any stainless steel particles present have been converted into oxide species during the sample preparation procedure for XRF analysis. Distinction is made only between the oxidation states of iron.

2.2. Experimental procedure

Specimens were vertically placed in an alumina crucible, and heated at 1.5 °C/min. in a vertical tube furnace (Fig. 1). The furnace was purged with dry air that entered the furnace from the bottom. A water-cooled copper finger was positioned inside the furnace to condense any volatile Cr-containing species. The condensate was subsequently dissolved in 50 ml nitric acid solution (1 mol/l). The total chromium concentration was determined using a UV–vis spectrophotometer.

Different types of clays, sintering temperatures, ratios of clay to waste and sintering times were evaluated in order to find the optimum sintering parameters (Table 2). The sintering temperatures ranged from 1000 to 1150 °C and the sintering time from 1 to 5 h. In order to find the optimum dust to clay ratio, different mixtures were made, ranging from 0 to 100 wt% dust. Lime was also added to the mixture to confirm the effect of basicity (mass% CaO/mass% SiO₂) on the leachability of Cr(VI) from the stabilised dust.

Since the Cr(VI) concentration in the sintered specimen 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 CrO₃ (1 wt% and

Table 2

Process parameters of the sintering experiments.

| Waste material | SPD |
|--|--|
| Clay type: | AS, MR, AC |
| Sinter temperature (°C): | 1000, 1050, 1100, 1150 |
| Sinter time (h): | 1, 3, 5 |
| Amount of steel plant dust (wt%): | 0, 40, 50, 60, 70, 100 |
| Spiked agent to 50%AS + 50%SPD mixture: | CrO ₃ , K ₂ Cr ₂ O ₇ , K ₂ CrO ₄ , CaCrO ₄ and K ₂ O |



Fig. 1. The furnace set-up.

10 wt%), K₂Cr₂O₇, K₂CrO₄ as well as synthetic CaCrO₄ (the same amount of Cr(VI) as in 1 wt%CrO₃), were spiked into the mixture of 50 wt% AS and 50 wt% SPD to study the stabilisation mechanisms of Cr(VI). K₂O (2.07 wt% and 4.07 wt%) was also spiked into certain 50%AS–50%SPD mixtures (added as K₂CO₃) to study the influence of alkaline metals on the leachability of Cr(VI).

2.3. Analytical methods

The chemical compositions of the clays and SPD were determined by X-ray fluorescence (XRF). A Malvern Mastersizer 2000 was used to analyse the particle size distributions of the clays in the–1 mm fraction.

Different leaching tests, such as the Toxicity Characteristics Leaching Procedure (TCLP) test [12] and the ASTM D 3987-85 test [13], have been developed to evaluate the leachability of toxic substances from wastes. These tests, which are also called availability tests [14], are often used to assess the leachability of toxic substances from the wastes. However, according to South African guidelines, which was published by the Department of Water Affairs and Forestry (DWAF) in 1998, the estimated environmental concentration (EEC) value is often used to evaluate whether the hazardous wastes are acceptable [15]. Thus, specimens that are constituted from stainless steel dust and clay can only be used when the EEC of Cr(VI) is lower than 0.02 ppm (acceptable risk level) [15]. The acceptable concentration of Cr(VI) in the leachates of the modified TCLP or the modified ASTM D3987-85 tests for the sintered specimens should be less than 0.013 mg/l [16]. This value was used in this paper to evaluate whether the stabilised products are environmentally acceptable. Two TCLP solutions were prepared for the modified TCLP tests: TCLP solution 2 has a pH of 2.98, and was only used for the sintered pure SPD specimen and the lime spiked specimen. However, TCLP solution 1 had a pH of approximately 4.93, and

was used for the remainder of the sintered samples. The modified ASTM D 3987-85 leaching solution consists of distilled water with a pH of approximately 6.

It was found that the Cr(VI) concentration in the leachate of the modified TCLP tests are below the detection limit of the UV-vis spectrometer for Cr(VI), while the Cr(VI) concentrations from the modified ASTM D 3987-85 test are significantly higher and therefore can be determined. 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 was added to the leachant, it could 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 from the samples, such as Fe²⁺ and organic components, can potentially reduce Cr(VI) species into Cr(III) species [17–19], thereby changing the Cr(VI) concentration in the leachate.

The Cr(VI) concentration in the leachate was determined photometrically using a UV–vis spectrometer. This method is reliable when Cr(VI) concentrations are higher than 0.01 mg/l although the detection limit of the method for Cr(VI) is 0.004 mg/l [20].

Owing to the fact that the concentrations of toxic substances (except Cr(VI)) which leached from the sintered specimens 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 Inductively Coupled Plasma Optical Emission Spectrometer (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 specimens with respect to the crystalline phases present, microstructure and chemical composition.

