

An NMR, XRD and EDS study of solidification/stabilization of chromium with Portland cement and C_3S

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Abstract

Solidification/stabilization (S/S) of chromium with Portland cement type I and tricalcium silicate (C_3S) was investigated by using the ^{29}Si solid state magic angle spinning/nuclear magnetic resonance (^{29}Si MAS/NMR), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). The present study confirms that chromium nitrate can increase the extent of C_3S hydration. It also confirms that the chromium ion is easily incorporated into the C_3S paste and hydrated Portland cement, and that it affects the characteristics of the hydration processes and their hydration products. The formation of calcium chromium silicate ($CaCrSi_4O_{10}$), calcium chromium oxide hydrate ($CaCrO_4 \cdot 2H_2O$), and calcium dichromate ($CaCr_2O_7$) during the hydration of chromium-doped C_3S indicates the probable substitution of chromium for silicon in the calcium silicate hydrate (C–S–H) and the interaction between Cr and Si. Furthermore, formation of $CaCrSi_4O_{10}$, aluminum chromium oxide hydroxide hydrate ($Al(OH)CrO_4 \cdot H_2O$), aluminum chromium oxide hydroxide ($Al_2(OH)_4CrO_4$), and $CaCr_2O_7$ during the hydration of chromium-doped cement reveals not only the probable substitution of chromium for silicon in the calcium silicate hydrate (C–S–H) but also the interaction among Cr, Si and Al. Apparently, the chromium ion (Cr^{3+}) may also be stabilized and solidified through these mechanisms in addition to those proposed by other investigators. © 1997 Elsevier Science B.V.

Keywords: NMR; XRD; EDS; Chromium; Solidification/stabilization; C_3S ; Cement

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1. Introduction

Portland cement has various chemical features that count for its widespread use in toxic waste immobilization processes [1]: it is tolerant of wet material, it is not flammable and it is durable in the natural environment. Moreover, it can be used as an activator for other potentially cementitious materials such as glassy slag or fly ash. Solidification/stabilization (S/S) refers to techniques that stabilize and/or solidify the waste. With the implementation of the Resource Conservation and Recovery Act (RCRA), 1976 of the USA, S/S processes have become essential for treating hazardous substances that are not eliminated by resource recovery, incineration and/or source reduction [2]. The S/S processes based on cement and other pozzolanic materials are being increasingly used for remedying sites contaminated by heavy metals, inorganic chemicals and organic compounds. It is specifically cited under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA; 40 CFR 300) of the USA as a method to be considered for remedying releases from contaminated soils and sediments.

The complexity of an S/S process results from the combined effects of dynamic cement chemistry with solution equilibria and kinetic processes coupled with the surface and near-surface phenomena [3]. The interaction between the cement and pollutants need to be determined and incorporated into detailed models of the process. Knowledge of the adsorption, precipitation, and other surface processes, however, is far from complete in dynamically reacting systems such as hydrating and setting cement. To gain insights into the mechanisms of the S/S processes, it requires extensive application of modern analytical techniques. It has been reported [3] that surface techniques, such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and Ion scattering spectrometry (ISS), bulk characterization techniques, such as X-ray diffraction (XRD), Energy dispersive spectroscopy (EDS) and Scanning electron microscopy (SEM), and optical spectroscopies, such as Fourier transform infrared (FTIR) and solid state magic angle spinning/nuclear magnetic resonance (MAS/NMR), can be effective in unveiling the chemistry of solidification, and lead to better understanding of its mechanisms. Note that each characterization method with its own set of limitations generally cannot delineate complex heterogeneous systems. A group of carefully selected characterization tools is needed.

XRD is an excellent tool to study the changes in crystallinity and appearance or disappearance of phases [4]. Any physical and chemical changes in cement caused by the addition of chromium-containing compounds can be characterized by comparing the XRD composite patterns that can be identified by the Joint Committee on Powder Diffraction Standards (JCPDS). The resolution limitation of the X-ray information, however, is that it is not always possible to determine whether waste metals are replacing other ions in certain cement phases or precipitating out as inclusions [1]. It is desirable to resort to EDS to identify materials of different compositions.

High resolution solid state ^{29}Si NMR techniques that can provide molecular information have been successfully applied to the characterization of the hydration products of Portland cement [5–8]. The chemical shift of ^{29}Si nuclei in various silica materials is dependent on the nature of the X group in Si–O–X units [7]. The orthosilicate unit

SiO_4^{4-} (Q^0) in Portland cement reacts with water to give silicate polymers. The chemical shifts of the major components in hydrated cement have been designated as Q^1 for terminal SiO_3^{3-} , Q^2 for internal SiO_2^{2-} , Q^3 for branching SiO^- , and Q^4 for cross-linking unit $\text{Si}(\text{OSi})_4$. Recently, numerous studies have been carried out on the mechanisms of cement hydration by the modern techniques, especially by means of MAS/NMR, which can provide useful structural information on silicon bonding [9–11]. In the work of Justnes et al. [11], they suggested that the degree (in terms of percentage) of hydration of cement clinker (C_3S and C_2S), α , be determined by the following:

$$\alpha = 100 - [I(Q^0)/I^0(Q^0)] \times 100 \quad (1)$$

where $I(Q^0)$ and $I^0(Q^0)$ represent the integral intensity of hydrated cement paste and cement powder, respectively, at a signal of -70 ppm (Q^0). Furthermore, they have defined the average length (in terms of the number of Si) of linear polysilicate anions in C–S–H gel, P_{Si} , as follows:

$$P_{\text{Si}} = 2[I(Q^1) + I(Q^2)]/I(Q^1) \quad (2)$$

where $I(Q^1)$ and $I(Q^2)$ are the integral intensity at -80 ppm (Q^1) and -87 ppm (Q^2).

