

Hexavalent chromium in tricalcium silicate

Part I *Quantitative X-ray diffraction analysis of crystalline hydration products*

O.E. OMOTOSO, D. G. IVEY

Department of Mining, Metallurgical and Petroleum Engineering, University of Alberta, Edmonton, Canada T6G 2G6

R. MIKULA

CANMET Western Research Centre, Devon, Alberta, Canada T0C 1E0

The hydration products of Cr^{VI}-doped tricalcium silicate (C₃S)* have been investigated. C₃S is the main constituent of Portland cement responsible for the strength and stability of hardened Portland cement paste. Chromium trioxide (CrO₃), added as a dopant to C₃S, simulates hexavalent chromium waste that may be stabilized in ordinary Portland cement. X-ray diffraction was used to monitor the development of the hydration reaction products from the early stages to the late reaction stages. Leaching studies were carried out to evaluate the stability of the Cr^{VI}-containing phases in the hydrated C₃S matrix.

In monolithic waste forms containing hexavalent chromium, CaCrO₄·2H₂O was found to form within a few minutes of the hydration reaction. With increasing concentration of Ca²⁺ in the pore solution, Ca₂CrO₅·3H₂O became the stable species. The chromium in this phase was found to be very mobile in a standard acetic acid leaching test.

1. Introduction

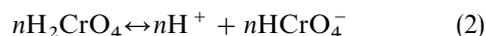
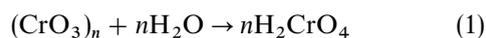
The disposal of hazardous heavy-metal liquid wastes in landfills is an age-long practice. Unfortunately, after some time, these wastes can be exposed to soil–water leaching action and end up as contaminants in ground water. This poses a threat to the environment since the toxicity of these heavy-metal ions (as elements or compounds) is not reduced. The use of cements as binding agents is the most successful method for the disposal of toxic heavy-metal ions in terms of economics and safety regulations. By making use of the resultant properties of cement–water reactions, liquid wastes are mixed with cement (usually ordinary Portland cement (OPC), to develop a high-strength monolithic cement–waste matrix. Depending on the heavy-metal ion, stabilization could be through chemisorption, precipitation, chemical incorporation in the hydrated cement components, physical entrapment or simultaneous occurrence of several of these possibilities [1–6]. Because of the specificity of heavy-metal ions' reaction with cement and the complexity of cement chemistry, it has been very difficult to optimize and even to understand the stabilization and solidification processes.

Containment of chromium in cement–alite has been investigated by several workers. When added in the hexavalent form (Cr^{VI}), Cr is leached from standard leachate solutions especially at high Cr^{VI} concentra-

tions [7–10]. Kindness *et al.* [10] reported that Cr^{VI} is immobilized in an OPC–blast furnace slag (BFS) blend with a OPC:BFS ratio of 1:9. No Cr was detected when the pore fluid was extracted and analysed after hydration for 250 days. They also reported the ability of blast furnace slag to reduce Cr^{VI} to Cr^{III}. The presence of Cr^{III} in the waste form is responsible for the partial stabilization of Cr^{VI} observed in the OPC–BFS matrix. However, no standard leachate test was conducted to determine its stabilization potential.

Despite the coordination similarities between CrO₄²⁻ and SiO₄⁴⁻, Cr^{VI} has not been found to replace silicon in the stable C–S–H, where silicon is tetrahedrally coordinated. Some investigations involving ettringite ([Ca₃(Al, Fe)(OH)₆·12H₂O]₂·(SO₄)₃·2H₂O), formed during the hydration of the calcium aluminate phase in OPC, suggest that CrO₄²⁻ can partially or wholly replace SO₄²⁻ [11–13]. This phase was reported to be potentially capable of reducing Cr^{VI} concentrations in the pore solution of OPC–Cr^{VI} waste forms.

