

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

Haiping Xiao

North China Electric Power University - Beijing Campus: North China Electric Power University

Yan Li

North China Electric Power University - Beijing Campus: North China Electric Power University

Mingwei Wang

North China Electric Power University - Beijing Campus: North China Electric Power University

Dahai Yan (✉ seavslan@163.com)

Chinese Research Academy of Environmental Sciences <https://orcid.org/0000-0001-5079-0707>

Zhong Liu

North China Electric Power University - Beijing Campus: North China Electric Power University

Research Article

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

Posted Date: February 11th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-217639/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Environmental Technology & Innovation on November 1st, 2021. See the published version at <https://doi.org/10.1016/j.eti.2021.101971>.

1 The migration and transformation of chromium during co-processing 2 of cement raw meal mixed with chrome-polluted soil

3 Haiping Xiao^a, Yan Li^a, Mingwei Wang^a, Dahai Yan^{b*}, Zhong Liu^a

4 ^a School of Energy, Power and Mechanical Engineering, North China Electric Power University,
5 Beijing 102206, China

6 ^b State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy
7 of Environmental Sciences, Beijing 100012, China

8 * **Corresponding author.** E-mail address: seavslan@163.com; Tel.: 86-15901376037; Fax: 86-
9 10-84913903

10
11 **Abstract:** To efficiently dispose of chrome-polluted soil, we tested the co-processing of raw meal
12 mixed with chrome-polluted soil in a tube furnace (laboratory experiments) and a cement rotary kiln
13 (field-scale experiments). The migration and transformation reactions of chromium were analyzed
14 and the environmental risk was evaluated. The average mass balance value was 91% for the
15 laboratory experiments. In field-scale experiments, the mass balance values were 110% for the
16 control experiments and 84% when 1% soil was treated. Therefore, only a small amount of Cr was
17 volatilized into the flue gas. The average total Cr concentration in the soil samples was 403.25
18 mg/kg, and the ratio of Cr(VI) to total Cr was 1.83% or less. On average, 45.15% of Cr(III) was
19 oxidized to Cr(VI) in laboratory experiments, while 87.94% of Cr(III) was oxidized in field-scale
20 experiments, and the difference could be a result of the different calcination conditions. The
21 materials in the cement rotary kiln make full contact with oxygen, and in this high temperature and
22 oxidizing atmosphere, abundant CaO and MgO promote the oxidation of Cr(III) to CaCrO₄. SiO₂,
23 Al₂O₃, and Fe₂O₃ reduce CaCrO₄, which inhibits Cr(III) oxidation. The Cr concentration in the
24 cement products was well below the Chinese standard limits. Therefore, the treatment of 1%
25 chrome-polluted soil with a cement rotary kiln is experimentally safe.

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

27 28 1 Introduction

29 Chromium is widely used in steel, leather, and other industries, and the resulting chromium
30 residue can cause serious pollution. In China, the annual production of chromium exceeds 160,000
31 tonnes, the cumulative amount of chromium residue is nearly six million tonnes, and the amount of
32 chrome-polluted soil exceeds 20 million tonnes(Wang et al. 2011). Cement kilns have some
33 advantages for the co-processing of solid waste, and can increase the capacity for solid waste
34 disposal and reduce the consumption of raw materials and fuel by the cement industry(Aranda Usón
35 et al. 2013; Kosajan et al. 2020). However, the migration and transformation of Cr and other heavy
36 metals during co-processing can threaten environmental and human health. Most chromium residue
37 is in the trivalent (Cr(III)) and the highly toxic hexavalent (Cr(VI)) forms. More importantly, some
38 Cr(III) will be oxidized to Cr(VI) during co-processing in a cement kiln(Fu et al. 2021; Gong et al.
39 2020; Li et al. 2018a). Therefore, the study of the transfer and transformations of Cr during co-
40 processing of waste is of great significance.

41 Alkali metal and alkali earth metal oxides affect the redox state of chromium. In cement raw
42 meal, coal, and chrome-polluted soil, chromium exists mainly in the forms CaCr₂O₄, Cr(OH)₃,

43 Cr₂O₃, Cr₂(SO₄)₃, CrO₃, and FeCr₂O₄.(Jiang et al. 2016) The components in cement raw meal
44 include CaO, SiO₂, Al₂O₃, Fe₂O₃, 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 Ca⁰ by assisting the electron transfer from
49 Cr(III) to O₂, and Ca⁰ is then oxidized by O₂ to Ca²⁺(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 CaCrO₄ 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). Cr₂O₃ and CaO were heated in a
53 muffle furnace. The X-ray adsorption near-edge spectroscopy spectra indicated that the initial
54 oxidation of Cr₂O₃ 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, CaCr₂O₄ is formed as an intermediate product, and the oxidation of CaCr₂O₄ 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). SiO₂ is an acidic oxide that can combine with O²⁻, while Al₂O₃ and Fe₂O₃ are neutral
60 oxides that can absorb O²⁻ under basic conditions. Therefore, SiO₂, Al₂O₃, and Fe₂O₃ reduce CaCrO₄
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). SiO₂ and Al₂O₃ favor the capture of Cr vapor, especially when the
63 ratio of Si:Al is 3:1. Fe₂O₃ 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 Na₂CrO₄ 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, Fe₂O₃, 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, SiO₂,
 94 Al₂O₃, Fe₂O₃, 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 ₂	13.08%	63.30%
Al ₂ O ₃	3.57%	11.90%
Fe ₂ O ₃	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 O₂ (5%) and N₂ (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**

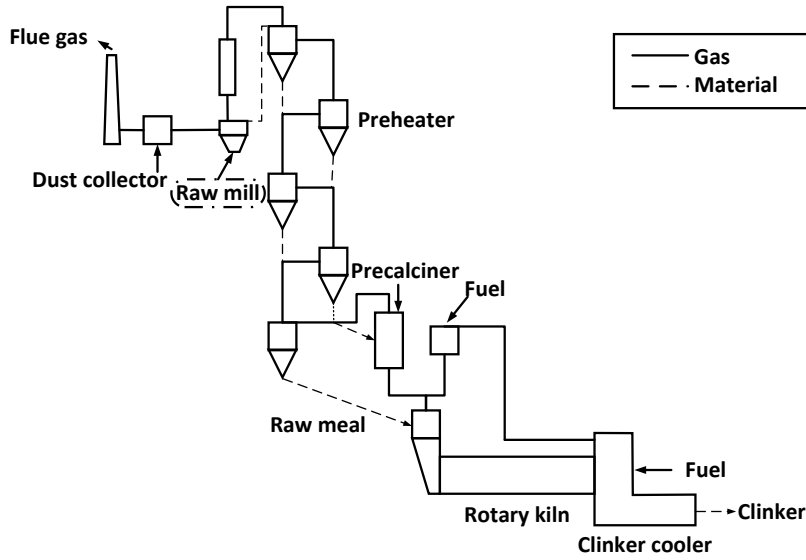
111 The field-scale experiments were carried out in a cement rotary kiln. The mixing of raw meal
 112 and chrome-polluted soil was conducted at various mass ratios indicated in Table 2.

