The migration and transformation of chromium during co-processing of cement raw meal mixed with chrome-polluted soil

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Abstract: To efficiently dispose of chrome-polluted soil, we tested the co-processing of raw meal mixed with chrome-polluted soil in a tube furnace (laboratory experiments) and a cement rotary kiln (field-scale experiments). The migration and transformation reactions of chromium were analyzed and the environmental risk was evaluated. The average mass balance value was 91% for the laboratory experiments. In field-scale experiments, the mass balance values were 110% for the control experiments and 84% when 1% soil was treated. Therefore, only a small amount of Cr was volatilized into the flue gas. The average total Cr concentration in the soil samples was 403.25 mg/kg, and the ratio of Cr(VI) to total Cr was 1.83% or less. On average, 45.15% of Cr(III) was oxidized to Cr(VI) in laboratory experiments, while 87.94% of Cr(III) was oxidized in field-scale experiments, and the difference could be a result of the different calcination conditions. The materials in the cement rotary kiln make full contact with oxygen, and in this high temperature and oxidizing atmosphere, abundant CaO and MgO promote the oxidation of Cr(III) to CaCrO₄. SiO₂, Al₂O₃, and Fe₂O₃ reduce CaCrO₄, which inhibits Cr(III) oxidation. The Cr concentration in the cement products was well below the Chinese standard limits. Therefore, the treatment of 1% chrome-polluted soil with a cement rotary kiln is experimentally safe.

Keywords: Chromium, Cement kiln, Chrome-polluted soil, Co-processing, migration, valence

1 Introduction

Chromium is widely used in steel, leather, and other industries, and the resulting chromium residue can cause serious pollution. In China, the annual production of chromium exceeds 160,000 tonnes, the cumulative amount of chromium residue is nearly six million tonnes, and the amount of chrome-polluted soil exceeds 20 million tonnes(Wang et al. 2011). Cement kilns have some advantages for the co-processing of solid waste, and can increase the capacity for solid waste disposal and reduce the consumption of raw materials and fuel by the cement industry(Aranda Usón et al. 2013; Kosajjan et al. 2020). However, the migration and transformation of Cr and other heavy metals during co-processing can threaten environmental and human health. Most chromium residue is in the trivalent (Cr(III)) and the highly toxic hexavalent (Cr(VI)) forms. More importantly, some Cr(III) will be oxidized to Cr(VI) during co-processing in a cement kiln(Fu et al. 2021; Gong et al. 2020; Li et al. 2018a). Therefore, the study of the transfer and transformations of Cr during co-processing of waste is of great significance.

Alkali metal and alkali earth metal oxides affect the redox state of chromium. In cement raw meal, coal, and chrome-polluted soil, chromium exists mainly in the forms CaCr₂O₄, Cr(OH)₃,
Together, CaO and oxygen will oxidize Cr(III) to Cr(VI), while only oxygen, at even 1500 °C, will not oxidize Cr(III). Lack of oxygen can inhibit the oxidation of Cr(III) to Cr(VI) (Kavouras et al. 2015; Verbinnen et al. 2013). CaO is converted to Ca\(^0\) by assisting the electron transfer from Cr(III) to O\(_2\), and Ca\(^4\) is then oxidized by O\(_2\) to Ca\(^2\) (Chen et al. 2012; Chen et al. 2013). During combustion of chromium-rich tannery sludge in an air atmosphere, the x-ray diffraction patterns indicate that CaCrO\(_4\) first appears at 400 °C, gradually increases in the range of 400–800 °C, and reaches a maximum concentration at 800 °C (Yang et al. 2020a). Cr\(_2\)O\(_3\) and CaO were heated in a muffle furnace. The X-ray adsorption near-edge spectroscopy spectra indicated that the initial oxidation of Cr\(_2\)O\(_3\) occurred at approximately 700 °C, and the intensity of the Cr(VI) peak increased dramatically with increasing temperature (Chen et al. 2013; Hu et al. 2018). During the heating process, CaCr\(_2\)O\(_4\) is formed as an intermediate product, and the oxidation of CaCr\(_2\)O\(_4\) is favored with increasing free Ca (Hu et al. 2018). In addition, CaO can capture Cr steam to form calcium chromite, thereby inhibiting Cr volatilization and promoting Cr enrichment in solid products (Chen et al. 2013). SiO\(_2\) is an acidic oxide that can combine with O\(^2\)-, while Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) are neutral oxides that can absorb O\(^2\)- under basic conditions. Therefore, SiO\(_2\), Al\(_2\)O\(_3\), and Fe\(_2\)O\(_3\) reduce CaCrO\(_4\) to form silicate, aluminate, and ferrite, respectively, and thereby inhibit the oxidation of Cr(III) (Mao et al. 2016; Wang et al. 2014). SiO\(_2\) and Al\(_2\)O\(_3\) favor the capture of Cr vapor, especially when the ratio of Si:Al is 3:1. Fe\(_2\)O\(_3\) can capture Cr vapor to form chromite, but the efficiency of this reaction is much lower than for the CaO reaction (Wang et al. 2012; Yang et al. 2020b). Therefore, in the process of co-processing solid waste in a cement kiln, oxides that are present in high concentrations in the cement raw meal will have a greater impact on the oxidation of Cr(III).