CrO₃, the most common form of Cr^{VI}, dissolves readily in water, giving a strong acid [14]:



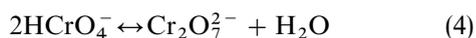
* The cement notation used throughout this paper is as follows: C = CaO; S = SiO₂; A = Al₂O₃; H = H₂O; F = Fe₂O₃; CH = Ca(OH)₂; C₃S = Ca₃SiO₅; C₃A = Ca₃Al₂O₆; C–S–H = calcium silicate hydrate.

In an alkaline solution typical of hydrating cement matrices, chromates are formed. These contain CrO_4^{2-} units in which the Cr is tetrahedrally coordinated:



It is known that chromium speciation is dominated by CrO_4^{2-} above pH 8. Calcium chromates are yellow and slightly soluble in water. The solubility product of CaCrO_4 is $0.023 \text{ mol}^3 \text{ l}^{-3}$ [15].

In acids, chromates are converted to dichromates. In the pH range 2–6, HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ are in equilibrium:



In this study, attempts are made to identify and quantify the crystalline Cr^{VI} containing phases in hydrated tricalcium silicate (C_3S) using X-ray diffraction. Leaching studies are also carried out to evaluate the stability of Cr^{VI} in C_3S paste.

2. Materials and methods

2.1. Production of tricalcium silicate

Stoichiometric ratios of analytical reagent grades of CaCO_3 (500 g) and SiO_2 (100 g) were mixed in a rotary shaker for 12 h to ensure homogenization. The mix was calcined in alumina crucibles at 1000°C for 4 h. The calcined mix was then transferred to a graphite crucible. Prior to sintering in a controlled-atmosphere high-temperature furnace, the sample was degassed for about 1 h at 1000°C after which the furnace was back-filled with argon. The sample was sintered at 1600°C for 24 h. The sintered product (C_3S) usually had some carbon adsorbed on the surface in contact with the graphite crucible. This was removed by decarbonation at 600°C for about 20 min. The colourless product obtained was ground in a ball mill with alumina balls for about 10 h. The ground product was sealed in a polyethylene container and stored under vacuum. Inadequate degassing may cause oxidation of the graphite crucible, forming carbon monoxide. The reducing atmosphere changes the thermodynamics of C_3S formation. An unidentified green carbonaceous substance was observed in inadequately degassed samples. This could not be removed even after re-sintering in a platinum crucible at 1450°C .

The Franke extraction procedure was used to determine the amount of free lime present in the ground

C_3S [16]. The free lime in the C_3S produced was found to be less than 0.1 wt%.

2.2. Preparation of chromium-doped samples

Table I shows the concentrations of the chromium solutions used in the stabilization–solidification experiments. Reagent-grade chromium trioxide was obtained from Aldrich Chemicals (Wisconsin, USA).

Industrial waste streams seldom contain more than $0.1 \text{ mol Cr}^{\text{VI}} \text{ dm}^{-3}$. However, to enhance the detection of the Cr-containing phases in hydrating C_3S pastes, and to observe the effects of varying concentrations on the hydration reaction, $1 \text{ mol Cr}^{\text{VI}} \text{ dm}^{-3}$ and $2 \text{ mol Cr}^{\text{VI}} \text{ dm}^{-3}$ solutions were used. First 10 g of C_3S were separately mixed with 5 ml of each chromium solution to make a paste. To serve as a standard, 5 ml of distilled water were also mixed with 10 g of C_3S . The paste was cast into plastic moulds and stored in a humidifying chamber plugged with ascarite and flushed with N_2 . Curing under N_2 was essential because carbonation occurs much more rapidly in the relatively small laboratory samples than in the very large quantities of waste–cement containment systems encountered in practice.

Except for the 60-day-old samples, all other samples were injected with isopropyl alcohol to stop the hydration reaction. This was followed by evacuation in a vacuum desiccator for 18 h. The 60-day-old samples were simply evacuated for 24 h. All samples were stored in a vacuum desiccator prior to analysis.

