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## Research Article

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# 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 CaCrO<sub>4</sub>. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> reduce CaCrO<sub>4</sub>, 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; Kosajan 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 CaCr<sub>2</sub>O<sub>4</sub>, Cr(OH)<sub>3</sub>,

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43 Cr<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, CrO<sub>3</sub>, and FeCr<sub>2</sub>O<sub>4</sub>.(Jiang et al. 2016) The components in cement raw meal  
44 include CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and MgO; CaO makes up more than 60% of the raw meal(Li  
45 2020).

46 Together, CaO and oxygen will oxidize Cr(III) to Cr(VI), while only oxygen, at even 1500 °C,  
47 will not oxidize Cr(III). Lack of oxygen can inhibit the oxidation of Cr(III) to Cr(VI)(Kavouras et  
48 al. 2015; Verbinnen et al. 2013). CaO is converted to Ca<sup>0</sup> by assisting the electron transfer from  
49 Cr(III) to O<sub>2</sub>, and Ca<sup>0</sup> is then oxidized by O<sub>2</sub> to Ca<sup>2+</sup>(Chen et al. 2012; Chen et al. 2013). During  
50 combustion of chromium-rich tannery sludge in an air atmosphere, the x-ray diffraction patterns  
51 indicate that CaCrO<sub>4</sub> first appears at 400 °C, gradually increases in the range of 400–800 °C, and  
52 reaches a maximum concentration at 800 °C(Yang et al. 2020a). Cr<sub>2</sub>O<sub>3</sub> and CaO were heated in a  
53 muffle furnace. The X-ray adsorption near-edge spectroscopy spectra indicated that the initial  
54 oxidation of Cr<sub>2</sub>O<sub>3</sub> occurred at approximately 700 °C, and the intensity of the Cr(VI) peak increased  
55 dramatically with increasing temperature(Chen et al. 2013; Hu et al. 2018). During the heating  
56 process, CaCr<sub>2</sub>O<sub>4</sub> is formed as an intermediate product, and the oxidation of CaCr<sub>2</sub>O<sub>4</sub> is favored  
57 with increasing free Ca(Hu et al. 2018). In addition, CaO can capture Cr steam to form calcium  
58 chromite, thereby inhibiting Cr volatilization and promoting Cr enrichment in solid products(Chen  
59 et al. 2013). SiO<sub>2</sub> is an acidic oxide that can combine with O<sup>2-</sup>, while Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are neutral  
60 oxides that can absorb O<sup>2-</sup> under basic conditions. Therefore, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> reduce CaCrO<sub>4</sub>  
61 to form silicate, aluminate, and ferrite, respectively, and thereby inhibit the oxidation of Cr(III)(Mao  
62 et al. 2016; Wang et al. 2014). SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> favor the capture of Cr vapor, especially when the  
63 ratio of Si:Al is 3:1. Fe<sub>2</sub>O<sub>3</sub> can capture Cr steam to form chromite, but the efficiency of this reaction  
64 is much lower than for the CaO reaction(Wang et al. 2012; Yang et al. 2020b). Therefore, in the  
65 process of co-processing solid waste in a cement kiln, oxides that are present in high concentrations  
66 in the cement raw meal will have a greater impact on the oxidation of Cr(III).

67 Fan et al.(Fan et al. 2014) explored the transformation of Cr in a cement kiln co-processing  
68 solid waste by adding Na<sub>2</sub>CrO<sub>4</sub> to the raw meal and calcining in a tube furnace. Chen et al.(Chen et  
69 al. 2013) studied the reaction thermodynamics of Cr-doped coal mixed with CaO, Fe<sub>2</sub>O<sub>3</sub>, or MgO  
70 during the combustion process in a lab-scale drop-tube furnace. Yang et al.(Yang et al. 2020a)  
71 studied the transformation of chromium after calcining chrome-rich tanning sludge in a crucible.  
72 Many studies have investigated the transformation of Cr at the laboratory scale, however few studies  
73 exist on the transfer and transformation of Cr during co-processing of solid waste in a cement plant.

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

## 80 **2 Materials and Methods**

### 81 **2.1 Materials**

82 Raw meal, clinker, coal, and cement were collected from a cement plant. Seven chrome-  
83 polluted soils, having different degrees of pollution, were collected from the original site of the  
84 Chongqing Special Steel Plant. The total Cr concentration was measured according to  
85 “Determination of metal elements in solid waste by inductively coupled plasma–mass spectrometry  
86 (ICP-MS)” from HJ 766-2015. The Cr(VI) concentration was measured according to

87 “Determination of alkali dissolution of solid waste from hexavalent chromium/flame atomic  
 88 absorption spectrophotometry” and the United States Environmental Protection Agency Method  
 89 3060 “Alkaline Digestion for Hexavalent Chromium.”

90 Cement raw meal was composed of calcareous and clayey solids and a small amount of  
 91 calibration material. The soil was composed mainly of silico-aluminates and oxides. The chrome-  
 92 polluted soil was air-dried and ground. After grinding, it was passed through a 100 mesh sieve and  
 93 dried in a blast drying oven at 110 °C for 2 h. The raw materials included the oxides CaO, SiO<sub>2</sub>,  
 94 Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and MgO. The properties of the raw materials are listed in Table 1(Li 2020; Li et al.  
 95 2009).

96  
 97 Table 1 General properties of raw meal and soil components

	Raw meal	Soil
Ignition loss	35.48%	8.18%
CaO	43.54%	5.05%
SiO <sub>2</sub>	13.08%	63.30%
Al <sub>2</sub> O <sub>3</sub>	3.57%	11.90%
Fe <sub>2</sub> O <sub>3</sub>	1.40%	4.90%
MgO	1.03%	2.40%
Else	1.89%	4.27%

98  
 99 **2.2 Laboratory experiments**

100 **2.2.1 Calcination experiments in a tube furnace**

101 The raw meal was mixed with 1%, 3%, or 5% chrome-polluted soil. The mixtures were  
 102 thoroughly homogenized, and 20–30 g was placed in a quartz crucible. The crucibles were preheated  
 103 on the top of a tube furnace, and then were placed in the furnace for 30 min. Two crucibles were put  
 104 into the furnace for each run, and calcination experiments were carried out twice for each mixing  
 105 ratio. The experiments were carried out in an atmosphere of O<sub>2</sub> (5%) and N<sub>2</sub> (95%) with the flow  
 106 rate of 1 L/min, and the temperature was set at 1450 °C. The mass of the samples was accurately  
 107 weighed before and after the experiments.