Fan et al. (Fan et al. 2014) explored the transformation of Cr in a cement kiln co-processing solid waste by adding Na\(_2\)CrO\(_4\) to the raw meal and calcining in a tube furnace. Chen et al. (Chen et al. 2013) studied the reaction thermodynamics of Cr-doped coal mixed with CaO, Fe\(_2\)O\(_3\), or MgO during the combustion process in a lab-scale drop-tube furnace. Yang et al. (Yang et al. 2020a) studied the transformation of chromium after calcining chrome-rich tanning sludge in a crucible. Many studies have investigated the transformation of Cr at the laboratory scale, however few studies exist on the transfer and transformation of Cr during co-processing of solid waste in a cement plant.

In this study, the cement raw meal was mixed with 1%, 3%, and 5% chrome-polluted soil, and the mixture was calcined at high temperature in a tube furnace. Based on the results from the laboratory experiments, field-scale experiments involving co-processing of chrome-polluted soil were carried out in a cement rotary kiln. This research will provide reference data and a theoretical basis for the development of co-processing solid waste technology.

2 Materials and Methods

2.1 Materials

Raw meal, clinker, coal, and cement were collected from a cement plant. Seven chrome-polluted soils, having different degrees of pollution, were collected from the original site of the Chongqing Special Steel Plant. The total Cr concentration was measured according to “Determination of metal elements in solid waste by inductively coupled plasma–mass spectrometry (ICP-MS)” from HJ 766-2015. The Cr(VI) concentration was measured according to...
Cement raw meal was composed of calcareous and clayey solids and a small amount of calibration material. The soil was composed mainly of silico-aluminates and oxides. The chrome-polluted soil was air-dried and ground. After grinding, it was passed through a 100 mesh sieve and dried in a blast drying oven at 110 °C for 2 h. The raw materials included the oxides CaO, SiO₂, Al₂O₃, Fe₂O₃, and MgO. The properties of the raw materials are listed in Table 1 (Li 2020; Li et al. 2009).

| Table 1 General properties of raw meal and soil components |
|----------------------------------------------------------|
| **Raw meal** | **Soil** |
| Ignition loss | 35.48% | 8.18% |
| CaO | 43.54% | 5.05% |
| SiO₂ | 13.08% | 63.30% |
| Al₂O₃ | 3.57% | 11.90% |
| Fe₂O₃ | 1.40% | 4.90% |
| MgO | 1.03% | 2.40% |
| Else | 1.89% | 4.27% |

### 2.2 Laboratory experiments

#### 2.2.1 Calcination experiments in a tube furnace

The raw meal was mixed with 1%, 3%, or 5% chrome-polluted soil. The mixtures were thoroughly homogenized, and 20–30 g was placed in a quartz crucible. The crucibles were preheated on the top of a tube furnace, and then were placed in the furnace for 30 min. Two crucibles were put into the furnace for each run, and calcination experiments were carried out twice for each mixing ratio. The experiments were carried out in an atmosphere of O₂ (5%) and N₂ (95%) with the flow rate of 1 L/min, and the temperature was set at 1450 °C. The mass of the samples was accurately weighed before and after the experiments.

### 2.3 Field-scale experiments

#### 2.3.1 Co-processing chrome-polluted soil in a cement rotary kiln

The field-scale experiments were carried out in a cement rotary kiln. The mixing of raw meal and chrome-polluted soil was conducted at various mass ratios indicated in Table 2.

| Table 2 Material parameters under two working conditions (t/h) |
|---------------------------------------------------------------|
| Working condition | Chrome-polluted soil | Raw meal | Coal | Clinker |
| Control | 0 | 180 | 16.8 | 111.8 |
| Add 1% soil | 1.8 | 180 | 16.8 | 111.8 |

#### 2.3.2 Cement kiln system

A schematic of the cement kiln calcining system is illustrated in Fig.1. The chrome-polluted soil was added to the raw mill, which homogenized the soil and raw meal.
3 Results and Discussion