Solidification/stabilization of chromium with cement has been investigated [12–18]. In the works of Bishop [12] and Shively et al. [13], they suggested the incorporation of Cr into the hydrated Portland cement and C_3S . Tashiro and Kawaguchi [14] and Tashiro et al. [15] reported that 10% or more of Cr_2O_3 (Cr^{3+}) could enter into solid solution with C–S–H. They suggested that Cr^{3+} substitute both Ca^{2+} and Si^{4+} , i.e., $2\text{Cr}^{3+} = \text{Ca}^{2+} + \text{Si}^{4+}$. Ivey et al. [16], however, suggested that the charge imbalance due to the substitute of Si^{4+} with Cr^{3+} be offset by the presence of other ions, e.g., by a H^+ or a hydrated H_3O^+ . In the work of Mollah et al. [17], they applied FTIR, SEM, and EDS to investigate S/S of chromium using Portland cement type V and type IP. They confirmed the dispersion of chromium below the surface of the ordinary Portland cement (OPC) matrix and chemical interaction with C–S–H through EDS and FTIR examinations of Cr–OPC systems. However, no speculation as to the mechanism of Cr incorporation into the C–S–H was made. Kindness et al. [18] combined pore fluid extraction, XRD, EDX, EM, SEM, and TEM/STEM techniques to investigate the immobilization mechanism of chromium in cement matrices. They concluded that Cr could be substituted for Al in most of the calcium aluminate hydrates; the Cr analogues were $\text{Ca}_2\text{Cr}(\text{OH})_7 \cdot 3\text{H}_2\text{O}$, $\text{Ca}_2\text{Cr}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$, and $\text{Ca}_2\text{Cr}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$. They also confirmed that Cr was widely dispersed throughout all the hydrates in the 39,000 ppm spiked OPC samples and in particular those containing Ca, Al, and SO_4 .

Portland cement is a mixture of four principal compounds: C_3S (Ca_3SiO_5) 50–70 wt.%; C_2S (Ca_2SiO_4) 20–30 wt.%; C_3A ($\text{Ca}_3\text{Al}_2\text{O}_6$) 5–12 wt.%; and C_4AF ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$) 5–12 wt.%. To gain better insights into the mechanisms of S/S of chromium with cement, it is desirable to separately investigate the mechanisms of S/S of chromium with its major compounds. The present study explores the mechanisms of immobilization involved in S/S of chromium with Portland cement and C_3S by using NMR, XRD and EDS.

2. Materials and methods

Portland cement type I (ordinary Portland cement, or OPC in short) and C_3S were used as the binding agents in this study. Their chemical compositions are listed in Table 1. A chromium solution was prepared by dissolving 200 g of an analytical grade of chromium nitrate nonahydrate, $Cr(NO_3)_3 \cdot 9H_2O$, in 1000 g of deionized water; it contained approximately 21,100 ppm of Cr^{3+} . This provided the source of chromium.

Samples were prepared by blending the chromium nitrate nonahydrate and water with Portland cement or C_3S , at different temperatures ($75^\circ C$ for Portland cement, $50^\circ C$ for C_3S) and stirring thoroughly until essentially homogenized. These samples were then stored in a sealed container under a relative humidity of 92% and a temperature of $25^\circ C$ for curing until testing at the age of 1, 3, 7, 14 and 28 days. The S/S treatment was terminated by quenching the samples with acetone and drying under vacuum at room temperature. The dried samples were then ground into powder prior to testing. Every sample prepared had a water-to-solid weight ratio (w/s) of 0.4. This is equivalent that each sample contains approximately 60,000 ppm of Cr^{3+} with a TCLP of 3000 mg/l before the reaction.

The XRD and MAS/NMR analyses were carried out by a Siemens D-5000 X-ray diffractometer with $CuK\alpha$ radiation and 2θ scanning ranging between 10° and 80° and with an MSL Bruker Solid State NMR-200 at 39.72 MHz of ^{29}Si , respectively. The ^{29}Si chemical shifts were expressed relative to the external liquid of tetramethylsilane (TMS). A Hitachi-S-570 scanning electron microscope (SEM) equipped with a Kevex EDS

Table 1
Chemical composition and constitution of C_3S and Portland cement type I

C_3S^a		Portland cement type I ^b	
Composition	wt. %	Composition	wt. %
SiO_2	25.21	SiO_2	20.38
Al_2O_3	0.08	Al_2O_3	6.77
Fe_2O_3	0.02	Fe_2O_3	3.48
CaO	72.28	CaO	64.93
MgO	< 0.01	MgO	0.95
SO_3	< 0.01	SO_3	1.92
Na_2O	< 0.01	Na_2O	0.15
K_2O	< 0.01	K_2O	0.59
TiO_2	0.01		
P_2O_5	< 0.01	LIO	0.50
Mn_2O_3	0.01	Total	99.67
SrO	< 0.01	Constituent	wt. %
LIO	1.36	C_2S	20.00
Total	98.98	C_3S	51.00
		C_3A	12.10
Alkalies as Na_2O	0.02	C_4AF	10.60
		Gypsum	1.50

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system containing a germanium detector and diamond window served the EDS analysis. All specimens for XRD, MAS/NMR and EDS analyses were prepared and analyzed by the specialists of the Institute following the standard procedures.