108  
 109 **2.3 Field-scale experiments**

110 **2.3.1 Co-processing chrome-polluted soil in a cement rotary kiln**

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

113  
 114 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

115  
 116 **2.3.2 Cement kiln system**

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

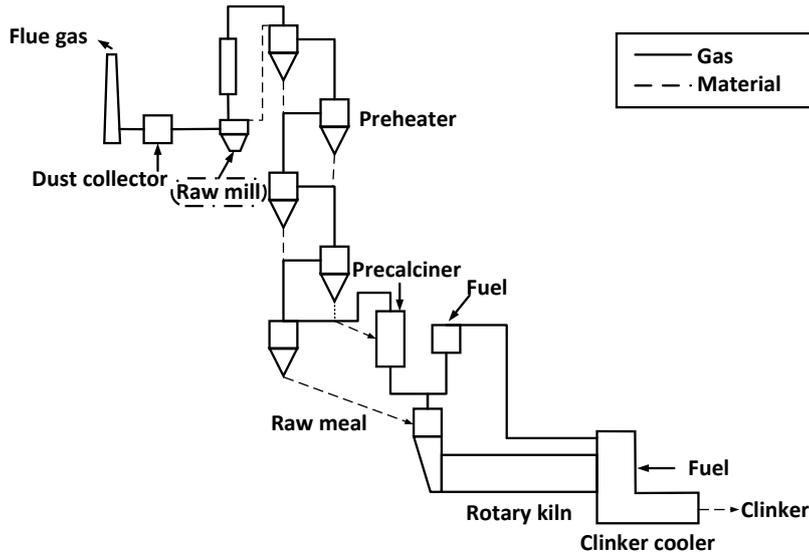


Fig.1 Schematic diagram of a cement kiln system

### 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.

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

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

7b	717.33	3.98	713.35
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### 136 3.1.2 Mass balance of Cr

137 Calcination experiments of raw meal and chrome-polluted soil were performed in a tube  
 138 furnace. The raw materials included cement raw meal and soil, and the combustion products  
 139 included clinker and flue gas. The mass and the total Cr concentration of these substances are listed  
 140 in Tables 4 and 5, respectively. The total Cr concentration in clinker was 1.52–4.67 times of that in  
 141 raw meal, and increased with the mixing ratio of soil. The total Cr concentration in clinker increased  
 142 under the influence of weight loss. The rate of weight loss in the calcination experiments ranged  
 143 from 35.02% to 36.27%, and was caused by the evaporation of crystalline water, the release of CO<sub>2</sub>  
 144 and SO<sub>2</sub>, and the loss of organic impurities.

145

146 Table 4 The mass of raw materials and products (g)

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

147

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

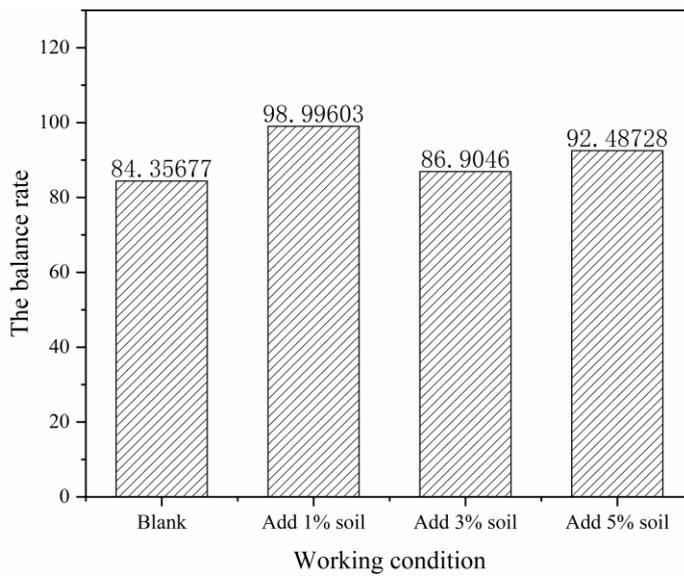
Working conditions	Raw materials		Products
	Raw meal	Soil	Clinker
Control	16.33	—	24.87
Add 1% soil	15.10	761.67	34.88
Add 3% soil	12.80	761.67	54.06
Add 5% soil	19.18	761.67	85.70

149

150 The mass balance ( $\eta$ ) of the total Cr was calculated by Eq. (2)

$$151 \eta = \frac{M_{cl} \cdot C_{cl}}{M_{rm} \cdot C_{rm} + M_s \cdot C_s} \times 100\% \quad (2)$$

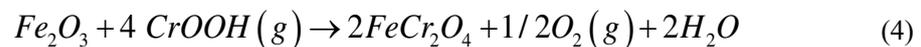
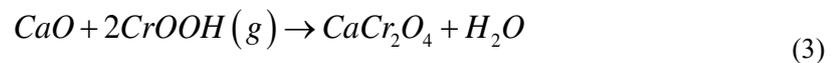
152 Where  $M_{rm}$ ,  $M_s$ , and  $M_{cl}$  represent the mass of raw meal, soil, and clinker, respectively.  $C_{rm}$ ,  $C_s$ ,  
 153 and  $C_{cl}$  represent the total Cr concentration in each of these three materials. The mass balance rate  
 154 of Cr under the four working conditions is shown in Fig.2. The average mass balance value was  
 155 91%, with a range of 70% to 130% over all the experiments.



**Fig.2** The mass balance value for Cr under different experimental conditions

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  $\text{CaCr}_2\text{O}_4$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{FeCr}_2\text{O}_4$ , 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  $\text{Cr}_2(\text{SO}_4)_3$  and  $\text{CrO}_3$ . 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  $\text{CrO}_3(\text{g})$ ,  $\text{CrOOH}(\text{g})$ , and  $\text{CrO}_2(\text{OH})_2(\text{g})$  (Nowak et al. 2012; Roy et al. 2013; Świetlik et al. 2014). Ryszard et al. (Świetlik et al. 2014) found that  $\text{CrOOH}$  and  $\text{CrO}_2(\text{OH})_2$  were the main gaseous forms in the combustion process. As shown in Table 1, the raw materials contain  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ .  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$  capture  $\text{CrOOH}$  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  $\text{CaO}$  could capture chromium steam and promote the enrichment of chromium in solid ash.



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  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  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.

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186

### 3.1.3 Migration and conversion of Cr

187

The Cr(VI) concentration in the raw materials and combustion products is shown in Table 6.

188

The Cr(VI) concentration in the clinker was increased significantly compared with the raw materials

189

during all experimental conditions. The increased Cr(VI) concentration can be explained as follows:

190

(1) Cr(VI) concentration increased under the influence of weight loss and (2) Cr(III) was oxidized

191

to Cr(VI) during calcination.

