

# A Potential of Chromium (VI) Reduction in Commercial Clinker Burning

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## ABSTRACT

Clinker burning methods for chromium reduction were examined in commercial plants by varying the coarse-sized secondary fuel consumption and/or the injection point of the secondary fuels into the rotary kiln. Because the total chromium amount in the clinker fluctuated during the trial periods, the chromium reduction was evaluated by the total or soluble chromium (VI) to total chromium ratio. The soluble chromium (VI) ratio in clinker was intentionally made variable by kiln operations. In particular, the injection of the secondary fuels into clinker flow in the cooling zone of the rotary kiln reduced the ratio of soluble chromium (VI) in the clinker.

## 1. INTRODUCTION

Chromium in Portland cement clinker may be classified into the following three types [1, 2].

- (1) "Chromium" means chromium as an element, regardless of the oxidizing state, that is, including chromium (III), (VI), and so on. In this paper, we use "total chromium" to refer to this chromium in order to avoid misunderstanding.
- (2) "Chromium (VI)" represents 50 to 80% of the total chromium in clinker [2]. It will mainly be incorporated into belite [3, 4] as (IV) and (V) and will become (VI) in water by disproportionation [5]. In this paper, we use "total chromium (VI)" to refer to this chromium.
- (3) "Soluble chromium (VI)" is the portion of the total chromium (VI) that rapidly dissolves in water. It represents, on average, approximately 20% of the chromium in clinker [6]. It is believed to exist as chromate [7].

Because soluble chromium (VI) in wet cement may cause a skin disease called "cement eczema [8]," the amount of soluble chromium (VI) in cement is regulated by EU directive 2003/53/EC. The cement manufacturers who supply cementitious materials to Europe often add reducing agents, e.g. ferrous (II) sulfate, that reduce soluble chromium (VI) to chromium (III), converting it to chromium (III) hydroxide precipitation

under the basic condition of wet cement. Cement eczema is rarely found in Japan, but Japan does have many weak foundations that can often be stabilized by using cementitious materials. It is necessary to confirm that the amount of chromium (VI) leached from a stabilized soil does not exceed the "Environmental Standard."

Based on our experience, adding a reducing agent is the perfect countermeasure for the rapid leaching of chromium (VI), the cause of cement eczema. Ferrous (II) sulfate, however, generally produces an unsatisfactory result for the slower leaching of chromium (VI) from long-aged soil stabilized by cementitious materials because ferrous (II) ion has only a short life in the air. Japanese cement manufacturers are therefore decreasing the total chromium (VI) amount in cement by decreasing the total chromium amount in the raw materials. However, we do not regard this approach as rational, since it has no selective effect for chromium (VI) and always restricts raw material selection. Environmental obligations may become more severe in the future regardless of the region. New technology can thus be expected for manufacturing clinker containing no chromium (VI) or only a small amount.

Here, we focus on the fact that clinker burning consumes a large amount of fuel that has a reducing potential. There might be a burning condition under which the total and/or soluble chromium (VI) in the clinker is reduced. In this study, we examined the potential for chromium (VI) reduction in clinker burning. First, we examined chromium (VI) reduction in the laboratory, re-burning clinker in a carbon-monoxide gas stream. Second, based on this result, we attempted chromium (VI) reduction in commercial burning systems by varying the consumption of secondary fuels and/or the injection point. Finally, we confirmed the degradation of chromium (VI) leaching from soils stabilized by cementitious materials fabricated from the chromium-reduced clinker.

## 2. EXPERIMENTAL

### 2.1 Determination of Chromium

#### (1) Total chromium: Absolute calibration method

The clinker sample was totally dissolved with a hydrochloric acid aquasolution, and the chromium was then measured with an inductively coupled plasma atomic emission spectrometer.