3. Results and discussion

3.1. S/S of chromium with C_3S

The XRD patterns of the pure and the hydrated samples of C_3S are shown in Fig. 1, left panel. The XRD patterns of the hydrated samples of C_3S , containing $Cr(NO_3)_3 \cdot 9H_2O$ with curing times of 1 day, 3 days, 7 days, and 14 days, are illustrated in Fig. 1, right panel. The appearances of $CaCrSi_4O_{10}$, $CaCrO_4 \cdot 2H_2O$, and $CaCr_2O_7$ in the samples at various days are identified according to the JCPDS pattern numbers of 39-213, 37-1367 and 1-0466, respectively. They are indicated by the peaks at A, B and C, respectively, in Fig. 1b. For example, the appearance of $CaCrSi_4O_{10}$ is identified by the peaks at $2\theta = 29.5$ and 51.6 , whereas $CaCrO_4 \cdot 2H_2O$ at $2\theta = 32.5$ and 44.4 , and $CaCr_2O_7$ at $2\theta = 32.2$ and 47.1 . Formation of new compounds in the reaction between Cr^{3+} and C_3S has also been reported by Bhatti [19]. The compounds, however, were not further characterized.

Fig. 2 presents the ^{29}Si MAS/NMR spectra of the hydrated samples of C_3S both with and without $Cr(NO_3)_3 \cdot 9H_2O$ prepared at $25^\circ C$ with a curing time of 28 days. The absorption peaks of the hydrated C_3S , containing $Cr(NO_3)_3 \cdot 9H_2O$, mainly appear at -68.9 , -71.6 , -72.6 , -73.4 , -73.6 , -74.4 , -79.7 and -85.0 ppm (see Fig. 2a). The hydrated C_3S absorption peaks, however, appear at -68.8 , -71.6 , -72.6 , -73.4 , -74.4 , -78.9 and -84.9 ppm (see Fig. 2b). Similarly, the ^{29}Si MAS/NMR spectra of the hydrated samples of C_3S containing $Cr(NO_3)_3 \cdot 9H_2O$ with curing times of 1 day and 3 days are shown in Fig. 3; the samples were prepared at $50^\circ C$. The absorption peaks of hydrated C_3S sample with 3 days curing mainly appear at -68.8 , -71.5 , -72.6 , -73.4 , -74.3 , -79.2 , -80.1 and -84.1 ppm (see Fig. 3a). The absorption peaks of the sample with one day curing, however, appear at -68.8 , -71.6 , -72.5 , -73.4 , -74.4 , -79.7 , -82.9 and -84.4 ppm (see Fig. 3b).

The integral intensities of Q^0 in hydrated and unhydrated C_3S , $I(Q^0)$ and $I^0(Q^0)$, are 37.2 and 81.8, respectively. The integral intensities of Q^1 and Q^2 in hydrated C_3S , $I(Q^1)$ and $I(Q^2)$, are 20.3 and 24.3, respectively. The degree of hydration of C_3S is 54.5% according to Eq. (1). The average length of linear polysilicate anions of hydrated C_3S is 4.4 from Eq. (2). These and the other results are summarized in Table 2. Note that the degree of hydration, α , is higher for C_3S with $Cr(NO_3)_3 \cdot 9H_2O$ than without; it is 70.4% for the former and 54.5% for the latter. This indicates that the chromium ion, Cr^{3+} , can increase the extent of C_3S hydration. However, the average length of linear polysilicate anions is lower for hydrated C_3S with $Cr(NO_3)_3 \cdot 9H_2O$ than without; it is 3.8 for the former and 4.4 for the latter. The degrees of hydration of C_3S containing $Cr(NO_3)_3 \cdot 9H_2O$ with 3 days curing and 1 day curing are 46.7% and 36.0%, respectively, and their average lengths of linear polysilicate anions are 3.5 and 4.2, respectively.

The EDS spectra of the hydrated samples of C_3S , containing $Cr(NO_3)_3 \cdot 9H_2O$ with curing times of 7 and 14 days, are illustrated in Fig. 4; the elements identified are calcium, chromium, and silicon. The weight percentages of Cr and Si are 8.68 and 9.51, respectively, for the sample with 7 days curing, and 7.49 and 9.24, respectively, for the sample with 14 days curing as shown in Table 3. The Cr:Si ratios in the samples with curing times of 7 and 14 days are 0.913 and 0.811, respectively, whereas the Ca:Si ratios are 8.603 and 9.012, respectively.

