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A method for the determination of total Cr(VI) in cement

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Abstract

Portland cement is often used to solidify wastes in order to prevent heavy metals from eluting, despite the fact that most cements contain traces of soluble Cr(VI). It was found that the leachability of Cr(VI) for the soil stabilized by cement was high in some cases, and the amount of Cr(VI) leached was larger than could be accounted for by the "soluble Cr(VI)" in the cement as determined by the standard method. Since the existing analytical standards only deal with "soluble Cr(VI)" in cement, we had to develop a new procedure to measure the total Cr(VI) in cement, making use of a complete dissolution in acid. Application of this method to several different ordinary Portland cements showed that 50–80% of their total Cr is typically extracted as Cr(VI). We also observed that the interstitial (calcium aluminate/ferrite) phase in Portland cement clinker usually contains higher concentrations of both Cr and Cr(VI) than the calcium silicate phases.

Keyword: Chromium

1. Introduction

Portland cement is frequently used to solidify wastes in order to prevent heavy metals from eluting, despite the fact that most cements contain traces of soluble Cr(VI). Concentrations of Cr(VI) in water and soil are regulated in many countries because it is highly toxic. The Cr(VI) in cement has become a serious issue, especially in relation to waste water from ready mixed concrete plants and as a possible cause of skin eczema in workers who have frequent contact with cement or fresh concrete.

Ten percent of the total cement produced in Japan is used as a soil stabilizer for construction. It was found that the leachability of Cr(VI) from soils stabilized by cement was high in some cases. In one case, with a "volcanic cohesive soil", it was estimated that the amount of leached Cr(VI) from the stabilized soil was much higher than that could be accounted for by the "soluble Cr(VI)" determined in the cement using the standard methods.[1]

The content of Cr(VI) in cement has been estimated as soluble Cr(VI). The analytical methods for soluble Cr(VI) have been widely published including Japan's JCAS I-51 and Germany's TRGS613. According to the JCAS I-51, the soluble Cr(VI) is determined by a kind of leaching test using deionized water, a high *L*/*S* (leachate to sample ratio = 100) and a short duration (=10 min). However, some part of Cr(VI), which is contained in the solid solution of the calcium silicate minerals, cannot be detected in this short leaching time.

It has been reported that Cr in cement exists as Cr(III), Cr(IV), Cr(V) and Cr(VI). Only Cr(III) and Cr(VI) are detected in the measurements because Cr(IV) and Cr(V) likely change to Cr(VI).[2] Sakurai estimated the valency of Cr in cement.[3] This valency was not determined by the direct measurement. The amount of Cr(VI) that was determined directly has not been reported.

In the recent PCA report[4] which summarized the determination methods for Cr(VI), Ellis and Freeman's method using Na_2SO_4 solution to leach the Cr(VI) from cement detected the highest Cr(VI) concentration.[5] However, this method left a large amount of insoluble residue, so it is hard to believe that all of Cr(VI) in the cement was dissolved.

In this report, a direct and precise method for the determination of total Cr(VI) is proposed, and the Cr(VI) content of several cements, as well as the distribution of total Cr and Cr(VI) in cement phases, were determined.

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Table 1
Chemical compositions of cement and clinker samples (mass%)