3.1 Laboratory experiments

3.1.1 Cr in chrome-polluted soil

Table 3 shows the distribution of Cr in the seven chrome-polluted soils. All samples were tested in parallel (a and b). The concentration of Cr(III) was calculated according to Eq. (1), where $\omega$ refers to the Cr(III) concentration. The average total Cr concentration in the samples was 403.25 mg/kg, and the average Cr(VI) concentration was 2.12 mg/kg. The ratio of Cr(VI) to total Cr was 1.83% or less. The soil sample used in the experiments was sample No.7 because it contained the most Cr.

$$\omega(Cr^{3+}) = \omega(Cr_{total}) - \omega(Cr^{6+})$$  \hspace{1cm} (1)

Table 3 The distribution of Cr in chrome-polluted soils (mg/kg)

| Samples of soils | $\omega$(Cr$_{total}$) | $\omega$(Cr$^{6+}$) | $\omega$(Cr$^{3+}$) |
|------------------|------------------------|---------------------|---------------------|
| 1a               | 416.40                 | 4.20                | 412.19              |
| 1b               | 421.79                 | 1.90                | 419.89              |
| 2a               | 385.56                 | 0.81                | 384.75              |
| 2b               | 408.91                 | -                   | 408.91              |
| 3a               | 339.85                 | 1.25                | 338.61              |
| 3b               | 329.63                 | -                   | 329.63              |
| 4a               | 123.44                 | 2.26                | 121.18              |
| 4b               | 130.48                 | 0.76                | 129.72              |
| 5a               | 325.65                 | 1.01                | 324.64              |
| 5b               | 354.61                 | -                   | 354.61              |
| 6a               | 445.22                 | 1.38                | 443.85              |
| 6b               | 440.56                 | 7.72                | 432.84              |
| 7a               | 806.00                 | 4.44                | 801.56              |
3.1.2 Mass balance of Cr

Calcination experiments of raw meal and chrome-polluted soil were performed in a tube furnace. The raw materials included cement raw meal and soil, and the combustion products included clinker and flue gas. The mass and the total Cr concentration of these substances are listed in Tables 4 and 5, respectively. The total Cr concentration in clinker was 1.52–4.67 times of that in raw meal, and increased with the mixing ratio of soil. The total Cr concentration in clinker increased under the influence of weight loss. The rate of weight loss in the calcination experiments ranged from 35.02% to 36.27%, and was caused by the evaporation of crystalline water, the release of CO₂ and SO₂, and the loss of organic impurities.

| Working conditions | Raw materials | Products |
|--------------------|---------------|----------|
|                    | Raw meal      | Soil     | Clinker  |
| Control            | 32.19         | —        | 17.83    |
| Add 1% soil        | 24.98         | 0.25     | 16.11    |
| Add 3% soil        | 25.22         | 0.78     | 14.74    |
| Add 5% soil        | 24.39         | 1.28     | 15.57    |

Table 5 The total Cr concentration in raw materials and products (mg/kg)

| Working conditions | Raw materials | Products |
|--------------------|---------------|----------|
|                    | Raw meal      | Soil     | Clinker  |
| Control            | 16.33         | —        | 24.87    |
| Add 1% soil        | 15.10         | 761.67   | 34.88    |
| Add 3% soil        | 12.80         | 761.67   | 54.06    |
| Add 5% soil        | 19.18         | 761.67   | 85.70    |

The mass balance (η) of the total Cr was calculated by Eq. (2)

\[ η = \frac{M_{cl} \cdot C_{cl}}{M_{rm} \cdot C_{rm} + M_{s} \cdot C_{s}} \times 100\% \]

Where M_{rm}, M_{s}, and M_{cl} represent the mass of raw meal, soil, and clinker, respectively. C_{rm}, C_{s}, and C_{cl} represent the total Cr concentration in each of these three materials. The mass balance rate of Cr under the four working conditions is shown in Fig.2. The average mass balance value was 91%, with a range of 70% to 130% over all the experiments.
No chromium was detected in the flue gas. Chromium belongs to an elemental group between the volatile and low volatility heavy metals. Chromium compounds include organic and inorganic forms, and organic chromium is more volatile. The cement raw meal is mainly composed of calcareous and clayey materials. Chromium is predicted to exist mainly in an inorganic form, such as CaCr2O4, Cr(OH)3, Cr2O3, FeCr2O4, or their complexes (Jiang et al. 2016). Chrome-polluted soils were collected from the original site of a special steel plant, and chromium is predicted to exist as Cr2(SO4)3 and CrO3. Therefore, most of chromium in the raw materials will be difficult to volatilize.