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.



119
120 **Fig.1** Schematic diagram of a cement kiln system

121
122 **3 Results and Discussion**

123 **3.1 Laboratory experiments**

124 **3.1.1 Cr in chrome-polluted soil**

125
126
127 Table 3 shows the distribution of Cr in the seven chrome-polluted soils. All samples were tested
128 in parallel (a and b). The concentration of Cr(III) was calculated according to Eq. (1), where ω refers
129 to the Cr(III) concentration. The average total Cr concentration in the samples was 403.25 mg/kg,
130 and the average Cr(VI) concentration was 2.12 mg/kg. The ratio of Cr(VI) to total Cr was 1.83% or
131 less. The soil sample used in the experiments was sample No.7 because it contained the most Cr.

132
$$\omega(Cr^{3+}) = \omega(Cr_{total}) - \omega(Cr^{6+}) \quad (1)$$

133
134 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
----	--------	------	--------

135

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 CO₂
 144 and SO₂, 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 (η) of the total Cr was calculated by Eq. (2)

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

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.

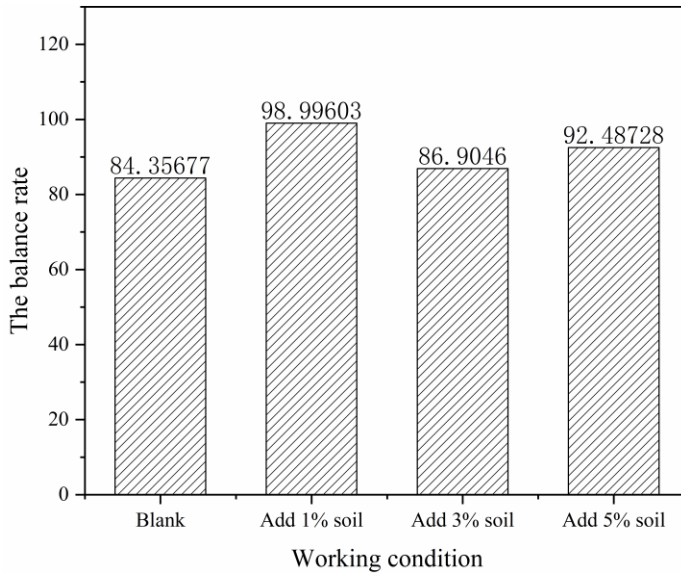
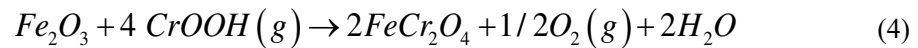
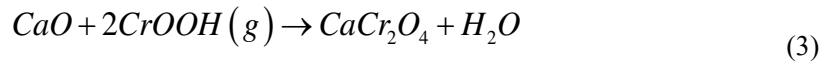


Fig.2 The mass balance value for Cr under different experimental conditions

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 CaCr_2O_4 , $\text{Cr}(\text{OH})_3$, Cr_2O_3 , FeCr_2O_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 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 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 CaO , SiO_2 , Al_2O_3 , and Fe_2O_3 . CaO and Fe_2O_3 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.



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 SiO_2 and Al_2O_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.

185

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

189

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

190

191

192

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

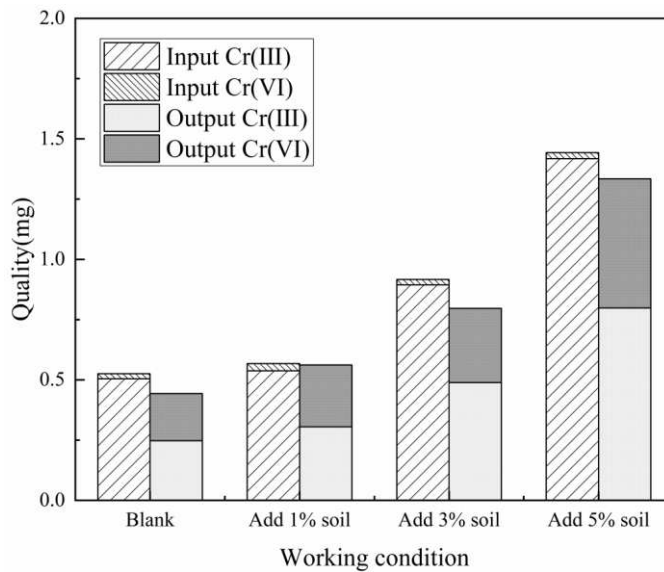
194

195

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.

196

197



198

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

199

200

201

202

CaO promotes the oxidation of Cr(III) to Cr(VI) according to Eq. (5) below. CaO may also promote the formation of unstable CaCr_2O_4 , while CaCr_2O_4 is oxidized to CaCrO_4 requiring less energy, as shown by Eq. (6) and Eq. (7) (Chen et al. 2012). CaO is converted to Ca^0 by assisting the electron transfer from Cr(III) to O_2 , and Ca^0 is then oxidized by O_2 to Ca^{2+} (Chen et al. 2013). Verbinnen et al. (Verbinnen et al. 2013) studied the oxidation of Cr(III) during the heating of Cr_2O_3 and CaO at temperatures between 100 °C and 1100 °C and observed that Cr(III) was oxidized, which is consistent with the thermodynamic calculation.