Sample		Ig. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Total
O-0	OPC	0.8	21.1	4.8	3.0	65.0	1.7	2.2	0.36	0.45	0.26	0.15	0.17	100.0
O-1	OPC	0.8	21.3	4.9	2.8	65.4	1.7	1.7	0.35	0.45	0.28	0.18	0.10	100.0
O-2	OPC	1.4	21.5	5.7	2.8	62.8	1.6	2.2	0.33	0.44	0.36	0.24	0.17	99.5
O-3	OPC	2.3	20.7	4.9	2.9	64.5	1.1	2.2	0.27	0.50	0.22	0.11	0.21	99.9
H-1	HPC	0.7	20.6	4.4	2.6	64.7	2.4	3.1	0.12	0.43	0.20	0.12	0.05	99.4
H-2	HPC	1.0	20.7	4.5	2.6	65.7	1.7	2.9	0.24	0.31	0.27	0.14	0.12	100.2
H-3	HPC	1.2	20.9	4.6	2.8	64.9	1.1	3.2	0.24	0.41	0.20	0.09	0.12	99.8
M-1	MC	0.7	22.6	4.0	4.4	63.1	2.2	1.8	0.10	0.38	0.16	0.09	0.04	99.6
M-2	MC	0.6	23.8	3.3	4.0	63.6	1.1	1.9	0.26	0.46	0.18	0.10	0.08	99.4
L-1	LC	1.0	25.2	3.2	3.5	62.7	0.9	2.4	0.27	0.36	0.15	0.05	0.11	99.8
C-L	5–10 mm[a]	0.2	22.2	5.1	3.3	66.1	1.2	0.6	0.29	0.39	0.25	0.11	0.17	99.9
	1.2–2.5 mm[a]	0.1	22.2	5.4	3.6	66.0	1.2	0.5	0.30	0.30	0.26	0.11	0.16	100.1
C-H	5–10 mm[a]	0.1	22.1	5.1	3.4	65.5	1.9	0.5	0.31	0.46	0.24	0.20	0.16	100.0
	1.2–2.5 mm[a]	0.1	22.0	5.4	3.6	65.4	2.0	0.3	0.32	0.34	0.26	0.21	0.17	100.1

[a] Grain size of clinker.

2. Experiment

2.1. *Determination of Cr(VI) in cement*

(1) Cement sample

The cement sample O-0 in Table 1 was used. Chemical compositions of major elements were determined by JIS R 5202-1999 and contents of Cr and soluble Cr(VI) were determined by CJAS I-51.

(2) Procedure of analysis

Main flow of the procedure is described in Fig. 1. The procedure consists of three parts as follows:

1. Dissolution of cement sample by HCl.
2. Elimination of interference matter in the solution.
3. Determination of Cr(VI) in the solution.

The dissolution is similar to the procedure for MgO or Fe_2O_3 in JIS R 5202. Diphenylcarbazide absorption spectroscopy was used for the determination of Cr(VI) in the final solution. In this method, Fe, Cu, V and Mo are regarded as interference materials in the solution.[6] As the content of Fe in cement is approximately 2%, it is necessary to eliminate Fe from the solution. The solution was neutralized by NH_4OH solution and precipitated $Fe(OH)_3$ was removed by filtration.

The preliminary experiment showed that the levels of Cu, V and Mo in the solution were considered low enough to ignore any influence on the determination of Cr(VI). Elimination of these elements was not executed.

Cr(VI) in the solution is easily reduced at a low pH and in the presence of a reducing agent. In order to make sure that Cr(VI) was not reduced during dissolution of the cement sample, an amount of Cr(VI) (0, 20 and 50 mg/kg cement) was added to the cement samples. The yield ratio of Cr(VI) in the dissolution was estimated by the slope of the regression line in Fig. 2. This was plotted to determine the stability of Cr oxidation states within the sample.

This procedure is regarded as the standard additional method described in JIS K 0115-1992 (general rules for molecular absorptiometric analysis). This method can compensate for the matrix effect in the analysis.

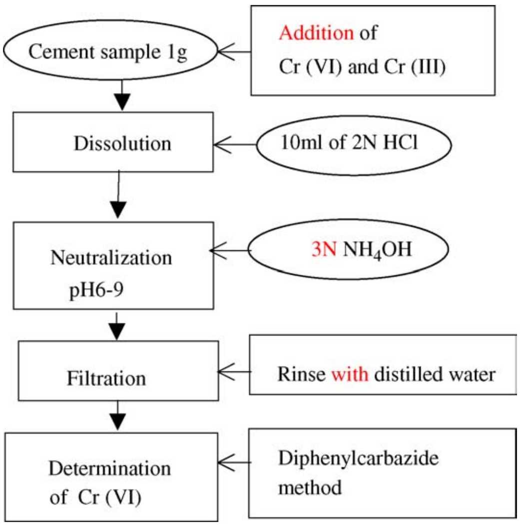

Fig. 1. Flow diagram of analysis procedure.