Chromium is volatilized mainly as a hydroxide in a high-temperature tube furnace. Thermodynamically stable Cr compounds include CrO3(g), CrOOH(g), and CrO2(OH)2(g) (Nowak et al. 2012; Roy et al. 2013; Świetlik et al. 2014). Ryszard et al. (Świetlik et al. 2014) found that CrOOH and CrO2(OH)2 were the main gaseous forms in the combustion process. As shown in Table 1, the raw materials contain CaO, SiO2, Al2O3, and Fe2O3. CaO and Fe2O3 capture CrOOH in flue gas through Eq. (3) and Eq. (4), respectively, thereby lowering the efficiency of Cr volatilization (Li et al. 2018b). Chen et al. (Chen et al. 2013) studied the capture of Cr by additives during oxy-fuel combustion and observed that CaO could capture chromium steam and promote the enrichment of chromium in solid ash.

\[ \text{CaO} + 2\text{CrOOH} (g) \rightarrow \text{CaCr}_2\text{O}_4 + H_2\text{O} \]  
(3)

\[ \text{Fe}_2\text{O}_3 + 4 \text{CrOOH} (g) \rightarrow 2\text{FeCr}_2\text{O}_4 + 1/2\text{O}_2 (g) + 2\text{H}_2\text{O} \]  
(4)

In addition, Wang et al. (Wang et al. 2012) studied the collection of heavy metals by different additives during the incineration of waste in a tube furnace, and observed the promoting effect of SiO2 and Al2O3 on capturing heavy metals. They (Wang et al. 2012) also observed that the heavy metal concentration in bottom ash reached a maximum value when the Si:Al atomic ratio was 3:1, increasing the Cr capture from 40% to 79%. In our experiments, the Si:Al atomic ratio in the raw materials was approximately 3:1, so Cr volatilization is reduced.

Together, these results indicate that only a small amount of Cr is volatilized into the flue gas and therefore can be ignored in future experiments.
3.1.3 Migration and conversion of Cr

The Cr(VI) concentration in the raw materials and combustion products is shown in Table 6. The Cr(VI) concentration in the clinker was increased significantly compared with the raw materials during all experimental conditions. The increased Cr(VI) concentration can be explained as follows: (1) Cr(VI) concentration increased under the influence of weight loss and (2) Cr(III) was oxidized to Cr(VI) during calcination.

Table 6 The total Cr(VI) concentration in raw materials and combustion products (mg/kg)

| Working conditions | Raw materials | Soil | Products |
|--------------------|---------------|------|----------|
| Control            | 0.66          | —    | 10.97    |
| Add 1% soil        | 1.14          | 4.21 | 15.91    |
| Add 3% soil        | 0.78          | 4.21 | 20.90    |
| Add 5% soil        | 0.79          | 4.21 | 34.46    |

The mass distribution of Cr(III) and Cr(VI) in raw materials and combustion products is shown in Fig. 3. The ratio of Cr(VI) to total Cr was between 1.71%–5.21% in the raw materials, and between 38.66%–45.61% in the clinker. On average, 45.15% of the Cr(III) in the raw materials was oxidized.

CaO promotes the oxidation of Cr(III) to Cr(VI) according to Eq. (5) below. CaO may also promote the formation of unstable CaCr₂O₄, while CaCr₂O₄ is oxidized to CaCrO₄ requiring less energy, as shown by Eq. (6) and Eq. (7) (Chen et al. 2012). CaO is converted to Ca⁰ by assisting the electron transfer from Cr(III) to O₂, and Ca⁰ is then oxidized by O₂ to Ca²⁺(Chen et al. 2013). Verbinnen et al. (Verbinnen et al. 2013) studied the oxidation of Cr(III) during the heating of Cr₂O₃ and CaO at temperatures between 100 °C and 1100 °C and observed that Cr(III) was oxidized, which is consistent with the thermodynamic calculation.
As shown in Eqs. (8) to (10), CaCrO₄ dissociates into cations and CrO₄²⁻ as the temperature increases, and CrO₄²⁻ easily dissociates into Cr₂O₃ and O²⁻. CrO₃ is thermodynamically unstable and dissociates into Cr₂O₃ and O₂ at 500 °C (Mao et al. 2016). The free cations and O²⁻ are captured by SiO₂, Al₂O₃, and Fe₂O₃ to form stable silicates, aluminates, and ferrites (Eqs. [11] to [13]). Mao et al. (Mao et al. 2016) believed that the potential of the metal oxides to promote Cr(VI) reduction was caused by their ability to combine with O²⁻. SiO₂ is an acidic oxide, while Al₂O₃ and Fe₂O₃ are neutral oxides. SiO₂ is more acidic than Al₂O₃ and Fe₂O₃ and can more easily combine with O²⁻ and therefore can promote Cr(VI) reduction. In addition, Mao et al. (Mao et al. 2016) studied the fate of Cr(VI) in the presence of SiO₂, Al₂O₃, and Fe₂O₃ and observed that SiO₂ can cause the release of CaCrO₄, Na₂CrO₄, and K₂CrO₄ at around 900 °C, 1000 °C, and 1000 °C, respectively, while Al₂O₃ and Fe₂O₃ could only promote the reduction of CaCrO₄.