203

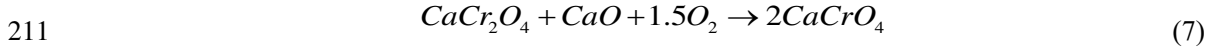
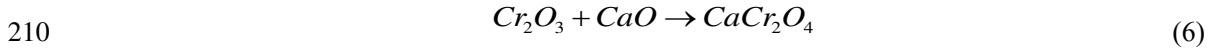
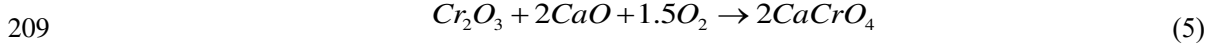
204

205

206

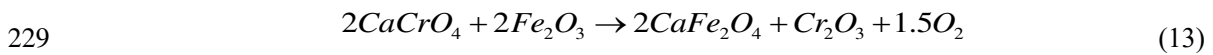
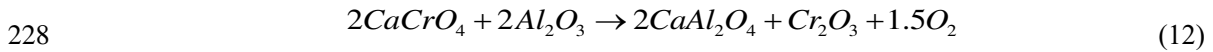
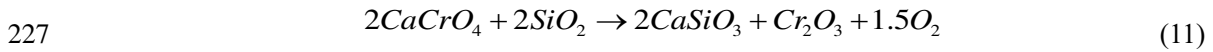
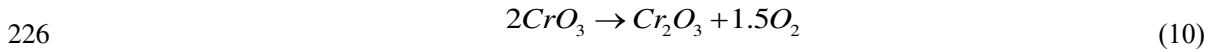
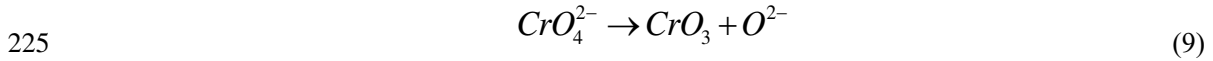
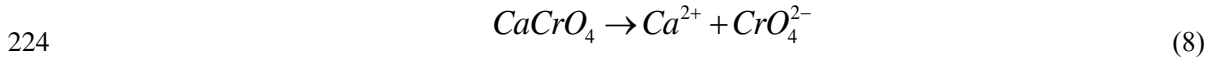
207

208

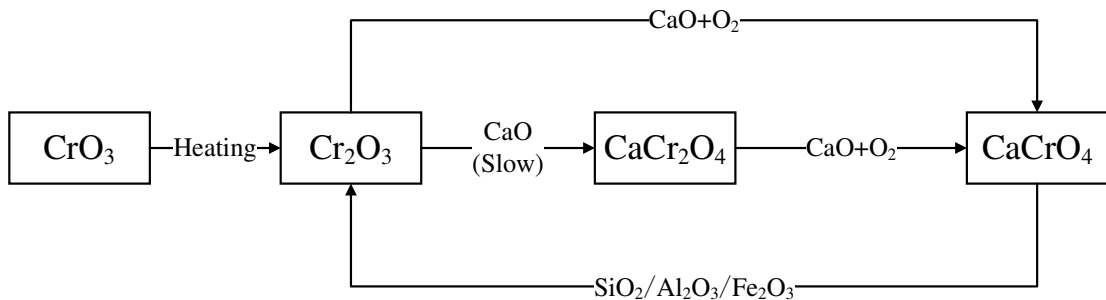


212 As shown in Eqs. (8) to (10), CaCrO_4 dissociates into cations and CrO_4^{2-} as the temperature
 213 increases, and CrO_4^{2-} easily dissociates into CrO_3 and O^{2-} . CrO_3 is thermodynamically unstable and
 214 dissociates into Cr_2O_3 and O_2 at 500 °C (Mao et al. 2016). The free cations and O^{2-} are captured by
 215 SiO_2 , Al_2O_3 , and Fe_2O_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 O^{2-} . SiO_2 is an acidic oxide, while Al_2O_3 and Fe_2O_3 are
 218 neutral oxides. SiO_2 is more acidic than Al_2O_3 and Fe_2O_3 and can more easily combine with 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 SiO_2 , Al_2O_3 , and Fe_2O_3 and observed that SiO_2 can cause the release of
 221 CaCrO_4 , Na_2CrO_4 , and K_2CrO_4 at around 900 °C, 1000 °C, and 1000 °C, respectively, while Al_2O_3
 222 and Fe_2O_3 could only promote the reduction of CaCrO_4 .

223 Therefore, SiO_2 , Al_2O_3 , and Fe_2O_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. CaO is a basic oxide, while SiO_2 , Al_2O_3 , and Fe_2O_3 are acidic or
 232 neutral oxides. The two have opposite effects on the conversion of Cr valence.



233

234

235

236

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

3.2 Field-scale experiments

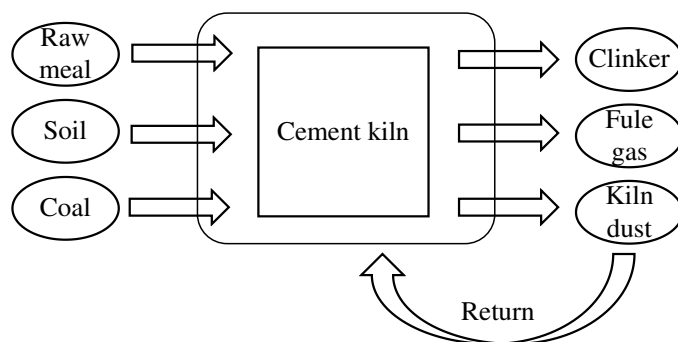
237

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

248

249

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

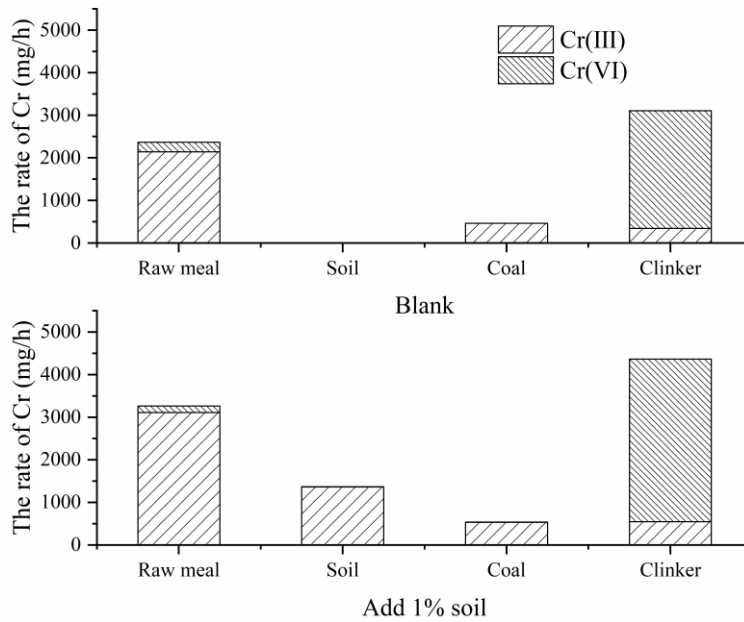
255

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.