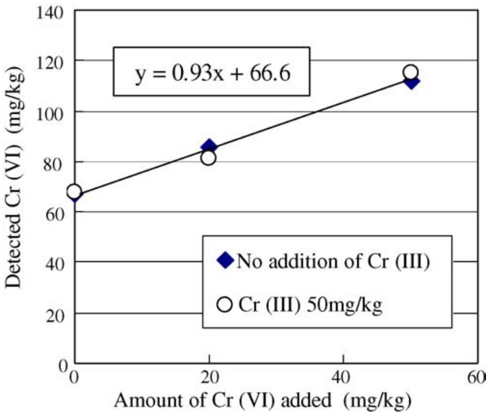

Fig. 2. Determined Cr(VI) concentration.

Table 2
Dosage condition of Cr and determined Cr(VI)

No.	Dosage of Cr (mg/kg cement)		Determined Cr(VI) (mg/kg cement)
	Cr(VI)	Cr(III)	
1	0	0	67.4
2	20	0	85.7
3	50	0	112.1
4	0	50	67.8
5	20	50	81.2
6	50	50	115.1

Additional amounts of Cr(III) (50 mg/kg cement) were also added to some of the cement samples. By comparing detected values of Cr(VI), it was confirmed that there was no redox reaction between Cr(III) and Cr(VI). This combination of added Cr(VI) and Cr(III) is shown in Table 2.

(3) Cr distribution in the analysis

The Cr distribution in the analytical procedure was investigated in samples No1 and No4 in Table 2. The precipitated $Fe(OH)_3$ containing Cr was dissolved by HCl solution and Cr in the solution was determined by ICP-AES. According to JIS K 0102-1995 (analytical methods for discharged water from plants), Cr contained in the precipitate was considered to be Cr(III) which was co-precipitated with $Fe(OH)_3$ as $Cr(OH)_3$. For this reason, Cr in the final solution is considered to be only Cr(VI). Cr(VI) in the final solution can be determined by ICP-AES or atomic absorption spectrometry.

2.2. *Evaluation of Cr(VI) in cement*

(1) Contents of Cr(VI) in cement samples

Cr(VI) levels in the four kinds of cement (OPC; ordinary Portland cement, HPC; high early Portland cement, MC; moderate heat Portland cement and LC; low heat Portland cement), shown in Table 1, were determined by the analytical method described in Section 2.1 (2). The chemical compositions of the cement samples determined by JIS R 5202-1999 are shown in Table 1. Content of Cr and soluble Cr(VI) were also determined by CJAS I-51.

OPC may contain ground blast furnace slag. Blast furnace slag contains S^{-2} (sulfide compound). Therefore, amount of S^{-2} represents the content of slag. Inorganic admixture, such as slag, content is regulated to be less than 5% in OPC in Japan. Amount of S^{2-} was determined by JIS R 5202-1999.

(2) Cr distribution in cement

Two lots of OPC clinker, shown in Table 1, were examined. One had a low concentration of total Cr (C-L) and the other a high concentration (C-H). Clinker samples were separated into two grain sizes: 5–10 mm and 1.2–2.5 mm. The chemical compositions of C-L and C-H are shown in Table 1. The calcium silicate phase and the interstitial phase in the clinker samples were extracted by the KOH-saccharose extraction method and the salicylic acid–ethanol extraction method, respectively. Cr in the two phases was determined by CJAS I-51 and the content of Cr(VI) in the calcium silicate phase was determined by the method described in Section 2.1 (2).