192

193

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

Working conditions	Raw materials		Products
	Raw meal	Soil	Clinker
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

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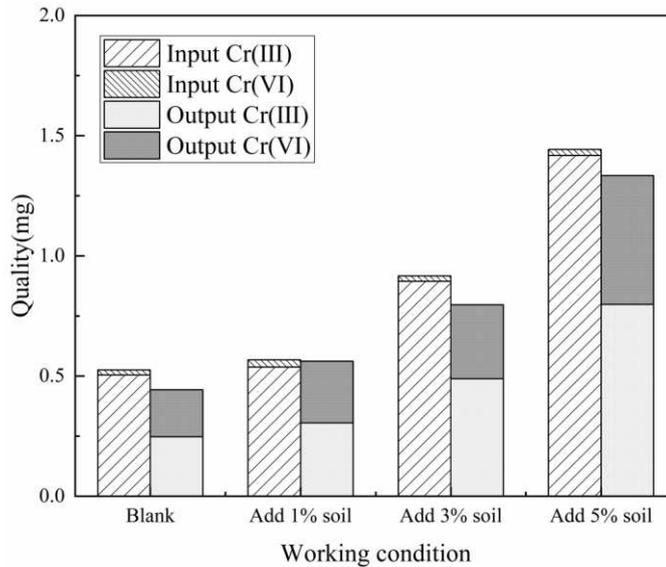
The mass distribution of Cr(III) and Cr(VI) in raw materials and combustion products is shown

196

in Fig.3. The ratio of Cr(VI) to total Cr was between 1.71%–5.21% in the raw materials, and between

197

38.66%–45.61% in the clinker. On average, 45.15% of the Cr(III) in the raw materials was oxidized.



198

Fig.3 The mass distribution of Cr(III) and Cr(VI) in raw materials and combustion products under

199

different experimental conditions

200

201

202

CaO promotes the oxidation of Cr(III) to Cr(VI) according to Eq. (5) below. CaO may also

203

promote the formation of unstable  $\text{CaCr}_2\text{O}_4$ , while  $\text{CaCr}_2\text{O}_4$  is oxidized to  $\text{CaCrO}_4$  requiring less

204

energy, as shown by Eq. (6) and Eq. (7) (Chen et al. 2012). CaO is converted to  $\text{Ca}^0$  by assisting the

205

electron transfer from Cr(III) to  $\text{O}_2$ , and  $\text{Ca}^0$  is then oxidized by  $\text{O}_2$  to  $\text{Ca}^{2+}$  (Chen et al. 2013).

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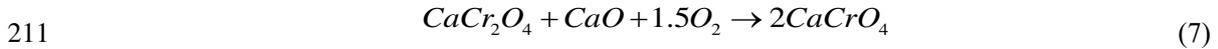
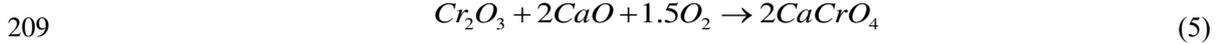
Verbinnen et al. (Verbinnen et al. 2013) studied the oxidation of Cr(III) during the heating of  $\text{Cr}_2\text{O}_3$

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and CaO at temperatures between 100 °C and 1100 °C and observed that Cr(III) was oxidized, which

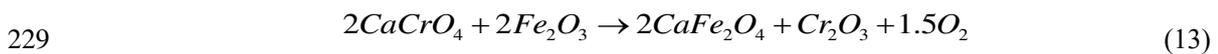
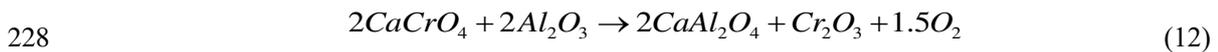
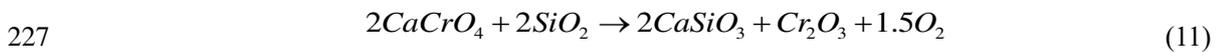
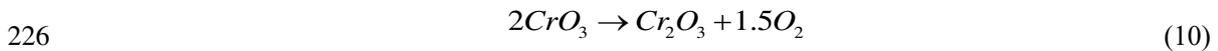
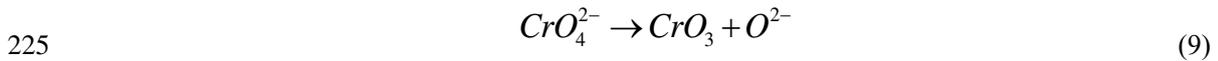
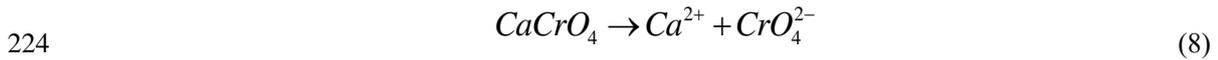
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is consistent with the thermodynamic calculation.