#### (2) Total chromium (VI): Standard addition method

This method was introduced by Hanehara et al. [1, 2]. A specified amount of standard chromium (VI) was added to the clinker; for example, 0, 20 and 50 micrograms of standard chromium (VI) per gram of each divided clinker powder. Each clinker was next totally dissolved with (1+1)

hydrochloric acid, and the pH of the solution was adjusted to 6 to 9 by using (1+4) ammonium hydroxide aqueous solution. The solution was subsequently filtered by a filter paper and rinsed with distilled water. The determination was performed by diphenylcarbazide spectrophotometry, a well-known procedure for chromium (VI) determination.

(3) Soluble chromium (VI): Absolute calibration method

Japan Cement Association Standard (JCAS) I-51-1981, "Determination Method of Minor Elements in Cement," was employed to determine the soluble chromium (VI). The soluble chromium (VI) is extracted by a suspension with a water-to-sample mass ratio of 100 and a stirring time of 10 minutes. The determination was performed by diphenylcarbazide spectrophotometry. In this procedure, if the time between the sulfuric acid addition and the diphenylcarbazide addition is too long, subsequent coloring will often be weakened because a redox reaction between chromium (VI) and sulfide advances in acidic conditions. We therefore added diphenylcarbazide immediately after the sulfuric acid addition and determined the absorbance within one minute or less.

2.2 Clinker Re-burning in the Laboratory

Clinker manufactured at a commercial cement plant was used as the starting material. Clinker particles approximately 5 mm in diameter were collected by using a sieve. Table 1 presents the chemical composition of the tested clinker, as determined by Japanese Industrial Standard R 5202-1999, "Methods for Chemical Analysis of Cements," and JCAS I-01-1997, "Determination Method of Free Calcium Oxide." The amounts of total chromium, total chromium (VI) and soluble chromium (VI) were 73 mg/kg, 40 mg/kg and 5.9 mg/kg respectively.

Fig. 1 schematically illustrates the apparatus and the heating pattern of temperature and atmosphere. The collected clinker was injected into a tubular electric furnace kept at a specified heating temperature and streaming a nitrogen gas. Subsequently, a mixed gas of 2 volume % carbon monoxide and nitrogen was input for 30 min. After that, the sample clinker was removed from the heating zone and quenched in the pure nitrogen gas stream.

Table 1 Chemical composition of initial clinker (%)

LOI	insol.	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>														
0.45	0.30	22.35	5.23	2.33	65.57	0.84	1.33														
<table border="1"> <thead> <tr> <th>Na<sub>2</sub>O</th> <th>K<sub>2</sub>O</th> <th>TiO<sub>2</sub></th> <th>P<sub>2</sub>O<sub>5</sub></th> <th>MnO</th> <th>Cl</th> <th>f.CaO</th> </tr> </thead> <tbody> <tr> <td>0.38</td> <td>0.49</td> <td>0.26</td> <td>0.20</td> <td>0.07</td> <td>0.004</td> <td>0.50</td> </tr> </tbody> </table>								Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	Cl	f.CaO	0.38	0.49	0.26	0.20	0.07	0.004	0.50
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### 2.3 Clinker Burning in Commercial Plants

We tried burning the chromium (VI) reduced clinker in two commercial cement plants, as depicted in Fig. 2. Plant A was built in 1971 and has a single rotary kiln system equipped with a four-stage preheater and calciner. Plant B, built in 1969, has a couple of rotary kiln systems equipped with a five-stage preheater and calciner. The clinker production capacities are 0.54 Mtpy and 1.12 Mtpy.