2.3. X-ray diffraction

X-ray diffraction patterns were recorded on a Rigaku X-ray diffractometer equipped with a rotating anode. All experiments were carried out with $\text{CuK}\alpha$ radiation at 40 kV and 110 mA. The solidified sample was ground with a mortar and pestle and spread on a glass slide coated with a thin layer of petroleum jelly. The diffractometer was scanned from 5° to 60° (2θ), with a step scan of 0.1° for 5 s. This procedure was used to characterize C_3S and to determine the phases present in the hydrated paste. The preliminary identification enabled the use of the correct primary standards for quantitative analysis.

The primary standards included C_3S which was taken from the stock kept under vacuum. CaCO_3 was

TABLE I Hydration experiments detailing concentrations of chromium solutions and hydration times

Solution (Solution/ C_3S about 0.5 by weight)	Molarity (mol dm^{-3})	Hydration periods used							
		5 min	6 h	1 day	3 days	60 days	4 months	14 months	
Cr^{VI}	CrO_3	0.1			*		*		
		1			*		*		
		2	*	*	*	*	*		
		2.75						*	
Standard	Distilled water				*		*	*	

* Hydration periods of sample.

taken from the same batch as the starting material for C_3S preparation. Commercial analytical reagent-grade CH was found unsuitable because of the very small crystallite size, which introduced excessive broadening of the CH peaks unmatched by those of the ground hydrated pastes. To obtain calcium hydroxide, $CaCO_3$ was calcined at $1000^\circ C$ until a constant weight was achieved. The resulting CaO was transferred to a stoppered flask and hydrated in excess distilled water for 24 h. The slurry was filtered in a CO_2 -free environment (glove bag) and dried at $105^\circ C$ for 1 h.

Five grams of each primary standard were mixed with 1 g of rutile (internal standard). The primary standard mix was packed with alumina balls in a 75 ml polyethylene bottle and tumbled in a rotary shaker. Cyclohexane was used as a grinding aid. Grinding for 2 h was found to be necessary to reduce the particle sizes to between 1 and $3\ \mu m$ with virtually no contamination from the alumina grinding balls. Then 5 g of each hydrated sample were ground in a similar manner with 1 g of rutile.

2.4. Data collection and analysis

The data collection strategy was similar to that used by Gutteridge [17]. A sample was loaded from the back into a cylindrical hole of 3 mm diameter and 20 mm depth drilled into a glass slide [18]. For all samples, diffraction intensities were obtained between 5° and 55° (2θ) at 40 kV and 110 mA. The diffractometer was step scanned at 0.05° intervals for 10 s per interval. For the primary standards, the background was fitted with a cubic spline and subtracted. In the hydrated samples, the amorphous C-S-H diffuse halo was simulated and subtracted from the pattern.

Also by using a cubic spline interpolation routine, the rutile (110) peak was aligned to $27.4501 \pm 0.0005^\circ$ (2θ). This required interpolating the original 1000 data points to 5000 data points. Each pattern was collected in triplicate. The rutile (110) peak was then normalized to 1000 counts. A linear least-squares procedure was used to fit the 5000 equations generated as shown below:

$$\sum_{i=1}^{5000} (y_i)_s = \sum_{j=1}^M w_j (y_i)_j + c_i \quad (5)$$

$(y_i)_s$ is the i th data point of sample s , $(y_i)_j$ is the i th data point of the primary standard j , w_j is the weight fraction of the primary standard j in the sample M is the number of primary standards and c_i is the contribution of the background to the i th data point. c_i also accounts for the amorphous halo. The coefficients w_j in the equation are obtained using a Gaussian elimination routine. The amorphous C-S-H was obtained by the difference ($1 - \text{sum of } w_j$). The reliability, R , is given as

$$R = \frac{\sum_{i=1}^{5000} \left[(y_i)_s - \left(\sum_{j=1}^M w_j (y_i)_j + c_i \right) \right]^2}{\sum_{i=1}^{5000} [(y_i)_s - c_i]^2} \quad (6)$$

The background subtraction routine was performed with a dedicated X-ray diffraction program Jade + (Materials Data Inc., CA). The alignment and least-squares routine are part of a macro written within a graphing program (Igor Pro 2.0.4).