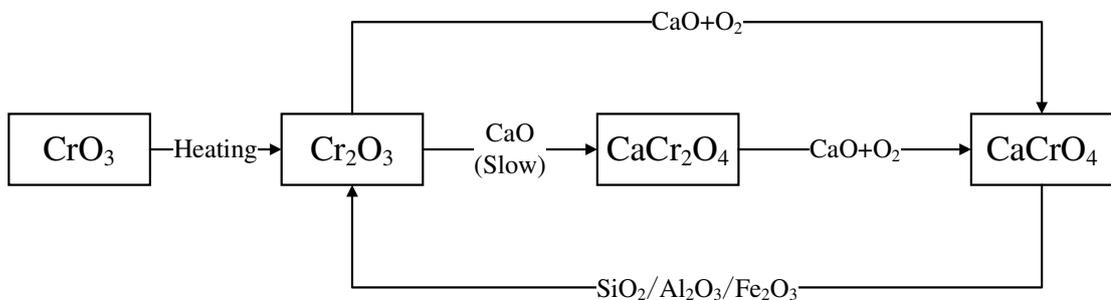


212 As shown in Eqs. (8) to (10),  $\text{CaCrO}_4$  dissociates into cations and  $\text{CrO}_4^{2-}$  as the temperature  
 213 increases, and  $\text{CrO}_4^{2-}$  easily dissociates into  $\text{CrO}_3$  and  $\text{O}^{2-}$ .  $\text{CrO}_3$  is thermodynamically unstable and  
 214 dissociates into  $\text{Cr}_2\text{O}_3$  and  $\text{O}_2$  at 500 °C (Mao et al. 2016). The free cations and  $\text{O}^{2-}$  are captured by  
 215  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  to form stable silicates, aluminates, and ferrites (Eqs. [11] to [13]). Mao et  
 216 al. (Mao et al. 2016) believed that the potential of the metal oxides to promote Cr(VI) reduction was  
 217 caused by their ability to combine with  $\text{O}^{2-}$ .  $\text{SiO}_2$  is an acidic oxide, while  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  are  
 218 neutral oxides.  $\text{SiO}_2$  is more acidic than  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  and can more easily combine with  $\text{O}^{2-}$  and  
 219 therefore can promote Cr(VI) reduction. In addition, Mao et al. (Mao et al. 2016) studied the fate of  
 220 Cr(VI) in the presence of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  and observed that  $\text{SiO}_2$  can cause the release of  
 221  $\text{CaCrO}_4$ ,  $\text{Na}_2\text{CrO}_4$ , and  $\text{K}_2\text{CrO}_4$  at around 900 °C, 1000 °C, and 1000 °C, respectively, while  $\text{Al}_2\text{O}_3$   
 222 and  $\text{Fe}_2\text{O}_3$  could only promote the reduction of  $\text{CaCrO}_4$ .

223 Therefore,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  can promote Cr(VI) reduction to different degrees.



230 Based on the experimental results, the possible reactions of Cr compounds in the calcination  
 231 experiment are shown in Fig.4.  $\text{CaO}$  is a basic oxide, while  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  are acidic or  
 232 neutral oxides. The two have opposite effects on the conversion of Cr valence.



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

### 3.2 Field-scale experiments

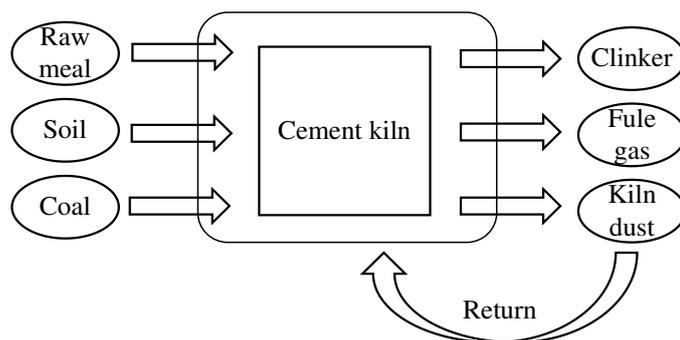
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### 3.2.1 Mass balance of Cr

238

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.

246



247

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

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250

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

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

251

252

**Table 8** Input and output rates of total Cr (g/h)

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

253

254

### 3.2.2 Migration and conversion of Cr

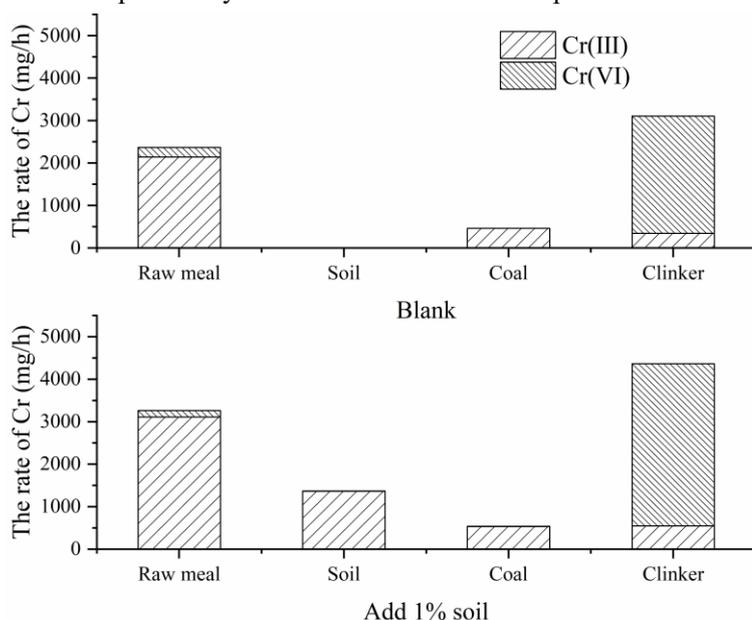
255

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

258

259 average, 87.94% of the Cr(III) in the raw materials was oxidized. In the laboratory experiments, the  
 260 ratio of Cr(VI) to total Cr in the clinker ranged from 38.66% to 45.61%. This is significantly lower  
 261 than for the field-scale experiments, and can be explained by the different calcination conditions.  
 262 The materials in the cement rotary kiln can make full contact with oxygen, while in a tube furnace,  
 263 the inside of the bulk material does not have full contact with oxygen.

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

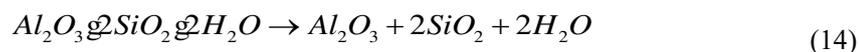


267 **Fig.6** The valence distribution of Cr in the cement kiln under the control condition and with 1%  
 268 chrome-polluted soil  
 269

### 271 3.2.3 Possible reactions of Cr in the cement kiln

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

276 During preheating, the raw meal is heated to approximately 750 °C, resulting in evaporation  
 277 of water and dehydration and decomposition of the clay particles. First, the raw meal is dried, and  
 278 the free water in raw meal evaporates at 100–150 °C, increasing the Cr concentration in the raw  
 279 meal. At around 450 °C, kaolin—the main component of clay—is dehydrated and decomposed into  
 280 free Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> (Eq. 14). Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> inhibit the oxidation of Cr according to the  
 281 thermodynamic equilibrium equation, which is consistent with the experimental results of Mao et  
 282 al. (Mao et al. 2016).



284 The temperature of the materials can reach approximately 870 °C in the pre-calciner, where  
 285 limestone is decomposed; here, approximately 90% of the raw meal is decomposed. CaCO<sub>3</sub> and  
 286 MgCO<sub>3</sub> are rapidly decomposed to free oxides and CO<sub>2</sub> in the pre-calciner. The decomposition of  
 287 CaCO<sub>3</sub> is reversible, so ventilation of the pre-calciner is necessary to promote the emission of CO<sub>2</sub>.