Therefore, SiO₂, Al₂O₃, and Fe₂O₃ can promote Cr(VI) reduction to different degrees.

\[
\text{CaCrO}_4 \rightarrow \text{Ca}^{2+} + \text{CrO}_4^{2-} \quad \text{(8)}
\]

\[
\text{CrO}_4^{2-} \rightarrow \text{CrO}_3 + \text{O}^{2-} \quad \text{(9)}
\]

\[
2\text{CrO}_3 \rightarrow \text{Cr}_2\text{O}_3 + 1.5\text{O}_2 \quad \text{(10)}
\]

\[
2\text{CaCrO}_4 + 2\text{SiO}_2 \rightarrow 2\text{CaSiO}_4 + \text{Cr}_2\text{O}_3 + 1.5\text{O}_2 \quad \text{(11)}
\]

\[
2\text{CaCrO}_4 + 2\text{Al}_2\text{O}_3 \rightarrow 2\text{CaAl}_2\text{O}_4 + \text{Cr}_2\text{O}_3 + 1.5\text{O}_2 \quad \text{(12)}
\]

\[
2\text{CaCrO}_4 + 2\text{Fe}_2\text{O}_3 \rightarrow 2\text{CaFe}_2\text{O}_4 + \text{Cr}_2\text{O}_3 + 1.5\text{O}_2 \quad \text{(13)}
\]

Based on the experimental results, the possible reactions of Cr compounds in the calcination experiment are shown in Fig.4. CaO is a basic oxide, while SiO₂, Al₂O₃, and Fe₂O₃ are acidic or neutral oxides. The two have opposite effects on the conversion of Cr valence.

![Diagram](image)

**Fig.4** The possible reactions of Cr compounds in the calcination experiment

### 3.2 Field-scale experiments
3.2.1 Mass balance of Cr

The material streams for the combustion experiment of chrome-polluted soil in a cement rotary kiln are shown in Fig.5. The raw materials included cement raw meal, soil, coal, and kiln dust, and the combustion products included clinker, flue gas, and kiln dust. The Cr mass balance calculation was carried out based on these material streams. The kiln ash was returned to the kiln and therefore not included in the mass balance calculation. The input and output rates of Cr were calculated according to Tables 2 and 7, as shown in Table 8. Similar to Eq. (2), the mass balance rate of Cr was 110% for the control condition and 84% with 1% chrome-polluted soil. The mass balance results ranged from 70% to 130%; therefore, the Cr is mass balanced and is not significantly volatilized into the flue gas. This is consistent with the results of the laboratory experiments.

![Material Streams](image)

**Fig.5** The material streams in the field-scale experiments

| Element | Conditions | Raw materials | Products |
|---------|------------|---------------|----------|
|         |            | Raw meal      | Soil     | Coal     | Clinker  |
| Total Cr| Control    | 13.16         | —        | 27.66    | 27.80    |
|         | Add 1% soil| 18.13         | 761.67   | 32.14    | 39.06    |
| Cr(VI)  | Control    | 1.27          | —        | —        | 24.73    |
|         | Add 1% soil| 0.86          | 4.21     | 0.44     | 34.16    |

| Table 7 Total Cr and Cr(VI) concentration in raw materials and products (mg/kg) |

| Conditions | Raw materials | Products |
|------------|---------------|----------|
| Raw meal   | Soil          | Coal     | Clinker  |
| Control    | 2368.80       | 464.69   | 3108.04  |
| Add 1% soil| 3263.40       | 1371.01  | 539.90   | 4366.91  |

3.2.2 Migration and conversion of Cr

Fig.6 shows the valence distribution of Cr in the cement kiln system for the control condition and with 1% chrome-polluted soil. In Fig.6, the distribution of Cr(III) and Cr(VI) in clinker under the control condition was almost the same as that with 1% chrome-polluted soil. The ratio of Cr(VI) to total Cr was 88.96% and 87.46%, respectively, for the control and experimental conditions. On
average, 87.94% of the Cr(III) in the raw materials was oxidized. In the laboratory experiments, the ratio of Cr(VI) to total Cr in the clinker ranged from 38.66% to 45.61%. This is significantly lower than for the field-scale experiments, and can be explained by the different calcination conditions. The materials in the cement rotary kiln can make full contact with oxygen, while in a tube furnace, the inside of the bulk material does not have full contact with oxygen.