2.5. Leaching

Leaching tests were carried out on the 60-day-old hydrated pastes using the standard toxicity characteristic leaching procedure (TCLP) of the Environmental Protection Agency [19]. A sample was ground to particles less than 0.5 mm in size and leached with acetic acid (pH 2.88). 200 ml of acetic acid were added to the 10 g sample in a high-density polyethylene bottle. The bottle and its contents were agitated in a rotary shaker at $30\ \text{rev min}^{-1}$ for 18 h. A Perkin-Elmer 4000 atomic absorption spectrometer was used to analyse the leachate solution. The leachate was acidified with 1 M HNO_3 to bring the pH to below 3. This prevented precipitation of the metal ions prior to analysis.

3. Results and discussion

In a blank (C_3S -water) paste, calcium hydroxide begins to appear within a few hours, and in a few days a diffuse band at about $28-31^\circ$ (2θ), corresponding to amorphous C-S-H, is apparent in the X-ray diffraction pattern. The completely hydrated paste comprises CH, C-S-H and some $CaCO_3$ formed as a result of partial carbonation of CH. The presence of $CaCO_3$ depends greatly on the hydration environment. The diffraction patterns from anhydrous C_3S and a fully hydrated blank paste (14 months old) are shown in Fig. 1.

Fig. 2 shows the diffraction patterns for 2 mol Cr^{VI} dm^{-3} pastes hydrated for various times. The paste hydrated for 5 min shows unreacted C_3S and strong peaks at 11.1 , 20.7 and 22.4° (2θ), matching

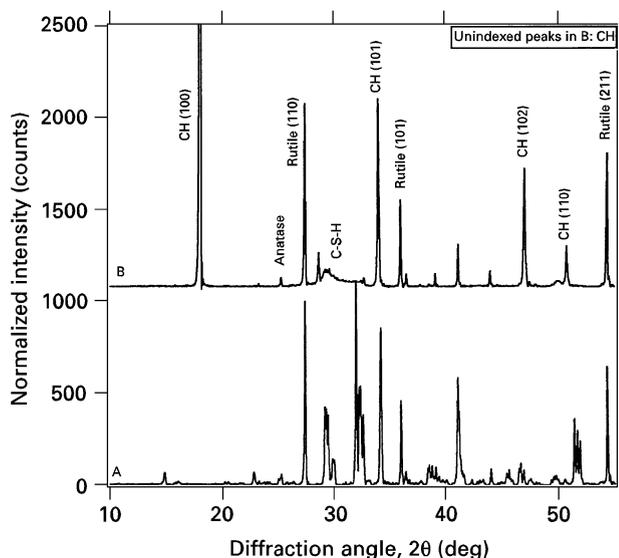


Figure 1 X-ray diffraction patterns of anhydrous C_3S (curve A) and 14-month old blank (C_3S-H_2O) paste (curve B). Anatase was an impurity in rutile.

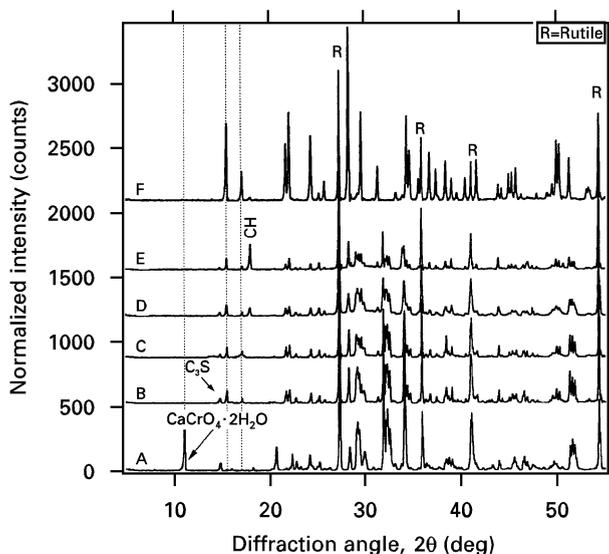
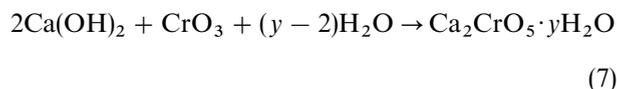