In order to control the burning atmosphere, large amounts of secondary fuels were injected into the rotary kiln systems. In these trials, two injection points, corresponding to the calcining zone and the cooling zone of the rotary kiln, were examined, as illustrated in Fig. 3. The one corresponding

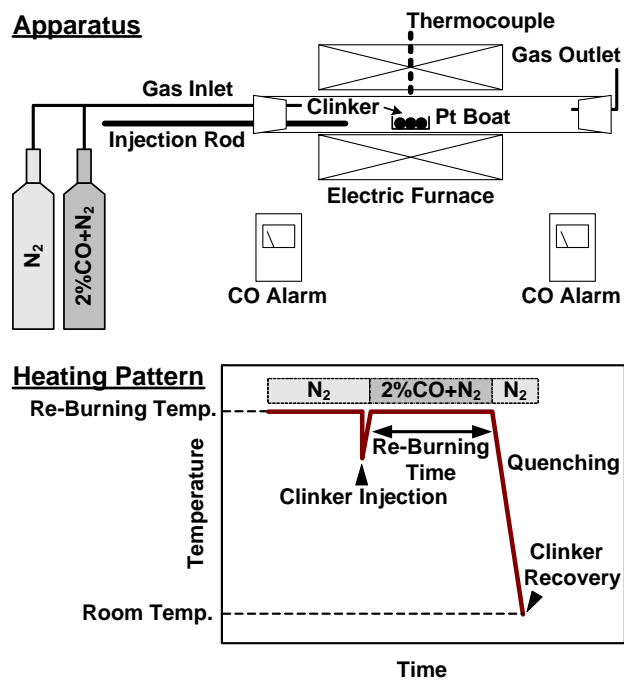


Fig. 1 Apparatus and heating pattern for the re-burning examination in laboratory.

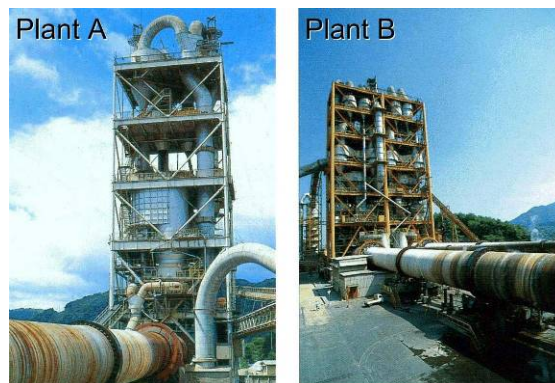


Fig. 2 Examined commercial plants; Mitsubishi Materials Corporation, Japan.

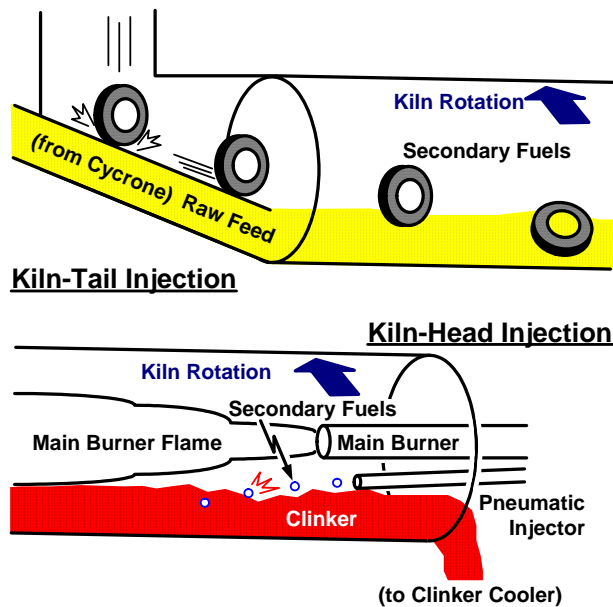


Fig. 3 Two methods of injecting the secondary fuels into the kiln system.

to the calcining zone was at the raw feed inlet of the rotary kiln, that is, underneath the final cyclone of the preheater. The other one, corresponding to the cooling zone, was at the clinker outlet of the rotary kiln, that is, adjacent to the main burner. We call these points “kiln-tail” and “kiln-head.” At the former injection point, waste tires were allowed to fall into the raw feed flow. For the latter, a mixture of coarse flammable waste (waste tire chips, waste plastics and waste wood chips) was pneumatically injected with a velocity of 60 m/s so that they directly impacted the clinker flow.