An explanation for the above XRD (Fig. 1), ^{29}Si NMR (Figs. 2 and 3), and EDS (Fig. 4) results would be the probable substitution of chromium for silicon in calcium silicate hydrates (C–S–H) and/or the interaction between Cr and Si.

3.2. S/S of chromium with cement

The XRD patterns of the hydrated samples of Portland cement, containing $Cr(NO_3)_3 \cdot 9H_2O$ with curing times of 1 day, 3 days, and 7 days are illustrated in Fig. 5. The samples were prepared at $75^\circ C$ followed by curing under a relative humidity of 92% and a temperature of $25^\circ C$. The appearances of calcium chromium silicate ($CaCrSi_4O_{10}$), aluminum chromium oxide hydroxide hydrate ($Al(OH)CrO_4 \cdot H_2O$), aluminum chromium oxide hydroxide ($Al_2(OH)_4CrO_4$), and calcium dichromate ($CaCr_2O_7$) are identified according to the JCPDS pattern numbers of 39-213, 26-14, 28-90, and 1-0466, respectively. They are indicated by the peaks at A, B, C and D, respectively, in Fig. 5.

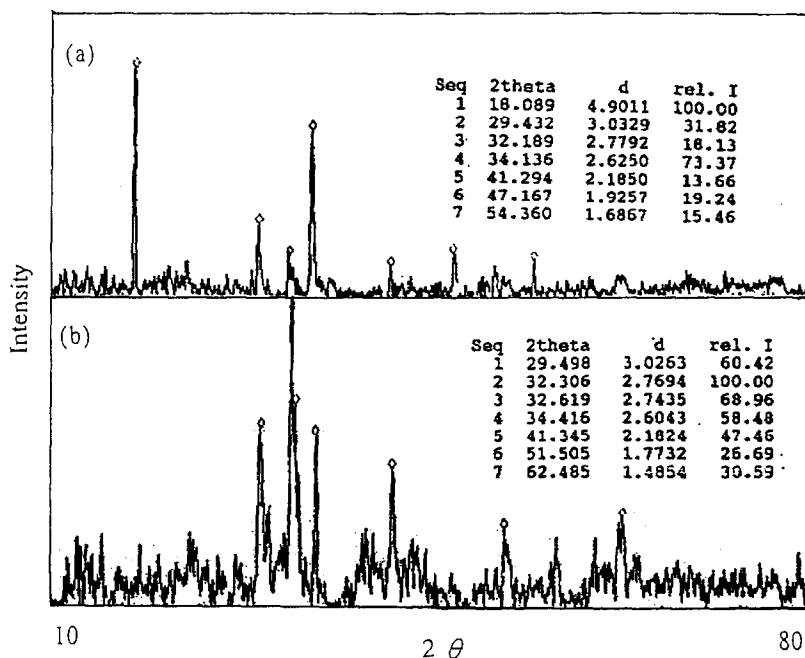
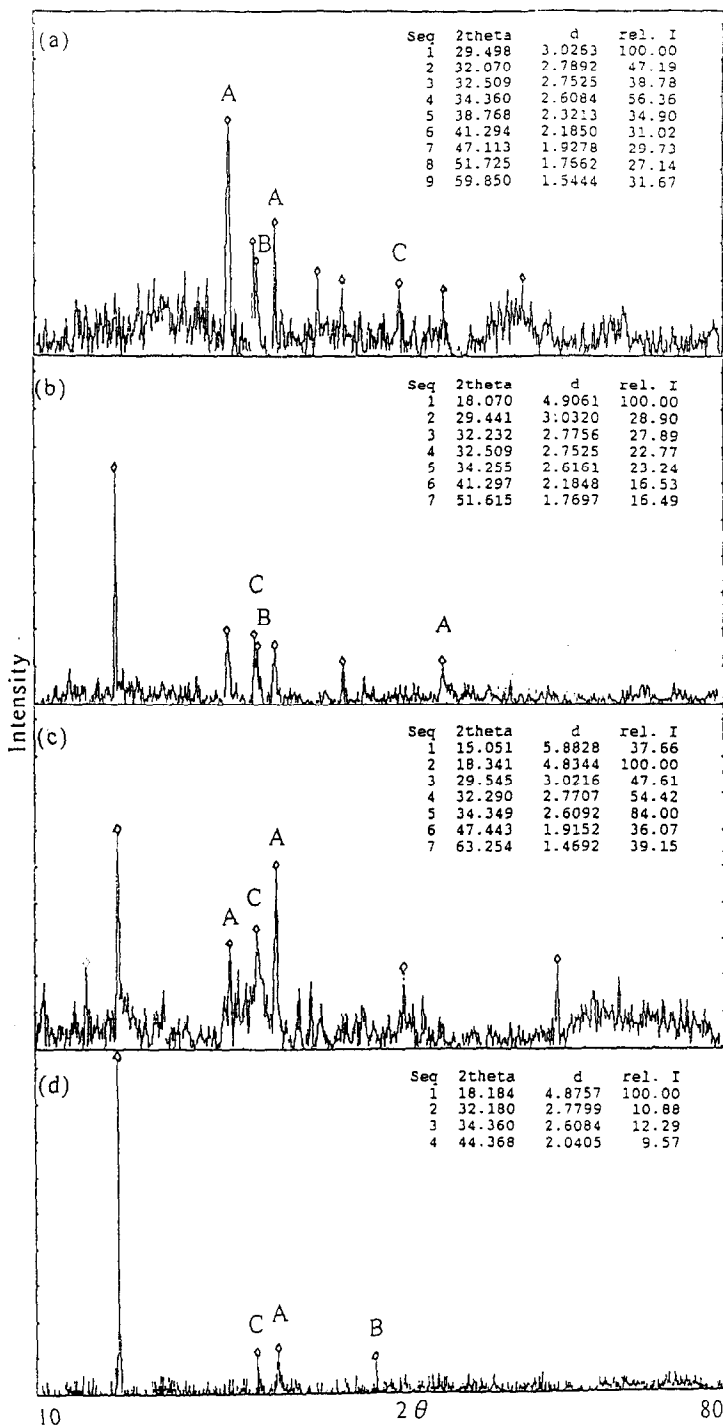