With the added 1% chrome-polluted soil, the Cr concentration in the clinker was higher than in the blank condition. Total Cr increased by 40.5%, and Cr(VI) increased by 38.13%. The increase in Cr can be explained by the addition of 1% chrome-polluted soil.

**Fig. 6** The valence distribution of Cr in the cement kiln under the control condition and with 1% chrome-polluted soil

### 3.2.3 Possible reactions of Cr in the cement kiln

The calcination process of raw meal in a cement kiln includes preheating, decomposition, sintering, and cooling, which are carried out in preheater, pre-calciner, rotary kiln, and clinker cooler, respectively. Based on the chemical reactions and reaction conditions of raw meal in a cement kiln, the possible reactions of Cr were analyzed in this study.

During preheating, the raw meal is heated to approximately 750 °C, resulting in evaporation of water and dehydration and decomposition of the clay particles. First, the raw meal is dried, and the free water in raw meal evaporates at 100–150 °C, increasing the Cr concentration in the raw meal. At around 450 °C, kaolin—the main component of clay—is dehydrated and decomposed into free Al₂O₃ and SiO₂ (Eq. 14). Al₂O₃ and SiO₂ inhibit the oxidation of Cr according to the thermodynamic equilibrium equation, which is consistent with the experimental results of Mao et al. (Mao et al. 2016).

\[
Al_2O_3 + 2SiO_2 + 2H_2O \rightarrow Al_2O_3 + 2SiO_2 + 2H_2O
\]  

The temperature of the materials can reach approximately 870 °C in the pre-calciner, where limestone is decomposed; here, approximately 90% of the raw meal is decomposed. CaCO₃ and MgCO₃ are rapidly decomposed to free oxides and CO₂ in the pre-calciner. The decomposition of CaCO₃ is reversible, so ventilation of the pre-calciner is necessary to promote the emission of CO₂.
The pre-calciner is an oxidizing atmosphere where free CaO and MgO are extremely active and can react with Cr.

In the pre-calcination process, a large amount of CaO promotes the oxidation of Cr(III) to CaCrO₄ and rapidly oxidizes any CaCr₂O₄ to CaCrO₄, as shown in Eqs. (5) to (7). Stam et al. (Stam et al. 2011) showed that the formation of Cr(VI) is a high-temperature process, and is affected by free CaO and the formation of solid chromate. Yang et al. (Yang et al. 2020a) studied the chromium speciation in chromium-rich tannery sludge under an air atmosphere at temperature of 300–1200 °C; they observed that CaCrO₄ first appeared at 400 °C, gradually increased in the range of 400–800 °C, and reached a maximum at 800 °C. This indicated the oxidation of Cr(III) to Cr(VI). Hu et al. (Hu et al. 2015) studied the distribution of Cr(VI) in municipal solid waste incineration ash and observed that the oxidation of Cr depended on the content of free CaO. They (Hu et al. 2015) also studied the effect of temperature on the oxidation of CaO to Cr₂O₃ and observed that the maximum oxygen consumption rate was increased with increasing temperature from 700 °C to 900 °C. This result indicated that CaO can promote the oxidation of most Cr(III) in this temperature range. In addition, MgO promotes the oxidation of Cr(III) into MgCrO₄.

The solid-solid and sintering reactions occur in a rotary kiln. In the transition zone of the rotary kiln, at a temperature of 900–1150 °C, free CaO, SiO₂, Al₂O₃, and Fe₂O₃ have multistage and complex solid reactions. SiO₂, Al₂O₃, and Fe₂O₃ reduce CaCrO₄, therefore inhibiting Cr(III) oxidation. In the sintering zone of the rotary kiln, a liquid phase will appear when the temperature of the materials rises to nearly 1300 °C. Because the melting point of CaO is 2570 °C, most of CaO is still in the solid phase; however, CaO can dissolve in the high-temperature liquid (Li 2020). Dissolved CaO has increased contact area with Cr, promoting the oxidation of Cr to a certain extent. In the cooling process of clinker, there is still a small amount of free CaO in the solidified material that has not been chemically reacted.

### 3.2.4 Environmental implications

The distribution of Cr in two cement products (P·C 32.5R and P·C 42.5R) with added 1% chrome-polluted soil is shown in Table 9. The Cr concentration in the cement products was lower than that in the clinker, as shown in Table 7. The total Cr for the two cement products decreased by 40.14% and 8.09%, and Cr(VI) fell by 61.59% and 62.64%, respectively. The decrease occurred because the Cr concentration in clinker was diluted after adding gypsum, and other additives. The standard Gb30760-2014 “Technical Specification for Collaborative Disposal of Solid Waste by Cement Kiln” indicates that the limit for Cr in clinker is 150 mg/kg. Therefore, adding 1% of chrome-polluted soil to the raw meal of a cement kiln conforms to Chinese safety standards.