Figure 2 XRD patterns of 2 mol $\text{Cr}^{\text{VI}} \text{dm}^{-3}$ pastes hydrated for various times. Curve A, 5 min; curve B, 6 hrs; curve C, 24 hrs; curve D, 72 hrs; curve E, 60 days; curve F, standard $\text{Ca}_2\text{CrO}_5 \cdot 3\text{H}_2\text{O}$.

$\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ in the powder file. As more C_3S reacted and dissolved in the pore solution, $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ disappeared in the 6 hour old and subsequent pastes, replaced by another phase with diffraction intensities at 15.5° , 28.5° and 34.6° (2θ) (the three most intense peaks). No matching compound was found in the powder file. To produce the pure phase, CH was reacted with a 1 mol $\text{CrO}_3 \text{dm}^{-3}$ solution ($\text{Ca}:\text{Cr} = 2$) according to



$\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ was produced in the same manner with a $\text{Ca}:\text{Cr}$ ratio of 1.

The diffraction pattern of the synthesized $\text{Ca}_2\text{CrO}_5 \cdot y\text{H}_2\text{O}$ is shown in Fig. 2f. The synthesized chromates were used as primary standards in the quantitative X-ray diffraction (QXRD) procedure. The compositions of the hydrated 2 mol $\text{Cr}^{\text{VI}} \text{dm}^{-3}$ pastes are listed in Table II. The amount of $\text{Ca}_2\text{CrO}_5 \cdot y\text{H}_2\text{O}$ increased to 18.1 wt% at 6 h and decreased to 10.8 wt% at 60 days. The appearance of CH at 3 days coincides with a rapid decrease in the amount of $\text{Ca}_2\text{CrO}_5 \cdot y\text{H}_2\text{O}$, suggesting that partial decomposition of $\text{Ca}_2\text{CrO}_5 \cdot y\text{H}_2\text{O}$ may have taken place. The amount of $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ formed at 5 min

is 8.8 wt%. The maximum amount of $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ that could be formed based on the Cr concentration in the original mix is 12.1 wt%. Obviously not all the chromium has reacted within 5 min.

It is reasonable to assume that all the Cr has reacted at 6 h to form $\text{Ca}_2\text{CrO}_5 \cdot y\text{H}_2\text{O}$ (18.1 wt%, shown in Table II). The number, y , of moles of lattice water in $\text{Ca}_2\text{CrO}_5 \cdot y\text{H}_2\text{O}$ was calculated on the basis of this assumption. For 0.5 ml of 2 mol $\text{Cr}^{\text{VI}} \text{dm}^{-3}$ solution,

number of moles of Cr = $(2 \times 0.5 \times 10^{-3}) = 0.001 \text{ mol}$

Then,

$$\begin{aligned} & \text{mass of } \text{Ca}_2\text{CrO}_5 \cdot y\text{H}_2\text{O} \\ &= \text{number of moles of Cr} \\ & \quad \times \text{molar mass of } \text{Ca}_2\text{CrO}_5 \cdot y\text{H}_2\text{O} \\ &= 0.001 \times (230.176 + \text{total molar mass of } \text{H}_2\text{O}) \\ &= \text{weight fraction of } \text{Ca}_2\text{CrO}_5 \cdot y\text{H}_2\text{O} \\ & \quad \times \text{total mass of initial mixture} \\ &= 0.181 \times 1.5757 \end{aligned} \quad (8)$$

As

$$\text{total molar mass of } \text{H}_2\text{O} = 55.026$$

therefore

$$y = \frac{55.026}{18.016} = 3.05$$

The formula is thus $\text{Ca}_2\text{CrO}_5 \cdot 3\text{H}_2\text{O}$.