Fig. 1. (Left panel) XRD patterns of (a) hydrated C_3S and (b) pure C_3S . (Right panel) XRD patterns of hydrated C_3S containing $Cr(NO_3)_3 \cdot 9H_2O$ (a) 1-day curing, (b) 3-day curing, (c) 7-day curing and (d) 14-day curing; A: $CaCrSi_4O_{10}$, B: $CaCrO_4 \cdot 2H_2O$ and C: $CaCr_2O_7$.



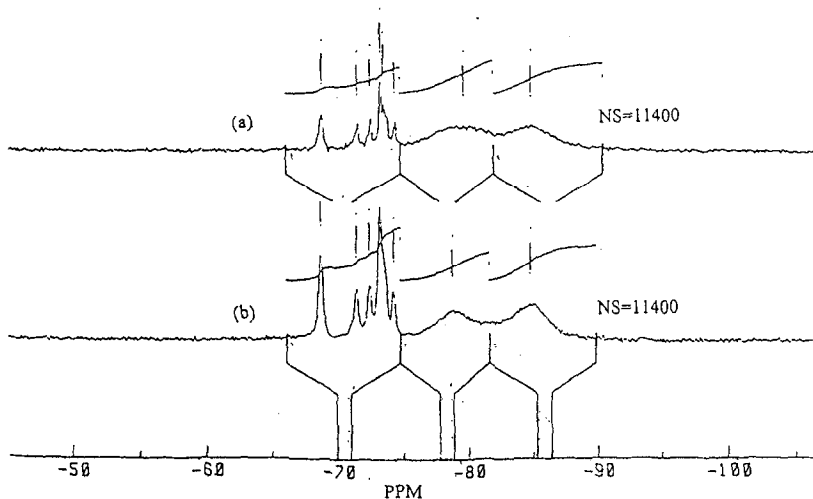


Fig. 2. ^{29}Si MAS/NMR spectra of hydrated (a) C_3S containing $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and (b) C_3S ; curing time, 28 days.

The ^{29}Si MAS/NMR spectra of the hydrated samples of Portland cement [20] show that the hydrated cement absorption peaks mainly appear at -80 , -82 , and -84 ppm and the hydrated cement containing $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ absorption peaks mainly appear at -79 and -84 ppm. The results of ^{29}Si MAS/NMR analyses of the S/S of chromium are also given in Table 2. As mentioned in the previous section, the degree of hydration (α) at 28 days is higher for C_3S with $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ than without. The degree of

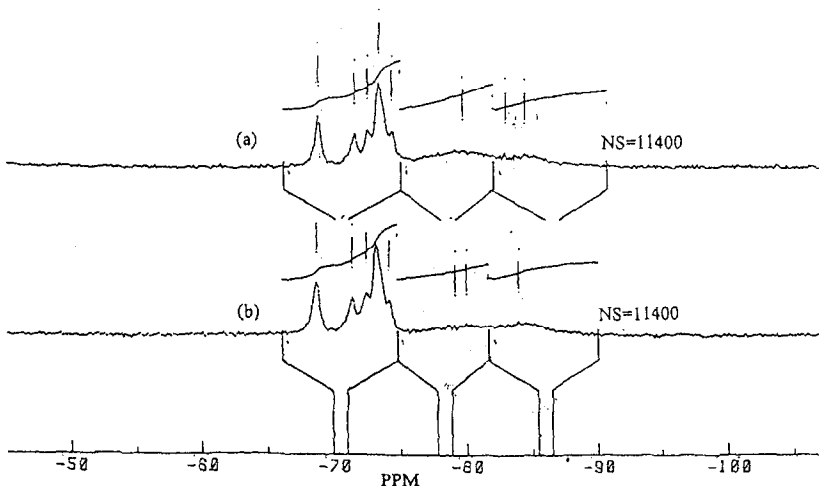


Fig. 3. ^{29}Si MAS/NMR spectra of hydrated C_3S containing $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (a) 3-day curing and (b) 1-day curing.