288 The pre-calciner is an oxidizing atmosphere where free CaO and MgO are extremely active and can  
289 react with Cr.

290 In the pre-calcination process, a large amount of CaO promotes the oxidation of Cr(III) to  
291 CaCrO<sub>4</sub> and rapidly oxidizes any CaCr<sub>2</sub>O<sub>4</sub> to CaCrO<sub>4</sub>, as shown in Eqs. (5) to (7). Stam et al. (Stam  
292 et al. 2011) showed that the formation of Cr(VI) is a high-temperature process, and is affected by  
293 free CaO and the formation of solid chromate. Yang et al. (Yang et al. 2020a) studied the chromium  
294 speciation in chromium-rich tannery sludge under an air atmosphere at temperature of 300–1200 °C;  
295 they observed that CaCrO<sub>4</sub> first appeared at 400 °C, gradually increased in the range of 400–800 °C,  
296 and reached a maximum at 800 °C. This indicated the oxidation of Cr(III) to Cr(VI). Hu et al. (Hu  
297 et al. 2015) studied the distribution of Cr(VI) in municipal solid waste incineration ash and observed  
298 that the oxidation of Cr depended on the content of free CaO. They (Hu et al. 2015) also studied the  
299 effect of temperature on the oxidation of CaO to Cr<sub>2</sub>O<sub>3</sub> and observed that the maximum oxygen  
300 consumption rate was increased with increasing temperature from 700 °C to 900 °C. This result  
301 indicated that CaO can promote the oxidation of most Cr(III) in this temperature range. In addition,  
302 MgO promotes the oxidation of Cr(III) into MgCrO<sub>4</sub>.

303 The solid-solid and sintering reactions occur in a rotary kiln. In the transition zone of the rotary  
304 kiln, at a temperature of 900–1150 °C, free CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> have multistage and  
305 complex solid reactions. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> reduce CaCrO<sub>4</sub>, therefore inhibiting Cr(III)  
306 oxidation. In the sintering zone of the rotary kiln, a liquid phase will appear when the temperature  
307 of the materials rises to nearly 1300 °C. Because the melting point of CaO is 2570 °C, most of CaO  
308 is still in the solid phase; however, CaO can dissolve in the high-temperature liquid (Li 2020).  
309 Dissolved CaO has increased contact area with Cr, promoting the oxidation of Cr to a certain extent.  
310 In the cooling process of clinker, there is still a small amount of free CaO in the solidified material  
311 that has not been chemically reacted.

312

### 313 3.2.4 Environmental implications

314 The distribution of Cr in two cement products (P·C 32.5R and P·C 42.5R) with added 1%  
315 chrome-polluted soil is shown in Table 9. The Cr concentration in the cement products was lower  
316 than that in the clinker, as shown in Table 7. The total Cr for the two cement products decreased by  
317 40.14% and 8.09%, and Cr(VI) fell by 61.59% and 62.64%, respectively. The decrease occurred  
318 because the Cr concentration in clinker was diluted after adding gypsum, and other additives. The  
319 standard Gb30760-2014 “Technical Specification for Collaborative Disposal of Solid Waste by  
320 Cement Kiln” indicates that the limit for Cr in clinker is 150 mg/kg. Therefore, adding 1% of  
321 chrome-polluted soil to the raw meal of a cement kiln conforms to Chinese safety standards.

322

323 Table 9 The distribution of Cr in two cement products (mg/kg)

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

324

## 325 4 Conclusions

326 For the four calcination experiments in a tube furnace, the Cr mass balance values ranged from  
327 84% to 99%, and the average mass balance was 91%. During the co-processing of chrome-polluted  
328 soil with raw meal in a cement rotary kiln, the mass balance values were 110% and 84% in the

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329 control condition and with added 1% chrome-polluted soil, respectively, for the two cement  
330 formulations used. Therefore, most of the Cr was fixed in the solid products, and very little Cr was  
331 volatilized into the flue gas. Most Cr compounds in the raw materials were difficult to volatilize. Cr  
332 hydroxides that may have been volatilized into the flue gas were captured by CaO and Fe<sub>2</sub>O<sub>3</sub>.

333 Most of the Cr(III) in the raw materials was oxidized to Cr(VI) after being calcined, and a  
334 higher proportion of Cr(III) was oxidized in cement kiln. The average concentration of total Cr was  
335 403.25 mg/kg, and the ratio of Cr(VI) to total Cr was 1.83% or less in the chrome-polluted soil  
336 samples. In laboratory experiments, the ratio of Cr(VI) to total Cr was between 38.66% and 45.61%  
337 in the clinker, and an average of 45.15% of Cr(III) in the raw materials was oxidized. In the field-  
338 scale experiments, 87.94% of Cr(III) was oxidized. The oxidation of Cr(III) can be explained as  
339 follows: in a high-temperature and oxidizing atmosphere, large amounts of CaO and MgO promote  
340 the oxidation of Cr(III) to Cr(VI), while SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> promote Cr(VI) reduction, leading  
341 to the oxidation of most of the Cr(III). The materials in the cement rotary kiln have full contact with  
342 oxygen, while in the tube furnace, the inside of the materials does not have full contact with oxygen,  
343 resulting in a higher proportion of Cr(III) oxidized in the cement kiln.

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

348

349 **Ethical Approval:** Not applicable.

350 **Consent to Participate:** Not applicable.

351 **Consent to Publish:** Not applicable.

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353 mechanism of chromium. YL and MWW analyzed the distribution of chromium systematically and  
354 were major contributors in writing the manuscript. DHY and ZL organized the experiments. All  
355 authors read and approved the final manuscript.

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358 **Competing Interests:** The authors declare that they have no competing interests.

359 **Availability of data and materials:** The datasets used and analyzed during the current study are  
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# Figures