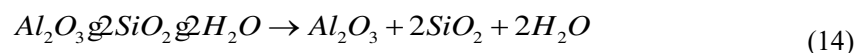


267 **Fig.6** The valence distribution of Cr in the cement kiln under the control condition and with 1%
 268 chrome-polluted soil
 269

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 Al₂O₃ and SiO₂ (Eq. 14). Al₂O₃ and SiO₂ 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. CaCO₃ and
 286 MgCO₃ are rapidly decomposed to free oxides and CO₂ in the pre-calciner. The decomposition of
 287 CaCO₃ is reversible, so ventilation of the pre-calciner is necessary to promote the emission of CO₂.

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 CaCrO₄ and rapidly oxidizes any CaCr₂O₄ to CaCrO₄, 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 CaCrO₄ 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 Cr₂O₃ 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 MgCrO₄.

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, SiO₂, Al₂O₃, and Fe₂O₃ have multistage and
305 complex solid reactions. SiO₂, Al₂O₃, and Fe₂O₃ reduce CaCrO₄, 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

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 Fe₂O₃.

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 SiO₂, Al₂O₃, and Fe₂O₃ 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.

352 **Authors Contributions:** HPX designed the experiments and analyzed the transformation
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.

356 **Funding:** This study was supported by the National Natural Science Foundation of China (No.
357 51676070).

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
360 available from the corresponding author on reasonable request.

References

- 361
362 Aranda Usón A, López-Sabirón AM, Ferreira G, Llera Sastresa E (2013) Uses of
363 alternative fuels and raw materials in the cement industry as sustainable waste management
364 options *Renewable and Sustainable Energy Reviews* 23:242-260
365 doi:10.1016/j.rser.2013.02.024
- 366 Chen J, Jiao FC, Zhang L, Yao H, Ninomiya Y (2012) Use of synchrotron XANES and Cr-
367 doped coal to further confirm the vaporization of organically bound Cr and the formation of
368 chromium(VI) during coal oxy-fuel combustion *Environ Sci Technol* 46:3567-3573
369 doi:10.1021/es204255h
- 370 Chen J, Jiao FC, Zhang L, Yao H, Ninomiya Y (2013) Elucidating the mechanism of Cr(VI)
371 formation upon the interaction with metal oxides during coal oxy-fuel combustion *J Hazard*
372 *Mater* 261:260-268 doi:10.1016/j.jhazmat.2013.07.023
- 373 Fan XG, Yang YF, Huang QF, Li ZW, Yu HJ (2014) The transformation of Cr form at
374 different temperatures in the co-treatment of Cr containing waste in cement kiln *Research of*
375 *Environmental Sciences* 27:272-278 doi:10.13198/j.issn.1001-6929.2014.03.08
- 376 Fu LJ, Feng AX, Xiao JJ, Wu Q, Ye QY, Peng S (2021) Remediation of soil contaminated
377 with high levels of hexavalent chromium by combined chemical-microbial reduction and
378 stabilization *Journal of Hazardous Materials* 403 doi:10.1016/j.jhazmat.2020.123847
- 379 Gong HY et al. (2020) The potential oxidation characteristics of CaCr₂O₄ during coal
380 combustion with solid waste in a fluidized bed boiler: A thermogravimetric analysis
381 *Chemosphere* 263:127974 doi:10.1016/j.chemosphere.2020.127974
- 382 Hu HY, Shi MY, Yang YH, Liu H, Xu M, Shen JH, Yao H (2018) Further Insight into the
383 Formation and Oxidation of CaCr₂O₄ during Solid Fuel Combustion *Environ Sci Technol*
384 52:2385-2391 doi:10.1021/acs.est.7b05538
- 385 Hu HY, Xu Z, Liu H, Chen DK, Li AJ, Yao H, Naruse I (2015) Mechanism of chromium
386 oxidation by alkali and alkaline earth metals during municipal solid waste incineration
387 *Proceedings of the Combustion Institute* 35:2397-2403 doi:10.1016/j.proci.2014.08.029
- 388 Jiang XG, Dong H, Lv GJ, Chi Y, Yan JH (2016) Oxidation mechanism and control method
389 of Cr during high temperature combustion *Chemical Industry and Engineering Progress* 35:1-
390 10 doi:10.16085/j.issn.1000-6613.2016.s2.001
- 391 Kavouras P et al. (2015) Incineration of tannery sludge under oxic and anoxic conditions:
392 Study of chromium speciation *Journal of Hazardous Materials* 283
- 393 Kosajan V, Wen Z, Fei F, Doh Dinga C, Wang Z, Zhan J (2020) The feasibility analysis of
394 cement kiln as an MSW treatment infrastructure: From a life cycle environmental impact
395 perspective *Journal of Cleaner Production* 267 doi:10.1016/j.jclepro.2020.122113
- 396 Li CP (2020) Practical technology for collaborative disposal of household garbage by
397 cement kiln. vol 05. China Building Industry Press, Beijing
- 398 Li L, Huang QF, zhang ZQ, Cai ML, Yan DH (2009) Study on the pollution discharge of
399 contaminated soil treated by cement kiln *Chinese Journal of Environmental Engineering* 3:891-
400 896
- 401 Li XY, Dong H, Chen J, Lu C, Luo G, Yao H (2018a) Transformation of Organically Bound
402 Chromium during Oxy-coal Combustion: The Influence of Steam and Mineral *Energy & Fuels*
403 32:1992-1998 doi:10.1021/acs.energyfuels.7b03123
- 404 Li XY, Dong H, Zhao XP, Chen J, Lu CM, Yao H (2018b) Effect of water vapor on mineral