Table 2
 ^{29}Si MAS/NMR results of the S/S of chromium with Portland cement and C_3S

Material	Integral intensities of Q^n , ^{29}Si NMR						α (%)	P_{Si}
	$I(Q^0)$	$I(Q^1)$	$I(Q^2)$	$I(Q^3)$	$I(Q^4)$	Total		
Cement powder	75.5 (100) ^a	—	—	—	—	75.5 (100)	—	—
Hydrated cement + $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (w/s = 0.4, 28 days ^b)	66.0 (41.9)	47.0 (29.8)	37.7 (23.9)	6.9 (4.4)	0.0 (0.0)	157.6 (100)	58.1	3.6
Hydrated cement (w/s = 0.4, 28 days ^b)	105.8 (26.2)	162.7 (40.3)	113.9 (28.2)	14.2 (3.5)	7.5 (1.8)	404.1 (100)	73.8	3.4
Hydrated C_3S + $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (w/s = 0.4, 28 days ^b)	18.8 (29.6)	23.4 (36.9)	21.3 (33.5)	0.0 (0.0)	0.0 (0.0)	63.5 (100)	70.4	3.8
Hydrated C_3S (w/s = 0.4, 28 days ^b)	37.2 (45.5)	20.3 (24.8)	24.3 (29.7)	0.0 (0.0)	0.0 (0.0)	81.8 (100)	54.5	4.4
Hydrated C_3S + $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (w/s = 0.4, 3 days ^c)	34.8 (53.3)	17.6 (26.9)	12.9 (19.8)	0.0 (0.0)	0.0 (0.0)	65.3 (100)	46.7	3.5
Hydrated C_3S + $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (w/s = 0.4, 1 day ^c)	39.6 (64.0)	10.6 (17.1)	11.7 (18.9)	0.0 (0.0)	0.0 (0.0)	61.9 (100)	36.0	4.2

^a Values inside the bracket indicate percentage.

^b Samples were prepared by blending C_3S and deionized water with/without chromium nitrate nonahydrate at 25°C for 10 min, then cured under a relative humidity of 92% and a temperature of 25°C.

^c Samples were prepared by blending C_3S , deionized water and chromium nitrate nonahydrate at 50°C for 10 min, then cured under a relative humidity of 92% and a temperature of 25°C.

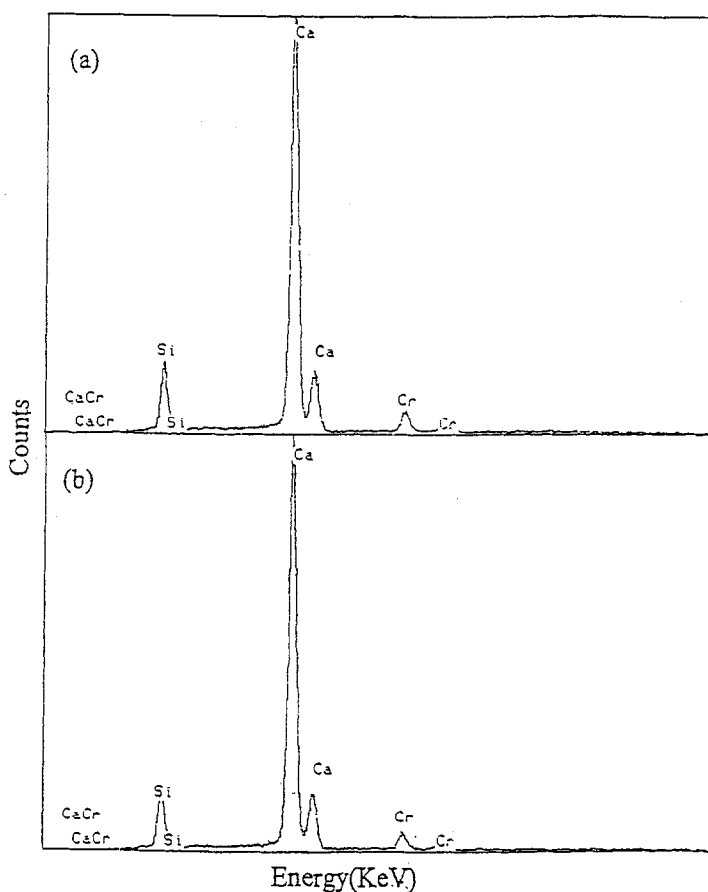


Fig. 4. EDS spectra of hydrated C_3S containing $Cr(NO_3)_3 \cdot 9H_2O$ (a) 7-day curing and (b) 14-day curing.

Table 3
EDS analyses of the S/S of Cr with Portland cement and C_3S

Element	Cement + $Cr(NO_3)_3 \cdot 9H_2O$ Curing time ^a (days)			C_3S + $Cr(NO_3)_3 \cdot 9H_2O$ Curing time ^b (days)	
	1	3	7	7	14
Cr	9.77	8.81	8.07	8.68	7.49
Ca	75.74	76.95	77.28	81.81	83.27
Si	6.95	7.36	7.43	9.51	9.24
Al	1.60	1.60	1.26		
Fe	5.95	5.26	5.95		
Mg		0.02			
Total	100.01	100.00	99.99	100.00	100.00

^aSamples were prepared by blending cement, deionized water, and chromium nitrate nonahydrate at 75°C for 10 min, then cured under a relative humidity of 92% and a temperature of 25°C.