No calcium chromate peaks were found in the 0.1 mol $\text{Cr}^{\text{VI}} \text{dm}^{-3}$ pastes hydrated for 1 day (Fig. 3). Strong peaks of $\text{Ca}_2\text{CrO}_5 \cdot 3\text{H}_2\text{O}$ could be seen in the 1 mol dm^{-3} paste. As expected, very small amounts of CH formed in the 1 mol dm^{-3} paste compared with the blank and 0.1 mol dm^{-3} pastes, since $\text{Ca}_2\text{CrO}_5 \cdot 3\text{H}_2\text{O}$ is preferentially precipitated from the pore solution. In the 60-day-old 1 mol dm^{-3} paste shown in Fig. 4, relatively large amounts of CH have formed and a marked reduction in the amount of $\text{Ca}_2\text{CrO}_5 \cdot 3\text{H}_2\text{O}$ in the 1 M Cr^{VI} paste, similar to the trend in 2 mol $\text{Cr}^{\text{VI}} \text{dm}^{-3}$ pastes, is evident. The composition of the pastes is shown in Table III. Increasing Cr^{VI} concentrations thus inhibits the formation of CH. It is probable that the calcium chromate level in the 0.1 mol $\text{Cr}^{\text{VI}} \text{dm}^{-3}$ paste is below the detection limit for the X-ray diffraction.

TABLE II QXRD of 2 mol $\text{Cr}^{\text{VI}} \text{dm}^{-3}$ pastes hydrated for various times

Hydration Time	C_3S (wt %)	$\text{Ca}(\text{OH})_2$ (wt %)	$\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$ (wt %)	$\text{Ca}_2\text{CrO}_5 \cdot 3\text{H}_2\text{O}$ (wt %)	Reliability (Equation 6)
5 min	72.6	ND	8.8	ND	0.01
6 h	52.4	ND	ND	18.1	0.01
1 day	41.1	ND	ND	16.3	0.02
3 days	32.4	1.3	ND	12.4	0.03
60 days	19.0	4.5	ND	10.8	0.04

ND, not detected.

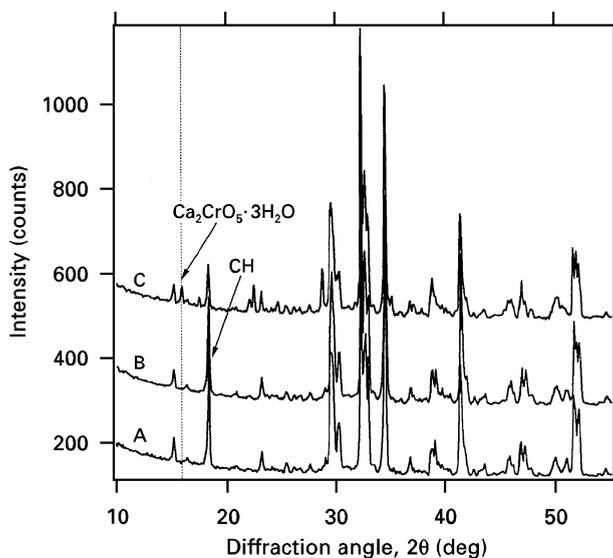


Figure 3 XRD patterns of 24-h-old Cr^{VI} pastes. Curve A, blank; curve B, 0.1 mol dm⁻³; curve C, 1 mol dm⁻³.