3. Results and discussion

3.1. Effect of clay type on the leachability of Cr(VI)

Clay AS had the best stabilisation capacity of Cr(VI), while clay AC the worst (Fig. 2). It can be due to the different basicity ratios (mass% CaO/mass% SiO₂) in the sintered specimens (0.15, 0.18, 0.21 for AS, MR and AC containing specimens respectively). In order to examine this hypothesis, a synthetic sample with a mass% CaO/mass% SiO₂ ratio of 0.5 was prepared by adding reagent grade CaO to the 50 wt% SPD-50 wt% AS mixture, after which it was sintered at 1100 °C for 5 h in the tube furnace. The Cr(VI) concentrations from the leachates of the modified TCLP and the modified ASTM



Fig. 2. The influence of different types of clays on the leachability of Cr(VI) from 50%clay–50%SPD specimens, sintered at $1100 \degree$ C for 5 h (using the modified ASTM D 3987-85 test).



Fig. 3. The influence of basicity ratio (mass% CaO/mass% SiO₂) on the leachability of Cr(VI) from the 50% clay-50% SPD specimens, sintered at 1100 $^{\circ}$ C for 5 h.

D 3987-85 tests increased to more than 7.6 mg/l when the mass% CaO/mass% SiO₂ ratio increased from 0.15 to 0.5 (Fig. 3), which confirmed that an increase in the basicity of the mixture increases the leachability of Cr(VI).

3.2. Effect of leaching time on the leachability of Cr(VI)

The effect of leaching time on the leachability of Cr(VI) from the 40%AS-60%SPD sample that was sintered at 1100 °C for 5 h, using the modified TCLP test, after spiking 2 mg/l Cr(VI) into the TCLP leachate is shown in Fig. 4. Cr(VI) recovery decreases with increasing leaching time, which indicates that the spiked Cr(VI) was reduced or transformed into Cr(III) during the leaching period.

The Eh-pH diagram for chromium species confirms 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) (Fig. 5, [21]). This presumably contributes some Cr(VI) to the final leachate. In addition, organic compounds and Fe(II) in the leachate can potentially reduce Cr(VI) components to Cr(III) [22].

3.3. Influence of sintering temperature on the leachability of Cr(VI)

The effect of sintering temperature on the leachability of Cr(VI) from 50%AS-50%SPD mixtures that were reacted for 5 h is shown in



Fig. 4. Cr(VI) concentration in the modified TCLP leachate as a function of leaching time (40%AS-60%SPD sample sintered at 1100 °C for 5 h, leachate spiked with 2 mg/l Cr(VI)).



Fig. 5. The Eh-pH diagram for Cr species calculated using STABCAL with 10–6 mol/l chromium concentration at $25 \,^{\circ}$ C [21].

Fig. 6. It shows that increasing sintering temperature promote 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 specimen was sintered at temperatures of 1050 °C and higher for 5 h. However, a detectable amount of Cr(VI) was found 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 specimens that were sintered at 1000 and 1050 °C are higher than the acceptable limit, while when the specimen was sintered at 1100 °C for 5 h, Cr(VI) was stabilised according to both the modified TCLP test and the modified ASTM D 3987-85 test [Cr(VI) concentration < 13 ppb].

The 50%AS–50%SPD specimen shrank significantly at sintering temperatures above $1100 \,^{\circ}$ C, which indicates that for this mixture, the optimum sintering temperature is $1100 \,^{\circ}$ C.

3.4. Influence of the SPD content of the specimen on the leachability of Cr(VI)

The leachability of Cr(VI) increases with increasing SPD content of the sintered specimen (Fig. 7). 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 specimen decreases with a reduction in the clay content of the mixture, and therefore increases the mass% CaO/mass% SiO₂ ratio in the mixture.



Fig. 6. The influence of sinter temperature on the leachability of Cr(VI) (50%AS-50%SPD sample sintered for 5 h; using modified ASTM D 3987-85 test).



Fig. 7. The influence of SPD content of the specimen on the leachability of Cr(VI).

Two reference samples, i.e., pure AS clay and pure stainless steel plant dust samples, were also sintered at 1100 °C for 5 h (Fig. 7). It was found that 4×10^3 mg Cr(VI) per kg SPD leached from the pure sintered SPD, 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 [3]). This indicates that an additional amount of Cr(VI) formed during the sintering process.

For the AS–SPD mixtures, the leachability of Cr(VI) from the specimens, which were sintered at 1100 °C for 5 h, 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 SPD as possible in the specimen, the optimum SPD content in the specimen is therefore 50 mass%.