405 chromium capture under oxygen-enriched combustion *CIESC Journal* 69:2714-2721
406 doi:10.11949/j.issn.0438-1157.20171460

407 Mao LQ, Deng N, Liu L, Cui H, Zhang WY (2016) Effects of Al₂O₃, Fe₂O₃, and SiO₂ on
408 Cr(VI) formation during heating of solid waste containing Cr(III) *Chemical Engineering Journal*
409 304:216-222 doi:10.1016/j.cej.2016.06.086

410 Nowak B, Frías Rocha S, Aschenbrenner P, Rechberger H, Winter F (2012) Heavy metal
411 removal from MSW fly ash by means of chlorination and thermal treatment: Influence of the
412 chloride type *Chemical Engineering Journal* 179:178-185 doi:10.1016/j.cej.2011.10.077

413 Roy B, Choo WL, Bhattacharya S (2013) Prediction of distribution of trace elements under
414 Oxy-fuel combustion condition using Victorian brown coals *Fuel* 114:135-142
415 doi:10.1016/j.fuel.2012.09.080

416 Stam AF, Meij R, Te Winkel H, Eijk RJ, Huggins FE, Brem G (2011) Chromium speciation
417 in coal and biomass co-combustion products *Environ Sci Technol* 45:2450-2456
418 doi:10.1021/es103361g

419 Świetlik R, Trojanowska M, Łożyńska M, Molik A (2014) Impact of solid fuel combustion
420 technology on valence speciation of chromium in fly ash *Fuel* 137:306-312
421 doi:10.1016/j.fuel.2014.08.010

422 Verbinnen B, Billen P, Van Coninckxloo M, Vandecasteele C (2013) Heating temperature
423 dependence of Cr(III) oxidation in the presence of alkali and alkaline earth salts and subsequent
424 Cr(VI) leaching behavior *Environ Sci Technol* 47:5858-5863 doi:10.1021/es4001455

425 Wang AY, Zhong GF, Xu GB, Liu ZX, Shen XB (2011) Effects of Chromium stress on
426 physiological characteristics and Chromium enrichment of Mustard rapeseed *Environmental*
427 *Science* 32:1717-1725

428 Wang WX, Hu HY, Zhu JJ, Yao H, XU MH, Qiao Y (2014) Study on the distribution and
429 leaching characteristics of Chromium in waste incineration bottom ash *Journal of Engineering*
430 *Thermophysics* 35:196-199

431 Wang XY, Huang YJ, Zhong ZP, Niu MM, Sun Y, Zhang Q (2012) Experimental study on
432 the influence of additives on heavy metal collection in waste incineration *Proceedings of the*
433 *CSEE* 32:15-21

434 Yang YL, Ma HR, Chen XP, Zhu C, Li XJ (2020a) Effect of incineration temperature on
435 chromium speciation in real chromium-rich tannery sludge under air atmosphere *Environ Res*
436 183:109159 doi:10.1016/j.envres.2020.109159

437 Yang Z, Wang CX, Li YM, Yang S, Zhang W, Li YL (2020b) Assessing the chromium
438 mobility in ashes through SiO₂-Al₂O₃-Fe₂O₃-CaO system: The role of composition
439 *Chemosphere* 257:127112 doi:10.1016/j.chemosphere.2020.127112
440