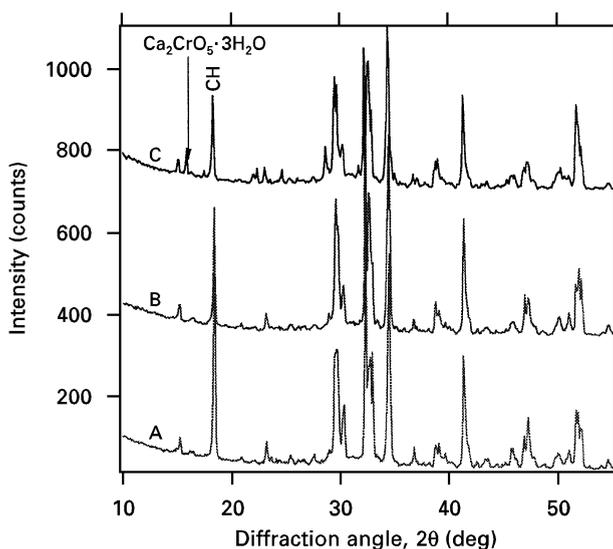


Figure 4 XRD patterns of 60-day-old Cr^{VI} pastes. Curve A, blank; curve B, 0.1 mol dm⁻³; curve C, 1 mol dm⁻³.

3.1. Leaching studies

The leaching studies carried out were aimed at confirming the similar leaching characteristics that exist between C₃S and the much investigated OPC.

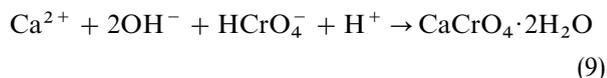
Four-month-old pastes containing 2.75 mol Cr^{VI} dm⁻³ were used for the leaching experiments. The

blank paste was hydrated for 14 months and contained virtually no unreacted C₃S. Results of atomic absorption spectroscopy (AAS) analysis of leachates are shown in Table IV. These represent the approximate leachate concentrations after 18 h of the TCLP. No Si was detected in the leachate in any of the samples (detection limit, about 2 ppm). Similar to the established notion, Cr^{VI} was very mobile in the leaching solution. In the blank pastes, the high pH and Ca contents of the leachates are primarily due to the partial dissolution of CH and some CaO units in the C–S–H. The blank paste still has some CH with a strong (001) preferred orientation (Fig. 5a). As shown in Fig. 5b, Ca₂CrO₅·3H₂O and CH were solubilized in the Cr^{VI} paste.

The Ca-to-Cr mole ratio in the Cr^{VI} paste leachate is about 4.6 which is higher than the Ca-to-Cr ratio in Ca₂CrO₅·3H₂O. The excess Ca comes from solubilized CH, C₃S and C–S–H. To verify whether Ca₂CrO₅·3H₂O dissolved congruently or through selective dissolution of CaO and CrO₄ units, pure Ca₂CrO₅·3H₂O was leached under the same conditions (Table IV). The Ca-to-Cr mole ratio is about 3.3, suggesting an incongruent dissolution of the metal ions. The leachate pH of 12.3, measured after 18 h, is similar to the pH of the pore solution in hydrating C₃S paste. It is conceivable that dissolution of Ca₂CrO₅·3H₂O is congruent when it first comes in contact with the acetic acid solution. Since the leachant does not have a buffer, increasing pH would result in an early saturation of Ca₂CrO₅·3H₂O in the leachate. Selective dissolution of the metal ions might ensue.

3.2. Proposed reaction mechanism

As Ca²⁺, O²⁻ and SiO₄⁴⁻ go into the pore solution containing HCrO₄⁻ ions, formation of OH⁻ increases the pH, leading to the formation of early C–S–H and calcium chromate. The formation of calcium chromate is represented by



As the pH increases and more Ca goes into solution, CaCrO₄·2H₂O becomes unstable and forms Ca₂CrO₅·3H₂O according to

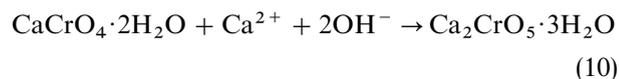


TABLE III QXRD analyses of partially hydrated blanks, 0.1 and 1 mol Cr^{VI} dm⁻³ pastes