| Elements | P·C 32.5R | P·C 42.5R |
|----------|-----------|-----------|
| Total Cr | 23.38     | 35.90     |
| Cr(VI)   | 13.12     | 12.76     |

### 4 Conclusions

For the four calcination experiments in a tube furnace, the Cr mass balance values ranged from 84% to 99%, and the average mass balance was 91%. During the co-processing of chrome-polluted soil with raw meal in a cement rotary kiln, the mass balance values were 110% and 84% in the
control condition and with added 1% chrome-polluted soil, respectively, for the two cement formulations used. Therefore, most of the Cr was fixed in the solid products, and very little Cr was volatilized into the flue gas. Most Cr compounds in the raw materials were difficult to volatilize. Cr hydroxides that may have been volatilized into the flue gas were captured by CaO and Fe₂O₃.

Most of the Cr(III) in the raw materials was oxidized to Cr(VI) after being calcined, and a higher proportion of Cr(III) was oxidized in cement kiln. The average concentration of total Cr was 403.25 mg/kg, and the ratio of Cr(VI) to total Cr was 1.83% or less in the chrome-polluted soil samples. In laboratory experiments, the ratio of Cr(VI) to total Cr was between 38.66% and 45.61% in the clinker, and an average of 45.15% of Cr(III) in the raw materials was oxidized. In the field-scale experiments, 87.94% of Cr(III) was oxidized. The oxidation of Cr(III) can be explained as follows: in a high-temperature and oxidizing atmosphere, large amounts of CaO and MgO promote the oxidation of Cr(III) to Cr(VI), while SiO₂, Al₂O₃, and Fe₂O₃ promote Cr(VI) reduction, leading to the oxidation of most of the Cr(III). The materials in the cement rotary kiln have full contact with oxygen, while in the tube furnace, the inside of the materials does not have full contact with oxygen, resulting in a higher proportion of Cr(III) oxidized in the cement kiln.

In the cement kiln experiment with added 1% chrome-polluted soil, the Cr concentration in the two tested cement products was 23.38 and 35.90 mg/kg, respectively, conforming to the Chinese safety standards. The co-processing technology poses no environmental risk at this lower mixing ratio.

**Ethical Approval:** Not applicable.

**Consent to Participate:** Not applicable.

**Consent to Publish:** Not applicable.

**Authors Contributions:** HPX designed the experiments and analyzed the transformation mechanism of chromium. YL and MWW analyzed the distribution of chromium systematically and were major contributors in writing the manuscript. DHY and ZL organized the experiments. All authors read and approved the final manuscript.

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**Availability of data and materials:** The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.
References

Aranda Usón A, López-Sabirón AM, Ferreira G, Llera Sastresa E (2013) Uses of alternative fuels and raw materials in the cement industry as sustainable waste management options Renewable and Sustainable Energy Reviews 23:242-260 doi:10.1016/j.rser.2013.02.024

Chen J, Jiao FC, Zhang L, Yao H, Ninomiya Y (2012) Use of synchrotron XANES and Cr-doped coal to further confirm the vaporization of organically bound Cr and the formation of chromium(VI) during coal oxy-fuel combustion Environ Sci Technol 46:3567-3573 doi:10.1021/es204255h

Chen J, Jiao FC, Zhang L, Yao H, Ninomiya Y (2013) Elucidating the mechanism of Cr(VI) formation upon the interaction with metal oxides during coal oxy-fuel combustion J Hazard Mater 261:260-268 doi:10.1016/j.jhazmat.2013.07.023

Fan XG, Yang YF, Huang QF, Li ZW, Yu HJ (2014) The transformation of Cr form at different temperatures in the co-treatment of Cr containing waste in cement kiln Research of Environmental Sciences 27:272-278 doi:10.13198/j.issn.1001-6929.2014.03.08

Fu LJ, Feng AX, Xiao JJ, Wu Q, Ye QY, Peng S (2021) Remediation of soil contaminated with high levels of hexavalent chromium by combined chemical-microbial reduction and stabilization Journal of Hazardous Materials 403 doi:10.1016/j.jhazmat.2020.123847

Gong HY et al. (2020) The potential oxidation characteristics of CaCr2O4 during coal combustion with solid waste in a fluidized bed boiler: A thermogravimetric analysis Chemosphere 263:127974 doi:10.1016/j.chemosphere.2020.127974

Hu HY, Shi MY, Yang YH, Liu H, Xu M, Shen JH, Yao H (2018) Further Insight into the Formation and Oxidation of CaCr2O4 during Solid Fuel Combustion Environ Sci Technol 52:2385-2391 doi:10.1021/acs.est.7b05538