The trial conditions are listed in Table 2. Trials #1 and #2 were performed continuously in Plant A. The consumption of secondary fuels injected from the kiln-tail point was kept constant during each trial period. Trial #1 was the usual condition during those days. In Trial #2, we examined the

Table 2 Trial conditions in the commercial plants.

Trial	Plant	Secondary Fuels	Consumption	Injection Point
#1	A	Waste Tire	25 kg/t-cli.	Kiln-Tail
#2	A	Waste Tire	26 kg/t-cli.	Kiln-Tail
		Flammable Wastes (25mm)*	8 kg/t-cli.	Kiln-Head
#3	B	Waste Tire	Max.50 kg/t-cli.	Kiln-Tail
#4	B	Waste Tire	25 kg/t-cli.	Kiln-Tail
		Flammable Wastes (20mm)*	Max.18 kg/t-cli.	Kiln-Head

\*: A mixture of chipped waste tires, plastics and wood. The brackets indicate the maximum diameter.

potential of additional kiln-head injection. Trials #3 and #4 in Plant B were performed over several days as we varied the injection amount of the secondary fuels at the corresponding injection point. Through all the trials, the total fuel consumption for clinker burning was kept constant as long as the amount of free lime in the clinker did not increase. We did not use the calciners in these trials. The oxygen concentration of the exhaust gas from the preheater was targeted at 2.7 volume %, taking the qualities of the cement and exhaust gas into account. The clinker output of the examined kiln systems was approximately 90 tph in Trials #1 and #2 and 60tph in Trials #3 and #4.

2.4 Fabrication of Stabilized Soil and an Examination of the Leaching Test  
In the laboratory, cementitious soil-stabilizer was fabricated from sampled clinker, industrial gypsum, and anhydrite. Typical volcanic cohesive soils from the capital area of Japan, commonly stabilized by cementitious materials, were stabilized by 200 kg/m<sup>3</sup> of the soil-stabilizer.

A leaching test for the stabilized soil was performed according to Notification No. 46-1993, "Environmental Quality Standards for Soil Pollution," as stipulated by the Director General of the Environment Agency of Japan. An outline of this test is as follows. A suspension with a water to stabilized soil mass ratio of 10 is shaken for 6 h. The soil is then removed by filtration, and the concentration of leached chromium (VI) in the water is measured with the above-mentioned spectrophotometry using diphenylcarbazide. After shaking, clinker causes the test water to indicate a base solution. The sulfide in the clinker does not reduce the chromium (VI) during shaking. In addition, the Environmental Quality Standards generally require the concentration of leached chromium (VI) in the test water not to exceed 0.05 mg/dm<sup>3</sup>.

### 3. RESULTS AND DISCUSSION

#### 3.1 Reduction of Chromium (VI) in the Laboratory

Fig. 4(a) illustrates the relationship between the re-burning temperature and the amount of total or soluble chromium (VI). Both of the chromium (VI) amounts simultaneously decreased with re-burning temperatures of 700 °C or more. Re-burning at 1000 °C or more produced no detectable chromium (VI). At this temperature or higher, the sulfide amount in the clinker increased, as seen in Fig. 4(b).

Here, it is not easy to judge whether the sulfide formation was a cause or a result of the soluble chromium (VI) reduction since co-existing sulfide often interferes with a soluble chromium (VI) determination using diphenylcarbazide spectrophotometry. We believe, however, that the soluble chromium (VI) reduction by the re-burning was not merely an