Figures

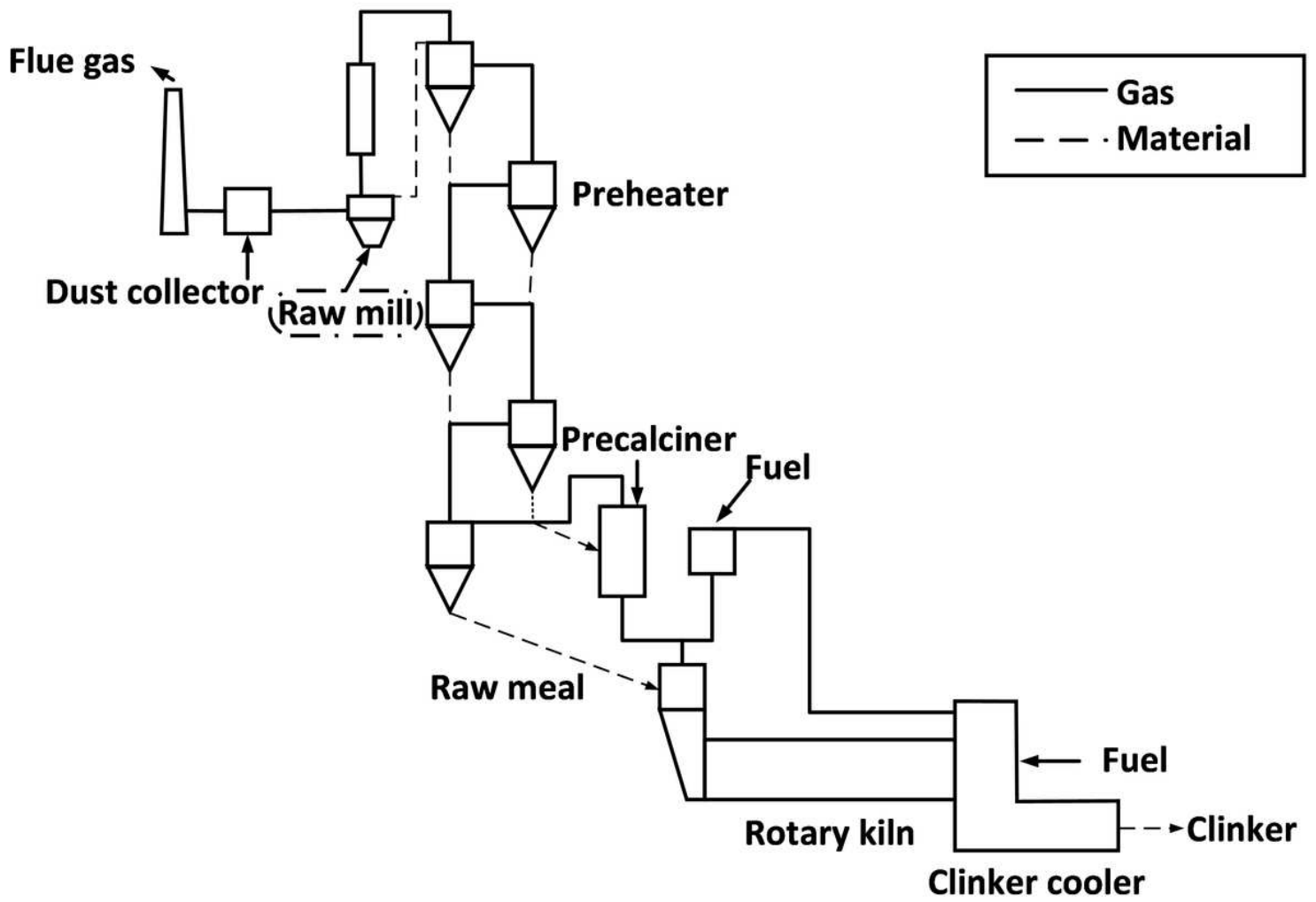


Figure 1

Schematic diagram of a cement kiln system

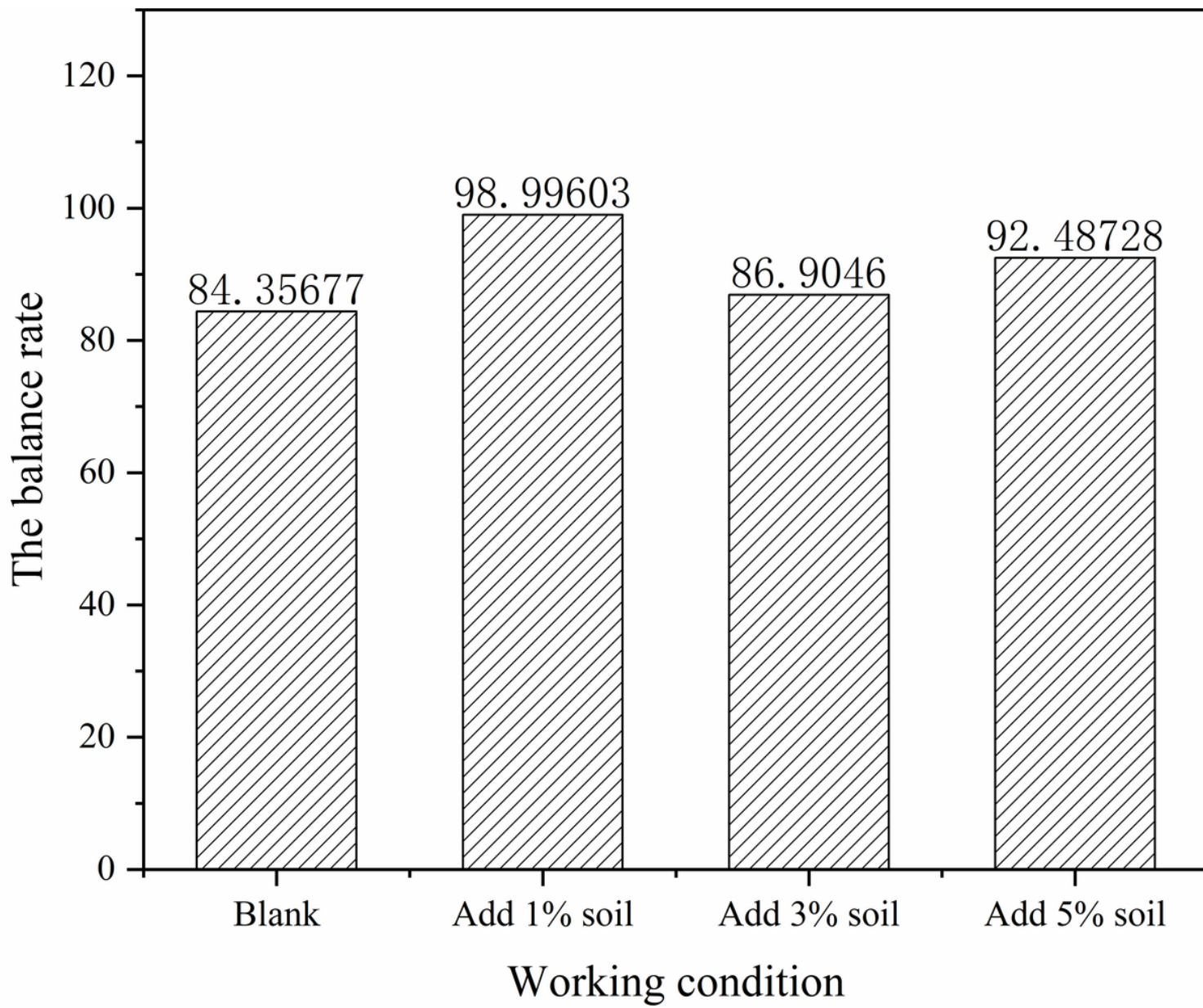


Figure 2

The mass balance value for Cr under different experimental conditions