Cr(VI) in the interstitial phase could not be determined because the yield ratio of the analysis was low in the preliminary experiment. It was supposed that some reducing materials remained from the procedure of salicylic acid–ethanol extraction method.

3. Results and discussion

3.1. *Determination of Cr(VI) in cement sample*

(1) Yield ratio of Cr(VI) in the analysis procedure

Determined content of Cr(VI) in samples which received addition of 0, 20 or 50 mg/kg cement of Cr(VI) and 0 or 50 mg/kg cement of Cr(III) are shown in Table 2 and plotted in Fig. 2. The *X*-axis in the figure represents Cr(VI) added and *Y*-axis represents amount of Cr(VI) in the cement sample which was estimated by the determined value.

The regression lines from determined Cr(VI) and the formula of the line are described in Fig. 2. The yield ratio of Cr(VI) is sufficiently high because of the slope of the line. It is considered that Cr(VI) in the samples was not reduced in this analysis procedure.

When samples with Cr(III) added and those without were compared, it was concluded that Cr(III) in the samples did not turn into Cr(VI).

The contents of total Cr, soluble Cr(VI) and determined Cr(VI) which was estimated by the standard additional method are described in Table 3. It was found that the content of Cr(VI) obtained with this method is about 70% of the total Cr in cement and eight times larger than the soluble Cr(VI). This result explains the concentration of Cr(VI) in the leachate from the leaching test using the stabilized soil.

(2) Cr distribution in the analysis procedure

The contents of Cr(VI) in the final sample solution and Cr(III) in the precipitation were determined and are shown in Table 4 as the concentration in the cement. Recovered Cr level in No1 and No4 were approximately 92%. Using the content of Cr(VI) by the standard additional method, the yield ratio was estimated at 97%. From this result, almost all Cr in cement sample can be

Table 3
Content of total Cr, soluble Cr(VI) and Cr(VI) in the OPC sample (mg/kg)

Sample	Total Cr	Soluble Cr(VI)	Cr(VI)[a]
O-0	101.3	9.3	72

[a] Estimated by standard additional method.

Table 4
Dosage condition, distribution and recovery ratio of Cr

Sample	Dosage (mg/kg)		Determined value (mg/kg)			Recovery ratio (%)
	Cr(VI)	Cr(III)	Cr(VI) (A)	Cr(III) (B)	Cr (A) + (B)	
O-0	0	0	67.4[a]	26.2	93.6	92.4
	0	50	67.8[a]	69.2	137.0	90.7[b]

[a] Determined by analytical curve method.
[b] Based on content of total Cr + dosage of Cr(III).

Table 5
Content of Cr and S^{2-} in cement samples and result of Cr(VI) analysis

No.	Type of cement	Total Cr (mg/kg)	Cr(VI) (mg/kg)	Conversion ratio (%)	Slope value of regression line	Content of S^{2-} (mass%)
O-1	OPC	116.5	62	53	0.81	0.004
O-2	OPC	96.5	–	–	–	0.051
O-3	OPC	123.1	96	78	0.89	0.003
H-1	HPC	72.5	39	54	0.85	[a]
H-2	HPC	118.9	81	68	0.89	[a]
H-3	HPC	109.2	82	75	0.84	[a]
M-1	MC	68.7	62	90	0.93	[a]
M-2	MC	128.1	101	79	0.91	[a]
L-1	LC	108.6	99	91	0.91	[a]

(–) Impossible to calculate.
[a] Unmeasured.

Table 6
Chemical compositions of extracted calcium silicate phase (mass%)

Sample	Grain size (mm)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Total
C-L	5–10	26.1	1.2	0.8	68.9	2.0	0.3	0.17	0.21	0.15	0.23	0.10	100.2
	1.2–2.5	26.6	1.0	0.6	69.6	1.2	0.3	0.15	0.21	0.16	0.13	0.09	100.0
C-H	5–10	26.7	0.9	0.5	69.8	1.2	0.3	0.14	0.15	0.15	0.13	0.08	100.1
	1.2–2.5	25.3	1.6	1.1	68.7	2.2	0.3	0.18	0.21	0.18	0.24	0.11	100.1

recovered as Cr(VI) in the final solution and Cr(III) in the precipitate by this method.