3.5. Influence of sintering time on the leachability of Cr(VI)

The effect of sintering time on the leachability of Cr(VI) was studied by sintering 50%AS–50%SPD mixtures at 1100 °C for 1, 3 and 5 h (Fig. 8). It shows that increasing sintering time increases the stabilisation of Cr(VI). The leachability of Cr(VI) from the specimens, which were sintered at 1100 °C for 5 h, is below the acceptable limit of 13 ppb. A 50%AS–50%SPD mixture that is sintered at 1100 °C, should therefore at least be reacted for 5 h in order to sufficiently stabilise the Cr(VI).



Fig. 8. The influence of sinter time on the leachability of Cr(VI) from 50%AS-50%SPD specimens that were sintered at 1100 $^\circ$ C (using the ASTM D 3987-85 test).

Table 3

Concentrations of toxic substances in the modified TCLP leachates from the 50%AS-50%SPD specimen that was sintered at 1100 $^\circ$ C for 5 h.

| Elements | As | Cd | Cr | Pb | Zn |
|---|------|--------|------|--------|------|
| Conc. (ppm) | <0.1 | < 0.05 | 0.16 | < 0.05 | 0.21 |
| Regulation limit in this study ^a | 0.28 | 0.02 | 3.05 | 0.065 | 0.45 |

^a These values were calculated with the same method as was used to calculate the regulation limit of Cr(VI).

3.6. The leachability of other toxic elements from the stabilised wastes

The leachabilities of As, Cd, Cr, Pb and Zn from the stabilised SPD (sintered with 50% clay AS at 1100 °C for 5 h) are below the regulation limits of South Africa, except for possibly cadmium (Table 3). It confirms that when Cr(VI) is stabilised with clay in a sintering process, other toxic elements such as arsenic, zinc and lead are also stabilised.

3.7. Further Cr(VI) addition to the 50%AS-50%SPD mixture

CrO₃, K₂Cr₂O₇, K₂CrO₄ and CaCrO₄ were spiked into 50%AS–50%SPD mixtures in order to evaluate how effective the stabilisation/solidification process with clay is. These mixtures were sintered at 1100 °C for 5 h. The modified TCLP and modified ASTM D 3987-85 tests were used to evaluate the leachability of Cr(VI) from these sintered specimens.

Fig. 9 shows the effect of the initial Cr(VI) concentration in the green specimen on the leachability of Cr(VI) in the stabilised SPD. It indicates that the Cr(VI) leachability only slightly increased when Cr(VI) was spiked into the 50%AS–50%SPD mixture. The amount of leachable Cr(VI) is 0.134 mg/l even though the specimen was spiked with 10 wt% CrO₃.

The influence of the mass% CaO/mass% SiO₂ ratio and mass% K₂O in the mixtures on the leachability of Cr(VI) under different initial Cr(VI) concentrations were also studied. This was done by examining 5321 mg Cr(VI)/kg mixtures (added as 1 wt% CrO₃, 1.46 wt% K₂CrO₄, 1.92 wt% K₂Cr₂O₇ and 1.55 wt%CaCrO₄) and 245.6 mg Cr(VI)/kg mixtures (added as 2.07 wt% K₂CO₃, 4.07 wt% K₂CO₃ and CaO). It was found that the leachability of Cr(VI) increases both with increasing mass% CaO/mass% SiO₂ ratio and with mass% K₂O in the mixtures (Figs. 10 and 11).

3.8. Microstructure of the stabilised steel plant dust

The XRD and EDS analyses of the stabilised 50%AS-50%SPD mixture that was sintered at $1100 \degree C$ for 5 h indicate that



Fig. 9. The influence of the initial Cr(VI) content on the leachability of Cr(VI).



Fig. 10. The influence of mass% CaO/mass% SiO₂ ratio on the leachability of Cr(VI) (Spiked 50%AS-50%SPD specimen, sintered at 1100 °C for 5 h).



Fig. 11. The influence of mass% K_2O in the mixture on the leachability of Cr(VI) (Spiked 50%AS-50%SPD specimen, sintered at 1100 °C for 5 h).

Table 4

EDS analyses of the phases present in the 50%AS–50%SPD specimen that was sintered at 1100 $^\circ C$ for 5 h (mass%).

| Phases | Fe_2O_3 | Cr_2O_3 | CaO | $Al_2O_3\\$ | SiO_2 | MgO | MnO | ZnO | NiO | K ₂ O |
|----------------|-----------|-----------|------|-------------|---------|-----|-----|------|-----|------------------|
| 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 |
| Glassy phase | 5.0 | 0 | 18.3 | 12.2 | 62.3 | 0 | 0 | 0 | 0 | 2.2 |
| | | | | | | | | | | |

the specimen consists of spinel solid solution phases $((Fe,Zn,Ni,Mg,Mn)(Fe,Cr,Al)_2O_4)$, hematite (Fe_2O_3) , augite $(Ca(Mg,Fe,Al)(Si,Al)_2O_6)$, anorthite $(CaAl_2Si_2O_8)$, quartz, cristobalite and glass (Table 4). EDS analysis indicated that the spinel, hematite and augite phases all contain chromium. The spinels include larger Cr-rich spinel crystals and very fine Fe-rich spinel crystals, while the hematite also contains some Cr_2O_3 , Al_2O_3 and