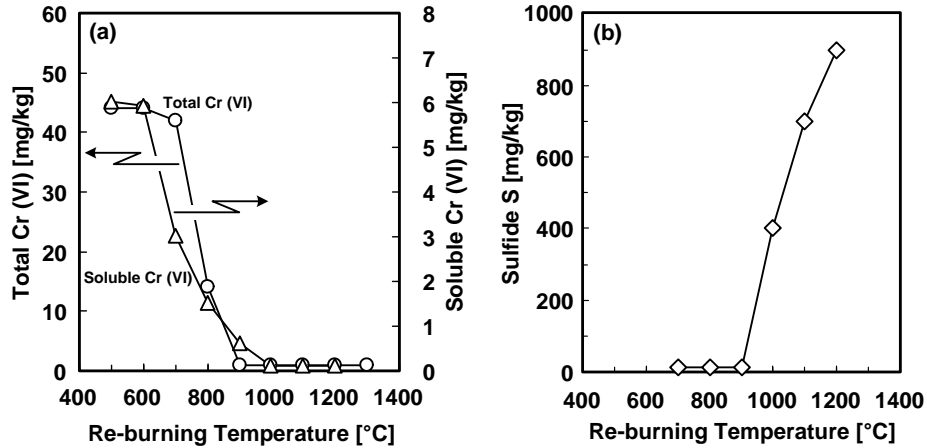


Fig. 4 Variations in the amount of chromium (VI), soluble chromium (VI) and sulfide as a function of re-burning temperature in a reducing atmosphere.

appearance but was actually in the clinker, and that the increase in the amount of sulfide was the result of a decrease in chromium (VI), because the total chromium (VI) amount, determined with the standard addition method to absolutely eliminate the sulfide interference, decreased under the same conditions.

A reducing atmosphere at 700 °C or higher will reduce the chromium (VI) amount in a commercial clinker. The amount of sulfide in the clinker might be usable as an indicator of a reducing atmosphere for clinker burning.

### 3.2 Reduction of Chromium (VI) in Commercial Plants

Based on the above results in the laboratory, we examined the chromium (VI) reduction in commercial plants, focusing on areas where the temperature was approximately 1000 °C. Here, the determination results for total or soluble chromium (VI) are expressed by ratios of the total or soluble chromium (VI) amount to the total amount of chromium, since each sampled clinker contained a different amount of elemental chromium.

Fig. 5 gives the hourly change in the ratios of total and soluble chromium (VI) in the sampled clinkers during Trials #1 and #2 in Plant A. As for the ratio of total chromium (VI), the difference between the averages of the ratio of each trial was very small. As a result, the difference between the averages of the ratio of total chromium (VI) was not able to be statistically confirmed by the t-test at a confidence level of 95% or greater. In contrast, the difference between the averages of the soluble chromium (VI) ratio was statistically confirmed by the t-test with a 99% or greater confidence probability. That is, the additional kiln-head injection of secondary fuels lowered the ratio of soluble chromium (VI) in clinker.

Pisters investigated the chromium amount in approximately 300 cements

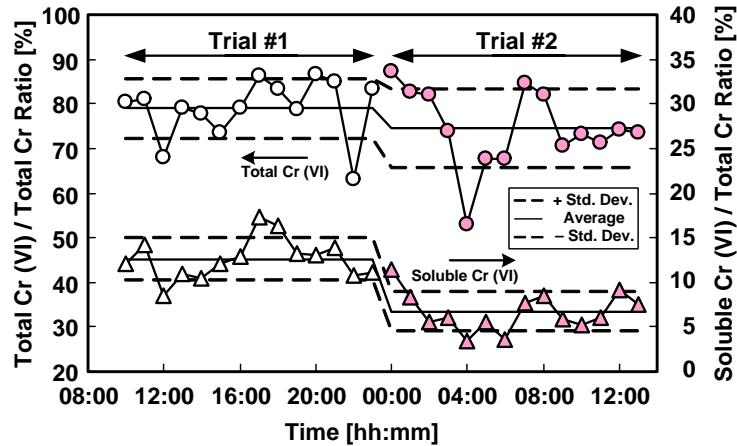


Fig. 5 Hourly change of the total and soluble chromium (VI) to chromium ratios in Trials #1 and #2.

and found that, on average, approximately 20% of the total chromium content exists as soluble chromium (VI) [6]. This relation is maintained to the present day, except for reducer-admixed cements. However, this is only true of the average. One, who knows that a constant amount of total chromium in clinker does not always give the same amount of soluble chromium in practice, would assume that this ratio might be variable by some intentional or un-intentional kiln operation. Our results in Plant A demonstrate the potential of this rather uncertain idea, that is, the amount of chromium (VI) in clinker and cement was made intentionally changeable by an operation focusing on the atmosphere of the burning process.