^bSamples were prepared by blending C_3S , deionized water, and chromium nitrate nonahydrate at 50°C for 10 min, then cured under a relative humidity of 92% and a temperature of 25°C.

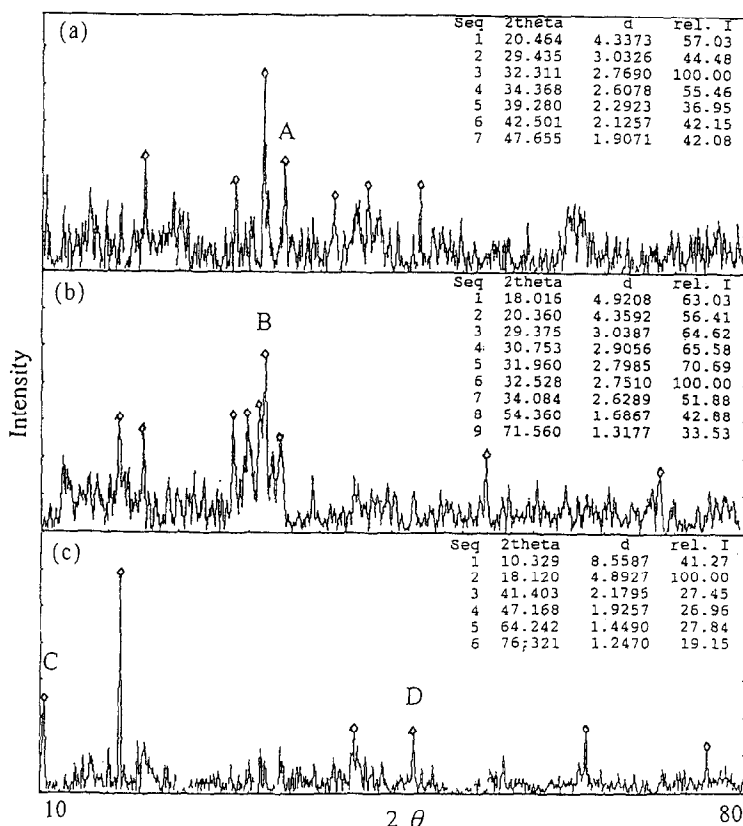


Fig. 5. XRD patterns of hydrated Portland cement containing $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (a) 1-day curing, (b) 3-day curing and (c) 7-day curing; A: $\text{CaCrSi}_4\text{O}_{10}$, B: $\text{Al}(\text{OH})\text{CrO}_4 \cdot \text{H}_2\text{O}$, C: $\text{Al}_2(\text{OH})_4\text{CrO}_4$ and D: CaCr_2O_7 .

hydration is, however, lower for cement with $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ than without; it is 58.1% for the former and 73.8% for the latter. This indicates that the chromium nitrate can increase the extent of C_3S hydration. It, however, decreases the extent of hydration of cement that contains 49 wt.% of other compounds such as C_2S , C_3A , C_4AF , and gypsum.

Fig. 6 shows the EDS spectra of the hydrated samples of Portland cement, containing $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with curing times of 1 day, 3 days and 7 days. The elements identified are calcium, chromium, silicon, aluminium, iron and magnesium. Note that the weight percentages of Al, Cr and Si are 1.60, 8.81 and 7.36, respectively, for the sample with 3 days curing, and 1.26, 8.07 and 7.43, respectively for the sample with 7 days curing, as shown in Table 3.

The above XRD (Fig. 5) and EDS (Fig. 6) results reveal the probable substitution of chromium for silicon and interaction among Cr, Si and Al in the hydrated Portland cement products. Similar results [14–17] have also been reported.

The reactions involved in the hydration of cement are heterogeneous and extremely