Table 5 EDS analyses of the phases present in the 100%SPD specimen that was sintered at 1100 $^\circ C$ for 5 h (mass%).

| Phases | Fe_2O_3 | Cr_2O_3 | CaO | $Al_2O_3\\$ | 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 |

| Table 6 | | | | |
|---------------|------------------|------------|------------|----------|
| Emission fact | tors of chromium | in various | industries | [23,24]. |

| Coal-fired industrial | Oil-fired industrial | Steel works | Municipal | Sewage sludge | Cement industry | This study |
|-----------------------|----------------------|---------------|---------------------|----------------------|-----------------|------------|
| boiler (g/ton) | boiler (g/10001) | (g/ton steel) | incinerator (g/ton) | incineration (g/ton) | (g/ton) | (g/ton) |
| 1.7 | 2.2 | 4.0-36.1 | 1.10 | 10 | 1.6 | 0.5-1.8 |

 Mn_2O_3 in solid solution. The Cr_2O_3 content in the spinel and hematite crystals ranged from approximately 8 to 54 wt%. It is assumed that hematite crystals formed due to the oxidation of spinel particles.

The sintered pure stainless steel plant dust (\sim 4,000 mg Cr(VI)/kg sintered steel plant dust) was also examined phase chemically (Table 5). The main crystalline phases of the sintered pure stainless steel plant dust are spinel, hematite, dicalcium silicate, and a glassy phase. EDS analysis indicated that chromium was present in the spinel, hematite and glassy phases. Small amounts of calcium and alkali oxides were also present in the spinel and glassy phases of this sample. The spinel phases in the stabilised dust sample however, do not contain any calcium and alkali oxides. It is presumed that CaO and alkali oxides can form Cr(VI) species in the sintered dust via the following reactions, which increased the extractable Cr(VI) from the sintered steel plant dust:

$$1/2FeCr_2O_4 + CaO + 7/8O_2 \rightarrow CaCrO_4 + 1/4Fe_2O_3$$
(1)

$$1/2FeCr_2O_4 + Na_2O/K_2O + 7/8O_2$$

 $\rightarrow Na_2CrO_4/K_2CrO_4 + 1/4Fe_2O_3$ (2)

3.9. Chromium emissions during the sintering process

Chromium emissions were very low in all the experiments, and low compared to other industrial sources (Table 6 [23,24]). 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) [25]. The total chromium emission factors from the stabilised waste during the sintering process is approximately 0.5 to 1.8 g/ton specimen produced at 1100 °C for 5 h, which is lower than the emission factors from steel plants (4.0–36.1 g/ton steel) and sewage sludge incineration (10 g/ton) [24], but similar to the cement industry (approximately 1.6 g/ton cement produced [23]). It indicates that under current experimental conditions the sintering process can be considered a safe process to treat SPD.

4. Conclusions

Cr(VI) in stainless steel plant dust was stabilised by mixing the dust with clay, and sintering it in air. The following conclusions with regard to the stabilisation of Cr(VI) can be drawn:

- (1) When the specimens were sintered at 1100 °C for 5 h with a 50 wt% SPD content, Cr(VI) in the stainless steel plant dust could be stabilised. It is assumed that this stabilisation/solidification process would also be successful if sintering is performed under more reducing conditions (as is associated with the use of combustible fuels), as less oxygen would be available for the conversion of Cr(VI).
- (2) Decreasing sintering temperature, increasing dust content and shorter sintering times increase the leachability of Cr(VI) from the stabilised stainless steel plant dust.
- (3) When Cr(VI) in the stainless steel plant dust is stabilised with clay in a sintering process, other toxic substances such as As, Zn and Pb are also stabilised. A sintering process whereby steel plant dust is mixed with clay is therefore considered to be an

effective process to stabilise toxic substances in stainless steel plant dust.

- (4) The leachability of Cr(VI) in the stabilised stainless steel dust increases with increasing mass% CaO/mass% SiO₂ ratio and alkali metal oxides content in the raw materials.
- (5) The chromium emission factor from the stabilised stainless steel dust is low and similar to those reported for the cement industry.
- (6) The stabilisation of Cr(VI) in stainless steel plant dust with clay was found to be more successful than is reported for cementation processes in which OPC is used [9,26,27]. This is due to the associated pore water which keeps some Cr(VI) in solution, when stabilisation/solidification is done using OPC. When OPC is used in the stabilisation process the dust also needs to be washed first to remove soluble chromium, Zn, Mg, K and Na, in order to effectively set the cement-waste product.

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