3.2. *Cr(VI) in cement samples*

(1) Content of Cr(VI) in four kinds of Portland cement

In four kinds of cement, the amount of total Cr, determined Cr(VI), conversion ratio to Cr(VI) and the slopes of the regression lines are shown in Table 5. For OPC samples, determined S^{2-} values are also shown in the table. Conversion ratio to Cr(VI) was calculated using the following equation: conversion ratio (%) = Cr(VI)/Cr × 100.

In OPC samples which contained a large amount of S^{2-} such as O-2, the slope of regression lines were much smaller than 1 and the content of Cr(VI) could not be determined. This was because Cr(VI) was reduced during the analytical process, particularly during the dissolving process which was carried out in low pH conditions. Other OPC samples had high slopes of the regression line nearly equal to 1 and almost all Cr(VI) was recovered. HPC, MC and LC are not permitted to contain any admixture such as ground blast furnace slag. Recovery ratio of Cr(VI) in these cements were sufficiently high.

Conversion ratios to Cr(VI) were 50–80% in OPC and HPC, and 80–90% in MC and LC.

As MC and LC have the small amount of Al and low SM (silica modulus), the amount of the interstitial phase in the clinker is small. This characteristic generates the small amount of liquid phase in the burning process of a rotary kiln. The grain size of MC and LC clinker are generally much smaller than that of OPC and HPC. MC and LC clinker have a bigger specific surface area. Furthermore, the pore of the MC and LC clinker is difficult to fill with melt during sintering. In the zone of high O_2 concentration by secondary air of a rotary kiln, near kiln burner, clinker grains consisting mainly of calcium silicate phase can be affected by the O_2.

Table 7
Weight ratio of extracted calcium silicate phase in clinker samples

Sample	Grain size of clinker (mm)	Weight ratio (%)
C-L	5–10	79
	1.2–2.5	78
C-H	5–10	78
	1.2–2.5	78

Table 8
Content of total Cr and Cr(VI) in clinker and calcium silicate phase

Sample	Grain size of clinker (mm)	Total Cr (mg/kg)		Cr(VI) (mg/kg)	
		Clinker	C-S phase[a]	Clinker	C-S phase
C-L	5–10	77	63	68	48
	1.2–2.5	76	63	55	39
C-H	5–10	230	171	165	92
	1.2–2.5	215	182	158	101

[a] C-S phase: calcium silicate phase.

Table 9
Cr distribution in calcium silicate phase and interstitial phase in clinker

Sample	Grain size of clinker (mm)	Cr (mg/kg)			Cr in clinker base (mg/kg clinker)		Cr distribution (%)	
		Clinker (A)	C-S phase	Interstitial phase[a]	C-S phase[b] (B)	Interstitial phase (C) = (A) − (B)	C-S phase	Interstitial phase
C-L	5–10	77	63	130	50	27	65	35
	1.2–2.5	76	63	119	49	26	65	35
C-H	5–10	230	171	439	133	97	58	42
	1.2–2.5	215	182	332	142	73	66	34

[a] Calculated by (C)/I (I: amount of interstitial phase in clinker).

[b] Calculated by (Cr content in C-S phase) × (amount of C-S phase).

The atmosphere in a rotary kiln has an influence on the oxidization number and distribution of Fe in cement minerals and consequently on the colors of cement. The clinker sintered in the oxidizing atmosphere has a dark color.[7] Ground powder of MC or LC clinker, which has almost the same fineness as OPC powder, generally has a darker color than OPC powder because of the influence of O_2 mentioned above. The conversion ratio to Cr(VI) is also influenced during sintering by an oxidizing condition. The ratios in MC and LC become bigger than those in OPC and HPC.