We confirmed the effect of secondary fuel injection on chromium reduction in Plant B. The results of Trials #3 and #4 are depicted in Fig. 6. Each plot indicates the result of a daily representative sample automatically collected with a sampling facility used for clinker inspection. In each trial, the ratio of soluble chromium (VI) clearly decreased with an increase in the secondary fuel consumption. In contrast, the decrease in the ratio of total chromium (VI) primarily corresponded to that of the ratio of soluble chromium (VI). We presume that there are a few essential effects of secondary fuel injection on the non-soluble chromium (VI). The soluble chromium will exist in the clinker matrix as a chromate [7]. The rest of the chromium (VI), that is, the non-

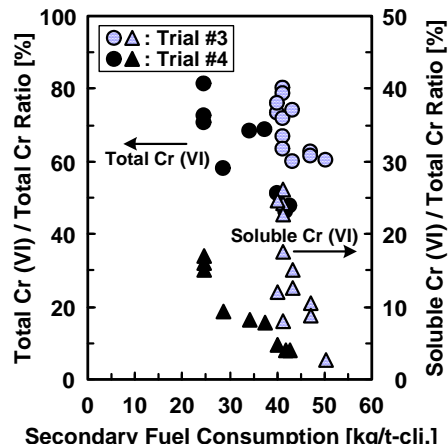


Fig. 6 Variations in the ratios of total and soluble chromium (VI) to chromium as a function of secondary fuels consumption in Trials #3 and #4.



soluble chromium (VI), will be incorporated into calcium silicates [3, 4]. As for the chromium reduction, the silicates will be less affected by the kiln atmosphere than the matrix [2]. Though the decrease in total chromium (VI) was not realized as we expected, we think that the obtained results involving the ratios of total and soluble chromium (VI) in commercial plants agree with the previous findings.

### 3.3 Mechanism of Chromium (VI) Reduction

In order to discuss the mechanisms of chromium reduction, we determined the soluble chromium amount in the separated core and shell of large clinkers (approximately 50mm in diameter) and in sieved clinkers. Fig. 7 illustrates the results for the separated core and shell of large clinkers burnt using the same secondary fuel consumption. A remarkable difference between Trials #3 and #4 was found in the ratios of the shell: the latter was smaller than the former. In contrast, for the cores, there was no difference between the trials. Next, the variations in the total and soluble chromium (VI) ratios as a function of the diameter of uncrushed clinker are plotted in Fig. 8. Clinker that had a smaller specific surface area, that is, a larger diameter, exhibited lower total and soluble chromium (VI) ratios in Trial #3, but there was no variation in the results of Trial #4. These relations present evidence of chromium oxidization from the clinker surface and the lack of oxidization on the cooling zone of the rotary kiln and/or the clinker cooler.

According to Fig. 6, kiln-tail injection, Trial #3, needed more secondary fuel than kiln-head injection, Trial #4, to obtain the same ratio of total or soluble chromium (VI). It should be noted that kiln-tail injection has no effect on these chromium (VI) ratios in the lower consumption ranges. In addition, with kiln-head injection, we sometimes observed flaming fuel

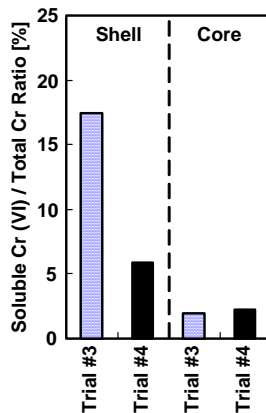


Fig. 7 Soluble chromium (VI) ratios in separated core and shell of large clinkers.