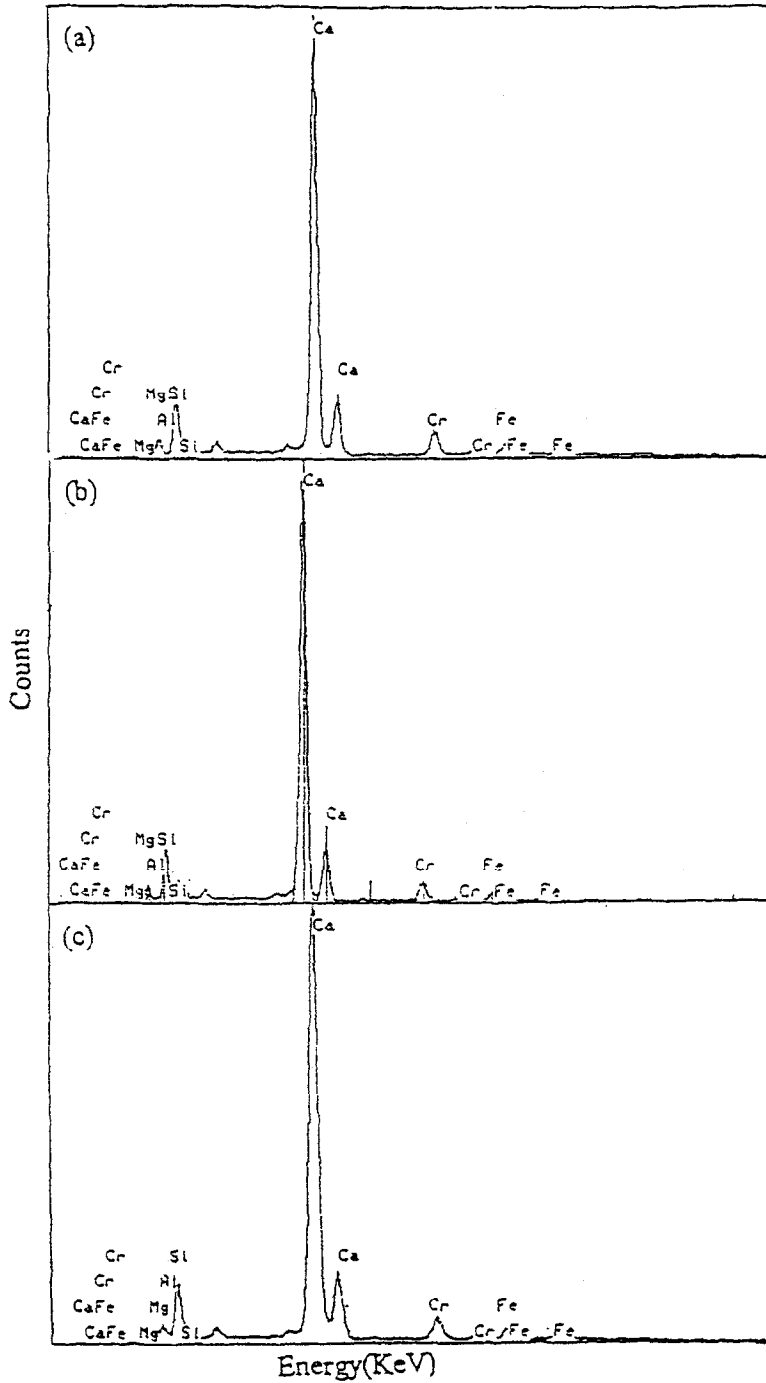


Fig. 6. EDS spectra of hydrated Portland cement containing $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (a) 1-day curing, (b) 3-day curing and (c) 7-day curing.

complex; their mechanisms are not yet well defined. In the present study, $\text{CaCrSi}_4\text{O}_{10}$, $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ and CaCr_2O_7 were identified in the hydrated samples of C_3S with $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, whereas $\text{CaCrSi}_4\text{O}_{10}$, $\text{Al}(\text{OH})\text{CrO}_4 \cdot \text{H}_2\text{O}$, $\text{Al}_2(\text{OH})_4\text{CrO}_4$, and CaCr_2O_7 were detected in the hydrated samples of Portland cement containing $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. These findings may provide a probable speculation on the mechanisms of cement hydration with chromium nitrate; i.e., the probable substitution of Cr for Si through Cr^{2+} and Cr^{6+} simultaneously, and the interaction among Cr, Si and Al in the hydrated Portland cement products that may enter into solid solution with C–S–H. Formation of $\text{CaCrSi}_4\text{O}_{10}$ (Cr^{2+}), $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ (Cr^{6+}), $\text{Al}(\text{OH})\text{CrO}_4 \cdot \text{H}_2\text{O}$ (Cr^{6+}), $\text{Al}_2(\text{OH})_4\text{CrO}_4$ (Cr^{6+}), and CaCr_2O_7 (Cr^{6+}) from $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Cr^{3+}), however, simultaneously involves the reduction and oxidation (Redox) processes. Although the coexistence of Cr^{2+} and Cr^{6+} is very unlikely, it would provide a possible mechanism for the immobilization of chromium in cement matrices. Nevertheless, additional investigations are needed to justify this hypothesis.

4. Conclusions

The solidification/stabilization of chromium was performed by using Portland cement type I and C_3S . Some significant findings are summarized in the succeeding paragraphs.

1. The present study confirms that chromium ion is easily incorporated into C_3S paste and hydrated type I Portland cement, and that it affects the characteristics of hydration and their hydration products.

2. $\text{CaCrSi}_4\text{O}_{10}$, $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ and CaCr_2O_7 are formed in the S/S of chromium with C_3S probably through the substitution of chromium for silicon in calcium silicate hydrate and/or the interaction between Cr and Si.

3. Formation of $\text{CaCrSi}_4\text{O}_{10}$, $\text{Al}(\text{OH})\text{CrO}_4 \cdot \text{H}_2\text{O}$, $\text{Al}_2(\text{OH})_4\text{CrO}_4$ and CaCr_2O_7 in the S/S of chromium with type I Portland cement reveals the interaction among Cr, Si and Al and/or the probable substitution of chromium for silicon in hydrated cement products.

4. Although the average length of linear polysilicate anions (P_{Si}) decreases, the degree of hydration (α) increases in the S/S of chromium with C_3S .

5. Formation of Cr^{2+} and Cr^{6+} from Cr^{3+} simultaneously involves the reduction and oxidation processes. Although the coexistence of Cr^{2+} and Cr^{6+} is very unlikely, it provides a possible mechanism for the immobilization of chromium in cement matrices.

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