(2) Distribution of Cr(VI) and the conversion ratio to Cr(VI) in clinker minerals

The chemical composition and the amount of the calcium silicate phase extracted by the saccharose–KOH method are shown in Table 6 and Table 7. Though the residue of the extraction contained Al_2O_3 and Fe_2O_3, it was confirmed by X-ray diffractometry (XRD) that the residues did not contain any interstitial phase such as C_3A phase and C_4AF phase. The amount of the calcium silicate phase, based on the extraction, was about 78% of the clinker. The content of Cr and Cr(VI) in the clinker and the calcium silicate phase are shown in Table 8. The distribution of Cr and Cr(VI) in each phase was calculated by the amount of the calcium silicate phase and the contents of Cr and Cr(VI) in the clinker and the calcium silicate phase.

The distribution of Cr and Cr(VI) is shown in Tables 9 and 10, respectively. Though the interstitial phase only accounted for 22% of the clinker by mass, Cr in the interstitial phase was about 60% of the total Cr in whole clinker. It was estimated that the concentration of Cr in the interstitial phase was about twice as high as in the combined calcium silicate phases (alite + belite).

As for Cr(VI), this tendency was stronger. The concentration of Cr(VI) in the interstitial phase was about three times as high as in the combined calcium silicate phases. The conversion ratio to Cr(VI) was 90% in the

Table 10
Cr(VI) distribution in calcium silicate phase and interstitial phase in clinker

Sample	Grain size of clinker (mm)	Cr(VI) (mg/kg)			Cr(VI) in clinker base (mg/kg clinker)		Cr(VI) distribution (%)	
		Clinker (A)	C-S phase	Interstitial phase[a]	C-S phase[b] (B)	Interstitial phase (C) = (A) − (B)	C-S phase	Interstitial phase
C-L	5–10	68	48 (76)	143 (110)	38	30	56	44
	1.2–2.5	55	39 (62)	112 (94)	30	25	55	45
C-H	5–10	165	92 (55)	424 (97)	72	93	43	57
	1.2–2.5	158	101 (55)	360 (92)	79	79	50	50

Values in parenthesis indicate conversion ratio (Cr(VI)/T-Cr) (%).

[a] Calculated by (C)/I (I: amount of interstitial phase in clinker).

[b] Calculated by (Cr content in C-S phase) × (amount of C-S phase).

interstitial phase, and 55–76% in the calcium silicate phase. It is considered that Cr in the interstitial phase reacts with O_2 more easily than the calcium silicate phase in a kiln. This is accounted for by the following reasons: the calcium silicate phase is a solid phase even at a high temperature and is covered by the liquid phase that turns to the interstitial phase. The calcium silicate phase is not influenced by O_2 directly. Moreover, the diffusion coefficient of O_2 in liquid phase is higher than that in a solid.

The grain size of the clinker did not make any difference in neither the amount of Cr nor the conversion ratio to Cr(VI). It is considered that the chemical composition of clinker has larger influence on the conversion ratio than the grain size.

4. Conclusion

The precise determination method of Cr(VI) in cement and clinker was developed based on the fully dissolving treatment in an acid solution. According to this method, it was estimated that the content of Cr(VI) in cement samples is about 50–90% of the total Cr. In an OPC sample, the amount of Cr(VI) was eight times larger than the soluble Cr(VI).

The distribution of Cr and Cr(VI) in the calcium silicate phase and the interstitial phase was investigate. The interstitial phase had higher concentrations of Cr and Cr(VI) than the calcium silicate phase. The conversion ratio to Cr(VI) in the interstitial phase was estimated at more than 90%, while in the calcium silicate phase it was estimated to be up to 76%. This is because the interstitial phase reacts with O_2 more easily in a kiln than the calcium silicate phase.

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