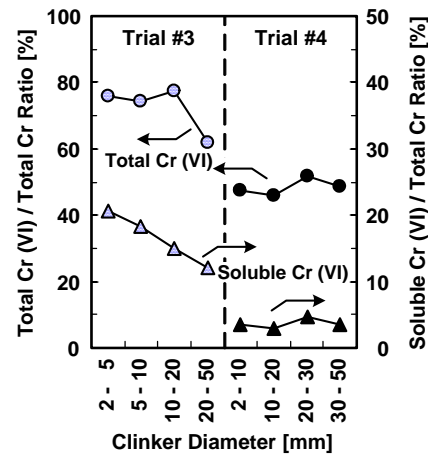


Fig. 8 Variations in the total and soluble chromium (VI) ratios as a function of the diameter of sampled clinkers.

particles on the clinker cooler.

Based on these facts, we summarize the chromium reduction in the kiln systems as follows. In the transition zone and the burning zone of a rotary kiln, chromium oxidation is restrained by the primary fuels from the main burner. Subsequently, chromium is oxidized by air from the clinker cooler in the cooling zone of the rotary kiln and/or the clinker cooler. The imperfectly flamed fuel particles that reach the kiln-head point, that is, the cooling zone, inhibit chromium oxidization in the cooling zone of the rotary kiln and/or the clinker cooler, thus realizing the chromium reduction.

### 3.4 Sulfide Amount as an Indicator of Reducing Atmosphere

Fig. 9 plots the variation in the sulfide amount as a function of the secondary fuel consumption for Trials #3 and #4. A small amount of secondary fuels never increased the sulfide amount, though the chromium (VI) amount was decreased in this range as seen in Fig. 6. This relation is similar to the results obtained in the laboratory as described in Section 3.1, that is, the temperature at which the sulfide amount increased was higher than that at which the chromium (VI) amount decreased. The sulfide amount should be regarded as a somewhat rough chromium reduction indicator.

Fig. 10 depicts the relationship between the sulfide amount and the chromium (VI) ratios. A negative correlation was found between the sulfide amount and the soluble chromium (VI) ratio in the trials. However, it seems that the same sulfide amount never produces the same ratio. The reason for this has not been studied, but detailed differences in kiln operations or facilities used during the trials may be considered causes. Furthermore, the sulfide amount and the total chromium (VI) is only weakly correlated.

For practical purposes, the sulfide amount should be used with restrictions as an indicator of a reducing atmosphere for the reduction of soluble chromium with certain conditions and facilities.

### 3.5 Chromium (VI) Leaching from Stabilized Soil

Leached chromium from soils stabilized by soil-stabilizers using selected clinkers from the trials was also evaluated to determine the leached chromium (VI) to chromium ratio.

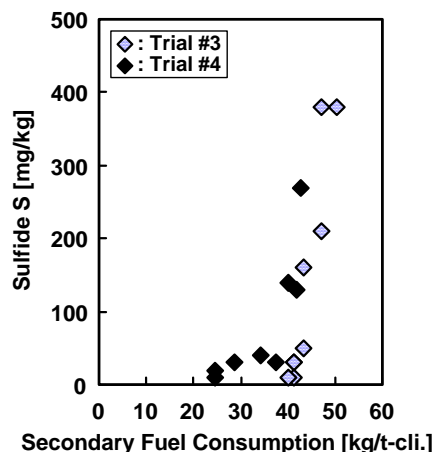


Fig. 9 Variation in the sulfide amount as a function of the secondary fuel consumption in Trials #3 and #4.