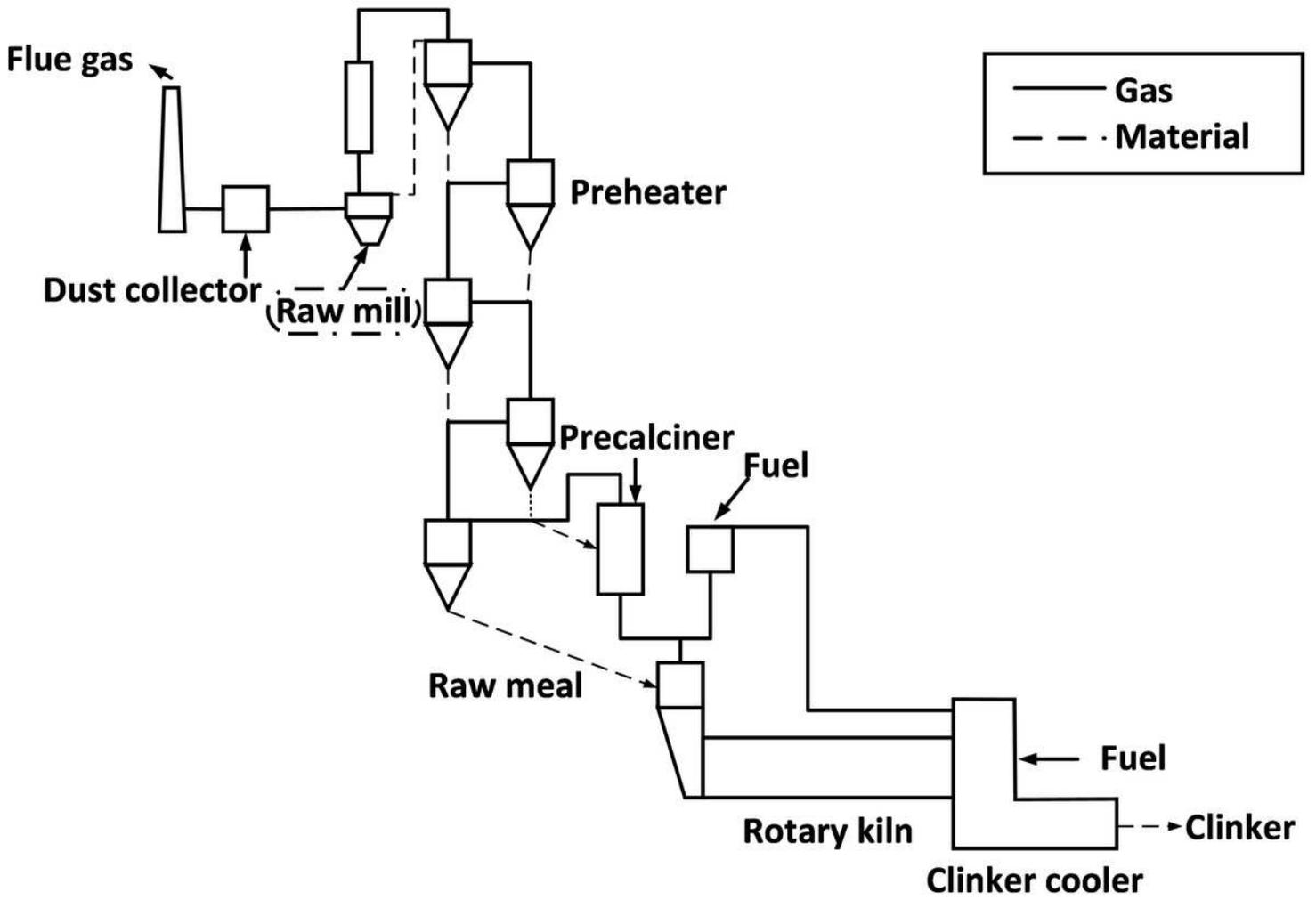


Figure 1

Schematic diagram of a cement kiln system

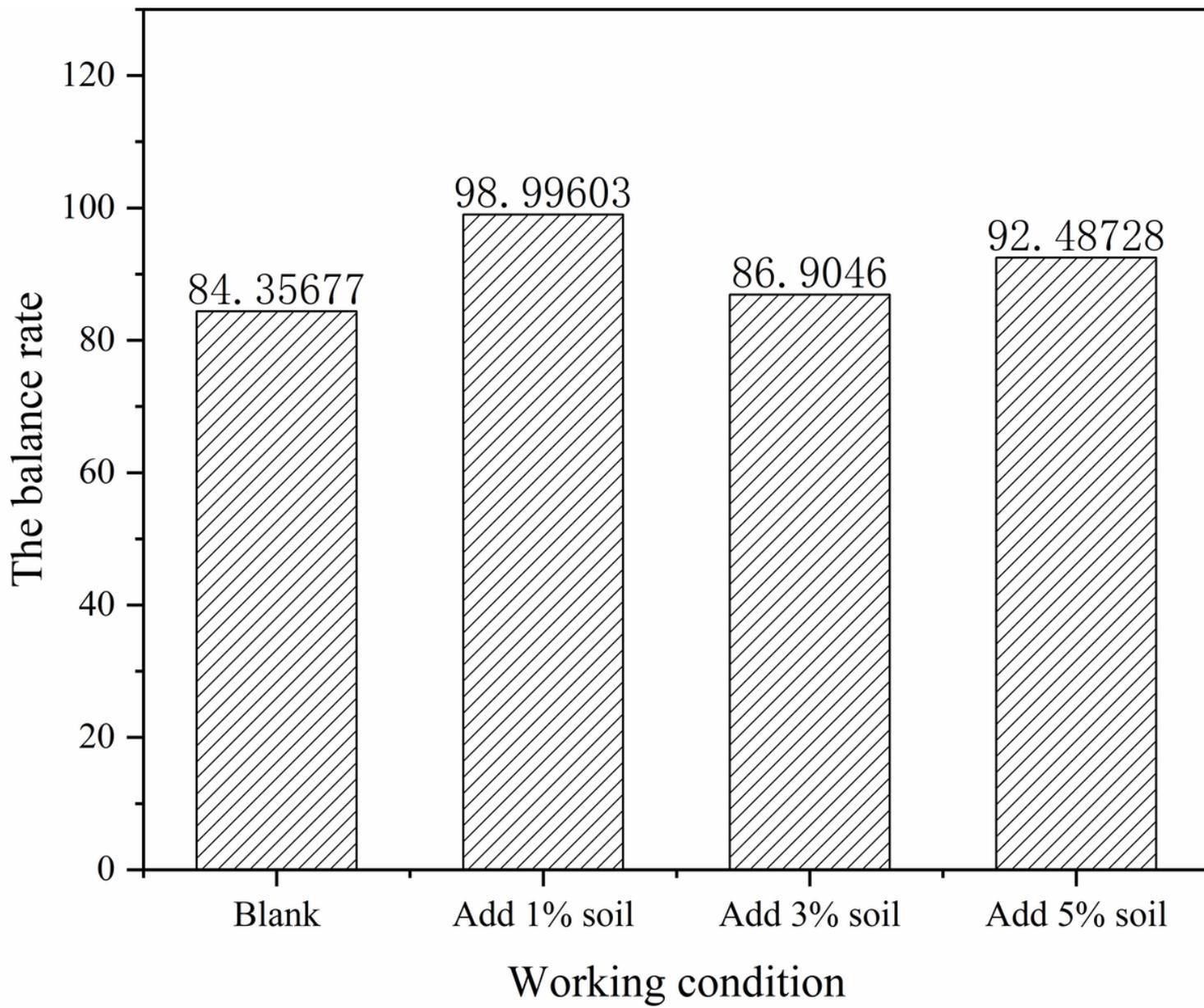


Figure 2

The mass balance value for Cr under different experimental conditions