Hu HY, Xu Z, Liu H, Chen DK, Li AJ, Yao H, Naruse I (2015) Mechanism of chromium oxidation by alkali and alkaline earth metals during municipal solid waste incineration Proceedings of the Combustion Institute 35:2397-2403 doi:10.1016/j.proci.2014.08.029

Jiang XG, Dong H, Lv GJ, Chi Y, Yan JH (2016) Oxidation mechanism and control method of Cr during high temperature combustIon Chemical Industry and Engineering Progress 35:1-10 doi:10.16085/j.issn.1000-6613.2016.s2.001

Kavouras P et al. (2015) Incineration of tannery sludge under oxic and anoxic conditions: Study of chromium speciation Journal of Hazardous Materials 283

Kosajan V, Wen Z, Fei F, Doh Dinga C, Wang Z, Zhan J (2020) The feasibility analysis of cement kiln as an MSW treatment infrastructure: From a life cycle environmental impact perspective Journal of Cleaner Production 267 doi:10.1016/j.jclepro.2020.122113

Li CP (2020) Practical technology for collaborative disposal of household garbage by cement kiln. vol 05. China Building Industry Press, Beijing

Li L, Huang QF, zhang ZQ, Cai ML, Yan DH (2009) Study on the pollution discharge of contaminated soil treated by cement kiln Chinese Journal of Environmental Engineering 3:891-896

Li XY, Dong H, Chen J, Lu C, Luo G, Yao H (2018a) Transformation of Organically Bound Chromium during Oxy-coal Combustion: The Influence of Steam and Mineral Energy & Fuels 32:1992-1998 doi:10.1021/acs.energyfuels.7b03123

Li XY, Dong H, Zhao XP, Chen J, Lu CM, Yao H (2018b) Effect of water vapor on mineral
chromium capture under oxygen-enriched combustion CIESC Journal 69:2714-2721
doi:10.11949/j.issn.0438-1157.20171460
Mao LQ, Deng N, Liu L, Cui H, Zhang WY (2016) Effects of Al2O3, Fe2O3, and SiO2 on
Cr(VI) formation during heating of solid waste containing Cr(III) Chemical Engineering Journal
304:216-222 doi:10.1016/j.cej.2016.06.086
Nowak B, Frias Rocha S, Aschenbrenner P, Rechberger H, Winter F (2012) Heavy metal
removal from MSW fly ash by means of chlorination and thermal treatment: Influence of the
chloride type Chemical Engineering Journal 179:178-185 doi:10.1016/j.cej.2011.10.077
Roy B, Choo WL, Bhattacharya S (2013) Prediction of distribution of trace elements under
Oxy-fuel combustion condition using Victorian brown coals Fuel 114:135-142
doi:10.1016/j.fuel.2012.09.080
Stam AF, Meij R, Te Winkel H, Eijk RJ, Huggins FE, Brem G (2011) Chromium speciation
in coal and biomass co-combustion products Environ Sci Technol 45:2450-2456
doi:10.1021/es103361g
Świetlik R, Trojanowska M, Lożyńska M, Molik A (2014) Impact of solid fuel combustion
technology on valence speciation of chromium in fly ash Fuel 137:306-312
doi:10.1016/j.fuel.2014.08.010
Verbinnen B, Billen P, Van Coninckxloo M, Vandecasteele C (2013) Heating temperature
dependence of Cr(III) oxidation in the presence of alkali and alkaline earth salts and subsequent
Cr(VI) leaching behavior Environ Sci Technol 47:5858-5863 doi:10.1021/es4001455
Wang AY, Zhong GF, Xu GB, Liu ZX, Shen XB (2011) Effects of Chromium stress on
physiological characteristics and Chromium enrichment of Mustard rapeseed Environmental
Science 32:1717-1725
Wang WX, Hu HY, Zhu JJ, Yao H, XU MH, Qiao Y (2014) Study on the distribution and
leaching characteristics of Chromium in waste incineration bottom ash Journal of Engineering
Thermophysics 35:196-199
Wang XY, Huang YJ, Zhong ZP, Niu MM, Sun Y, Zhang Q (2012) Experimental study on
the influence of additives on heavy metal collection in waste incineration Proceedings of the
CSEE 32:15-21
Yang YL, Ma HR, Chen XP, Zhu C, Li XJ (2020a) Effect of incineration temperature on
chromium speciation in real chromium-rich tannery sludge under air atmosphere Environ Res
183:109159 doi:10.1016/j.envres.2020.109159
Yang Z, Wang CX, Li YM, Yang S, Zhang W, Li YL (2020b) Assessing the chromium
mobility in ashes through SiO2-Al2O3-Fe2O3-CaO system: The role of composition
Chemosphere 257:127112 doi:10.1016/j.chemosphere.2020.127112