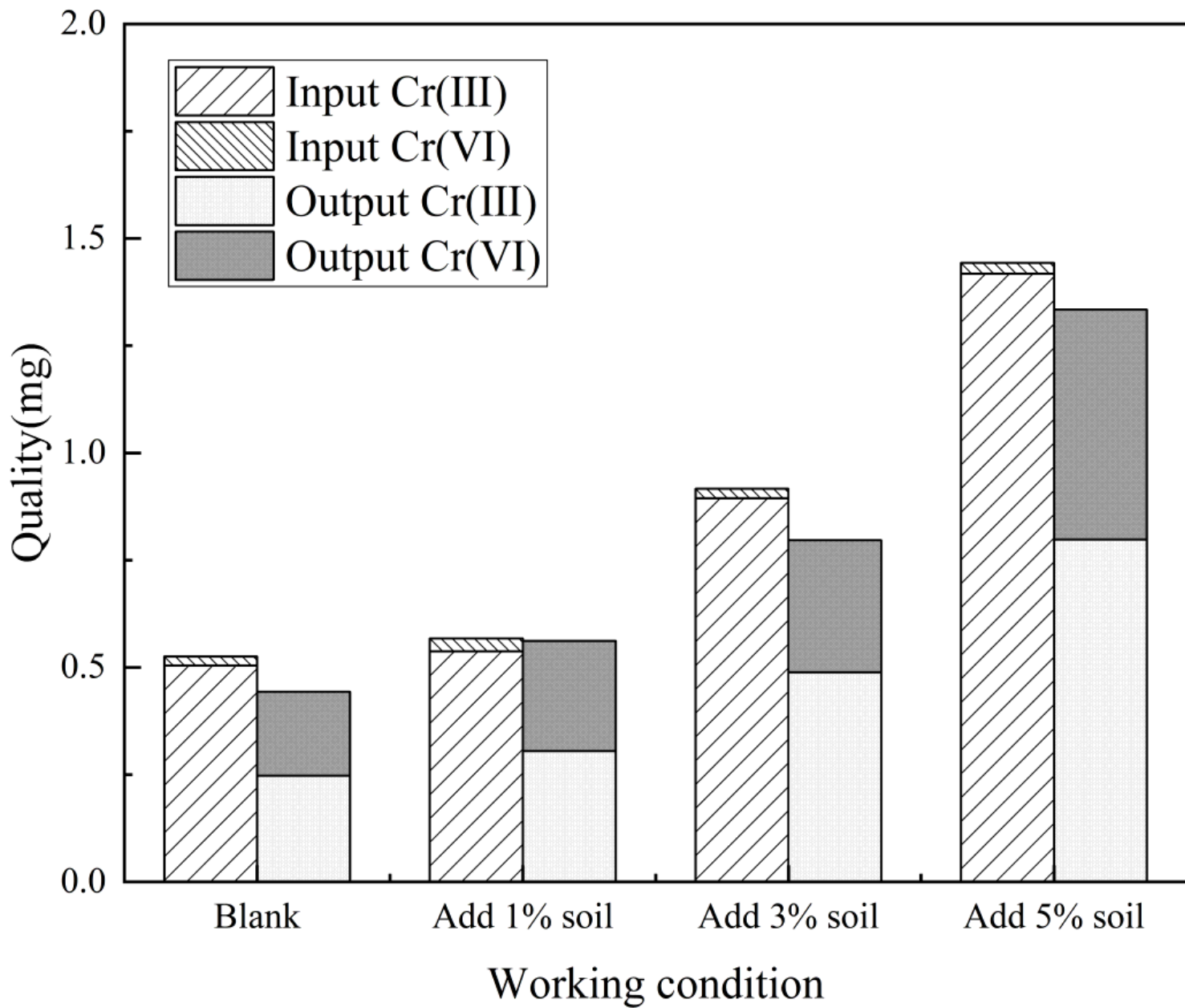


Figure 3

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

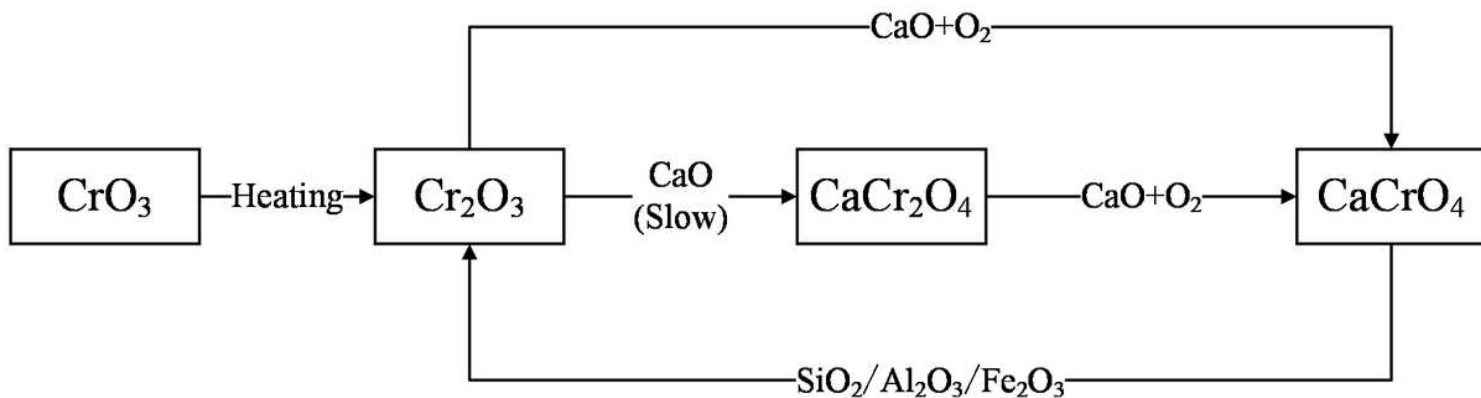


Figure 4

The possible reactions of Cr compounds in the calcination experiment