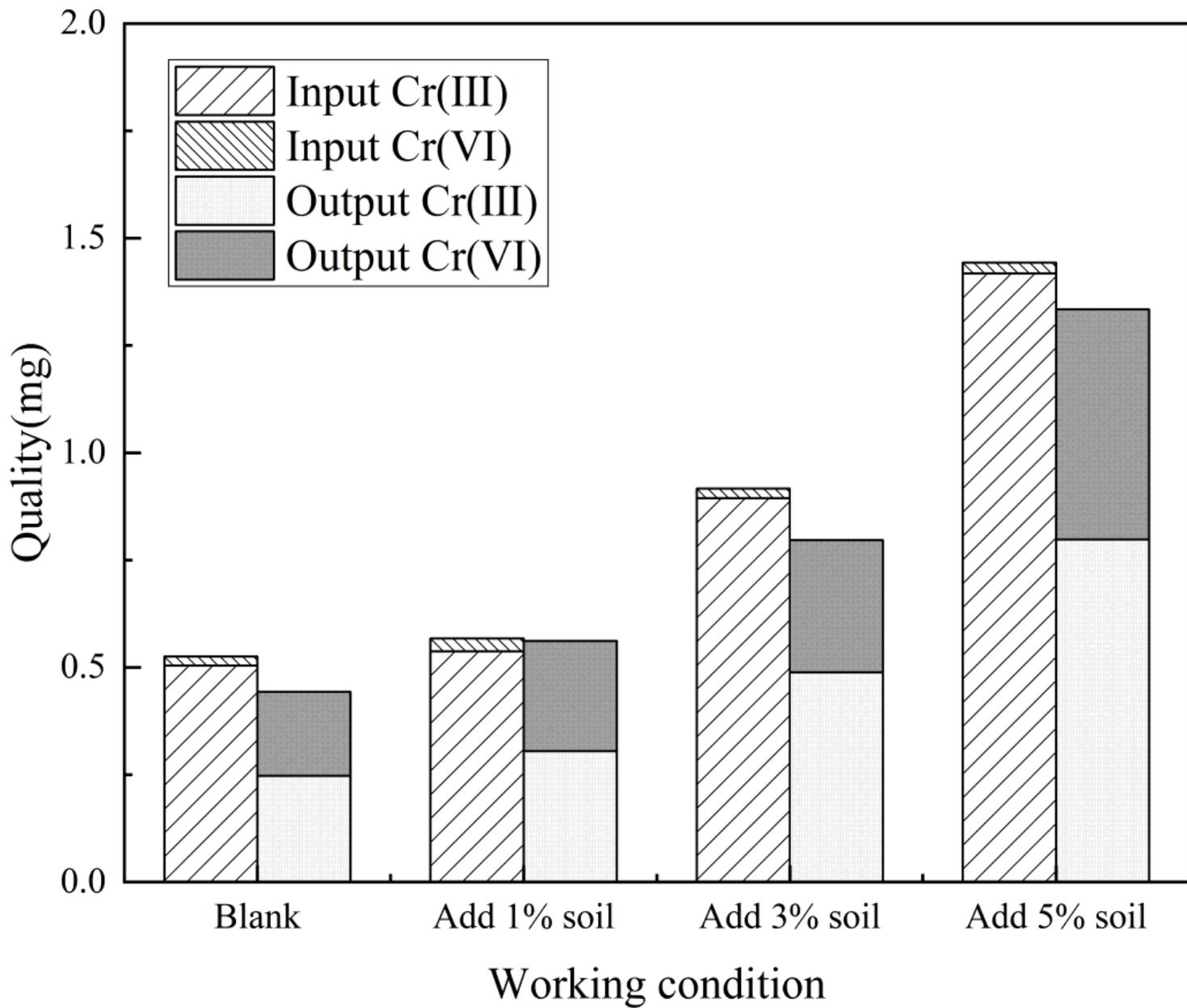


Figure 3

The mass distribution of Cr(III) and Cr(VI) in raw materials and combustion products under different experimental conditions