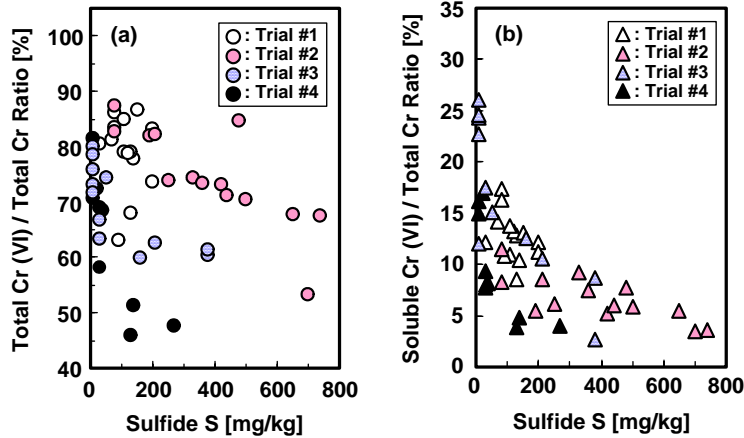


Fig. 10 Relationships between the sulfide amount and (a) the total chromium (VI) ratio and (b) the soluble chromium ratio.

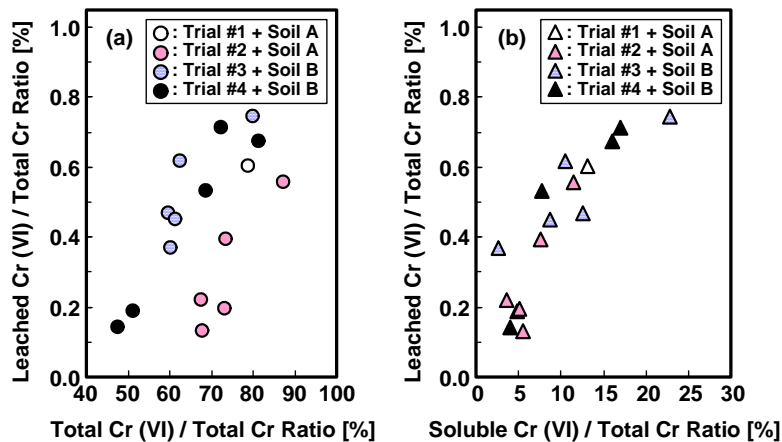


Fig. 11 Variation in the leached chromium (VI) to chromium ratio in stabilized soils as a function of (a) the chromium (VI) to chromium ratio and (b) the soluble chromium (VI) to chromium ratio in the used clinker. The leaching test was performed 28 days after solidification.

Fig. 11 illustrates the relationships between the leached chromium (VI) ratio from the stabilized soils and the chromium (VI) ratio or the soluble chromium (VI) ratio in the clinkers. The leached chromium (VI) ratio exhibited a decreasing trend with a decrease in the total or soluble chromium (VI) ratio. It was confirmed that chromium (VI) leaching from stabilized soil can be degraded by chromium reduction burning.

#### 4. SUMMARY

We examined chromium (VI) reduction in a laboratory and in commercial burning systems by controlling the burning atmosphere, aiming at a more rational and effective reduction method for chromium (VI) in Portland

cement clinker. The present study results are summarized as follows.

- (1) Chromium (VI) in clinker was able to be reduced at 700 °C or higher temperature in a reducing atmosphere.
- (2) The amount of chromium (VI) in clinker was intentionally made variable via kiln operation. Increasing coarse-sized secondary fuel consumption, injecting secondary fuels into the clinker flow in the cooling zone of rotary kiln, or both reduced chromium (VI) in commercial clinker.
- (3) Imperfectly flamed fuel particles that reached the cooling zone would decrease chromium oxidization in the cooling zone of a rotary kiln and/or clinker cooler, realizing a chromium reduction in the clinker.
- (4) The amount of sulfide in clinker is a somewhat rough chromium reduction indicator. It should be applied with restrictions to local conditions and facilities.
- (5) Chromium (VI) leaching from soils stabilized by using the clinker described in (2) was decreased.

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