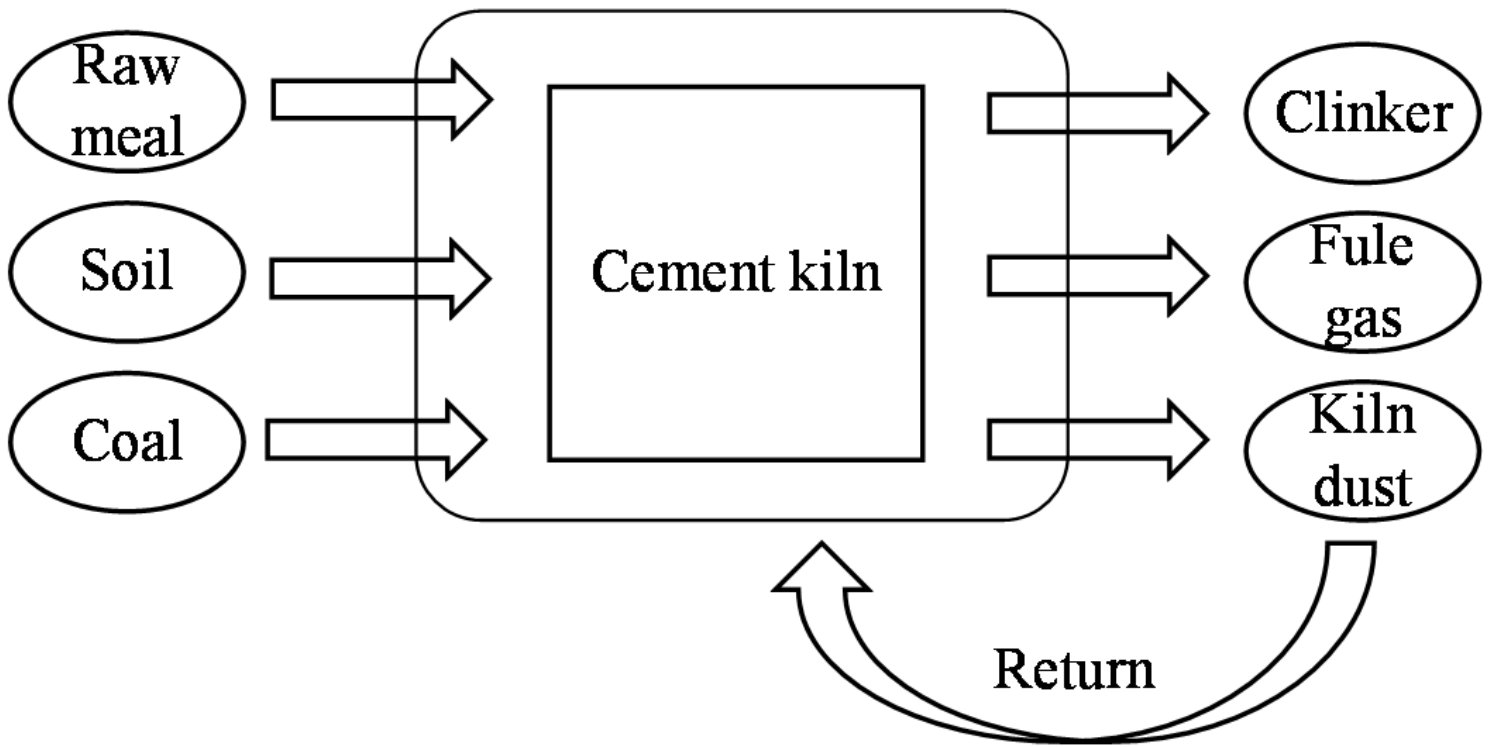


Figure 5

The material streams in the field-scale experiments

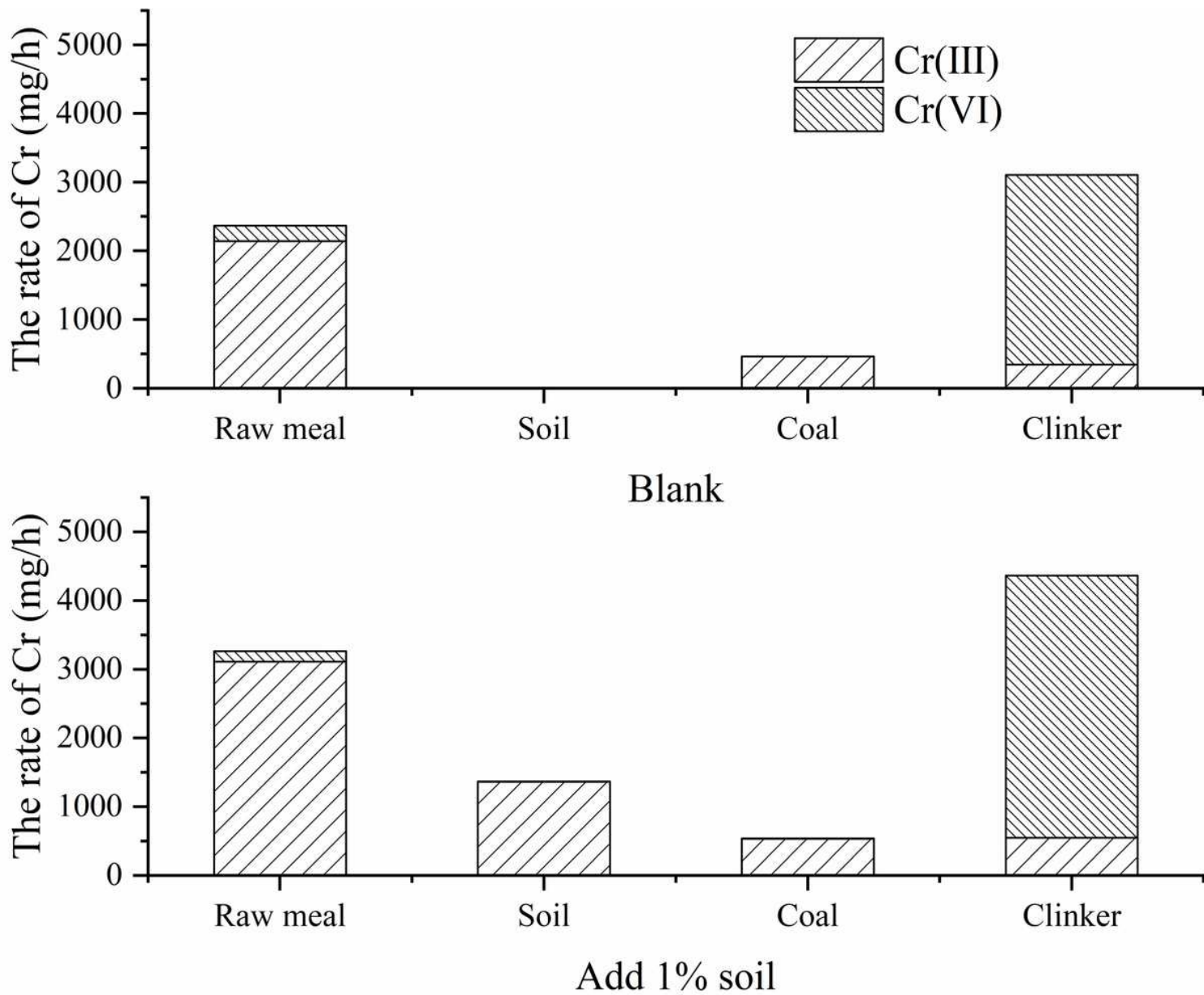


Figure 6

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