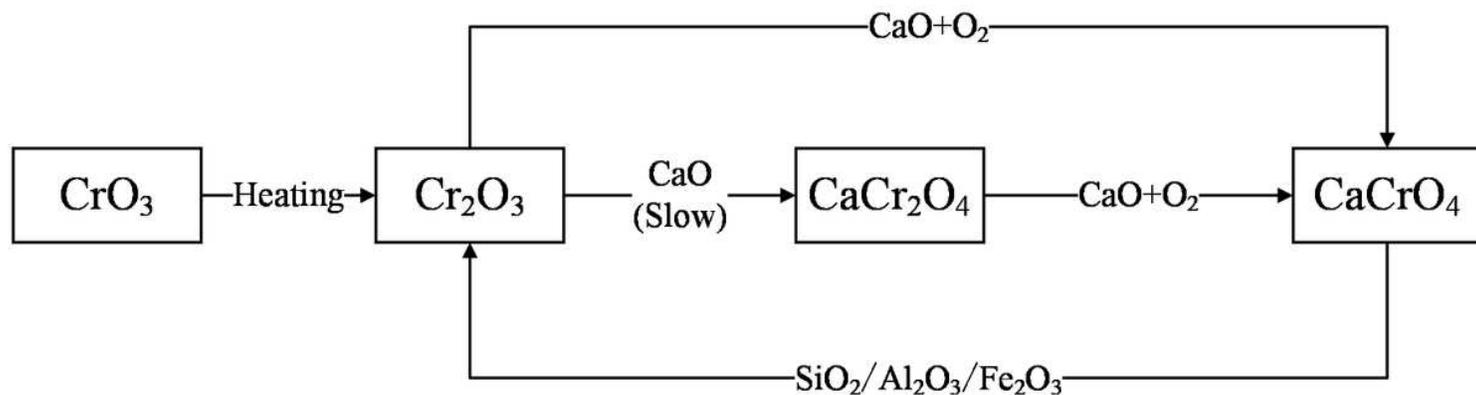


Figure 4

The possible reactions of Cr compounds in the calcination experiment

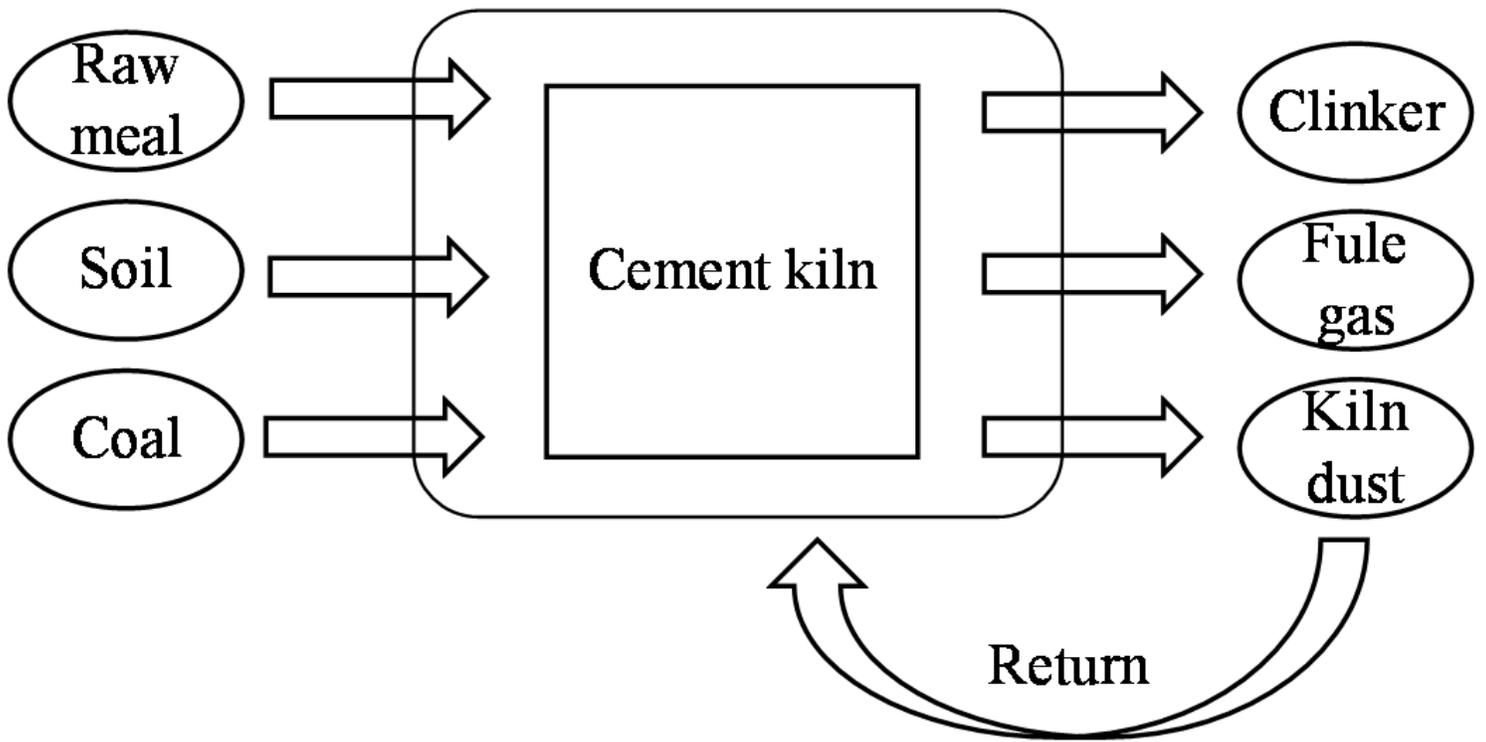
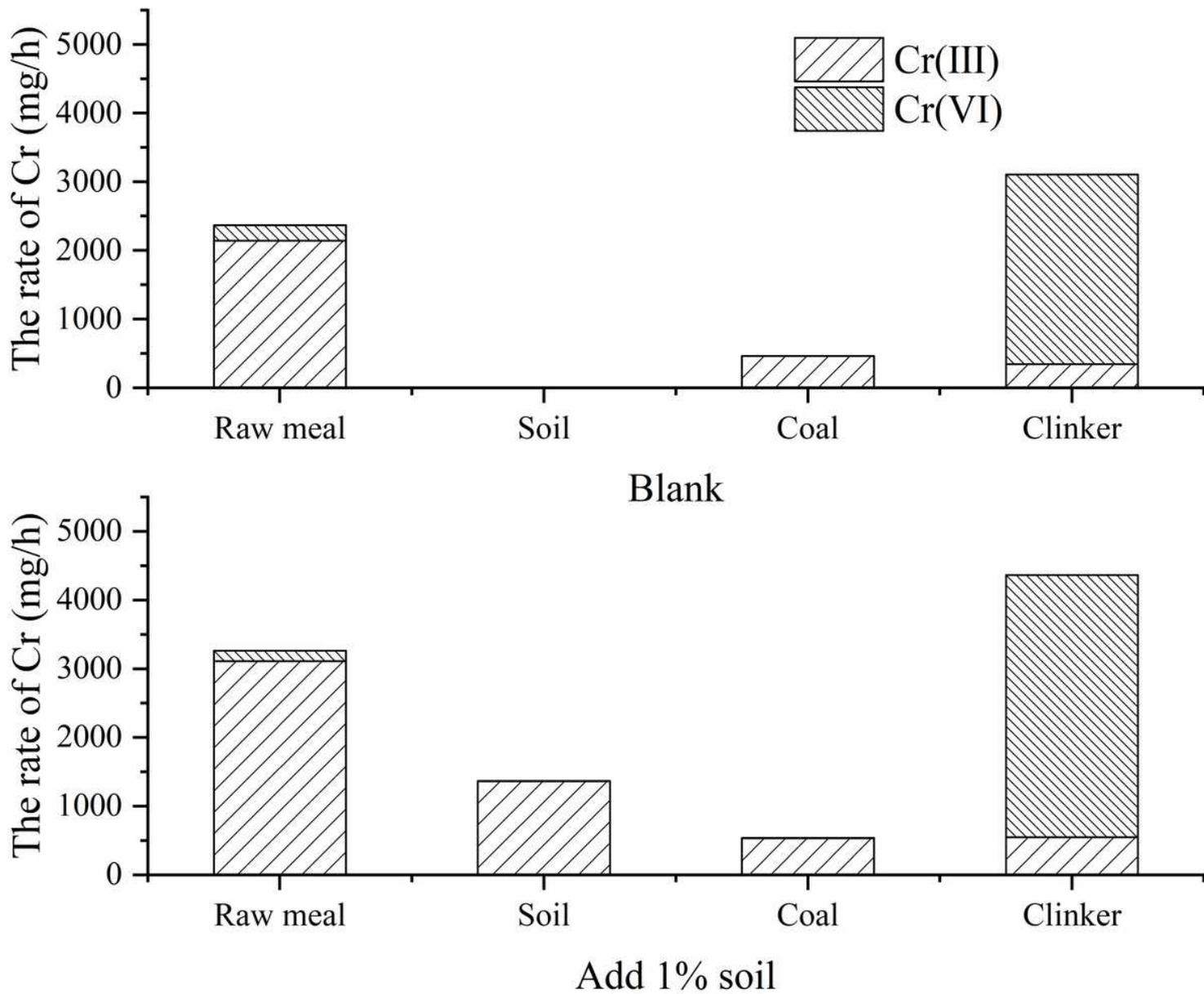


Figure 5

The material streams in the field-scale experiments



**Figure 6**

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