Sample	C ₃ S (wt%)	Ca(OH) ₂ (wt%)	CaCO ₃ (wt%)	Ca ₂ CrO ₅ ·3H ₂ O (wt%)	Reliability
Blank, 1 day	72.2	9.5	ND	ND	0.016
0.1 mol dm ⁻³ , 1 day	68.9	4.2	ND	ND	0.01
1 mol dm ⁻³ , 1 day	70.4	0.7	ND	9.4	0.016
Blank, 60 days	44.5	17.7	0.8	ND	0.007
0.1 mol dm ⁻³ , 60 days	55.2	8.2	1.0	ND	0.008
1 M, 60 days	41.2	6.0	ND	5.0	0.015

ND, not detected.

TABLE IV AAS leachate analyses of standard and Cr^{VI}-doped pastes subjected to TCLP

Sample	Ca (mol dm ⁻³)	Cr (mol dm ⁻³)	Si (mol dm ⁻³)	pH
2.75 mol dm ⁻³ , 4 months	0.14	0.03	< 3.85 × 10 ⁻⁵	12.6
Ca ₂ CrO ₅ ·3H ₂ O	0.16	0.05	< 3.85 × 10 ⁻⁵	12.3
Blank, 14 months	0.09	< 3.85 × 10 ⁻⁶	< 3.85 × 10 ⁻⁵	12.5

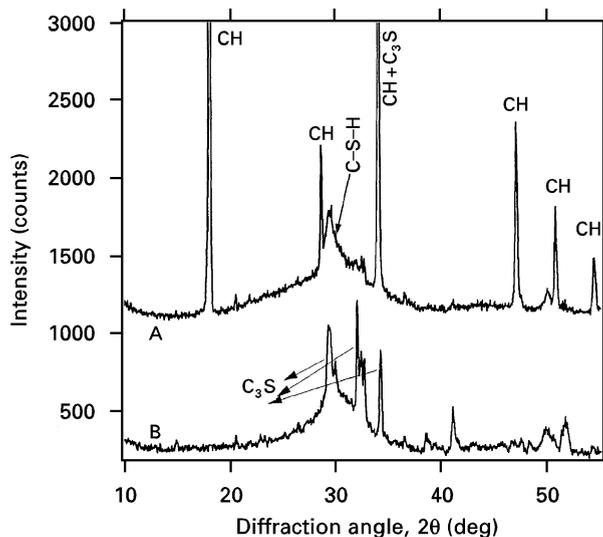


Figure 5 XRD patterns of leached pastes. Curve A, 14-month-old blank; curve B, 4-month-old 2.75 mol Cr^{VI} dm⁻³.

This phase persisted throughout the hydration period. As soon as all the Cr has been consumed, CH starts to form.

It appeared as if some of the Ca₂CrO₅·3H₂O redissolved in the strongly alkaline environment of the hydrating paste (pH about 12). The decrease in Ca₂CrO₅·3H₂O observed (Table II) could not be attributed to experimental errors or the loss of water when the reaction was stopped with isopropyl alcohol. The decrease is linear for both the 1 mol dm⁻³ and the 2 mol dm⁻³ pastes, despite the fact that both experiments were carried out 2 years apart using different batches of Cr^{VI} solutions. The location of the Cr^{VI} ions rejected from Ca₂CrO₅·3H₂O is not evident from the experiments carried out. No other diffraction intensities were observed in the leached residue and the only amorphous halo between 28 and 31° (2θ) corresponds to the stable C–S–H phase. However, the CrO₄²⁻ ions released by Ca₂CrO₅·3H₂O during the course of hydration may be forming an amorphous material not detected by powder diffraction techniques or they may be incorporated in the tetrahedral silicate sites in the C–S–H without creating too much distortion within the C–S–H. This could account for the absence of Ca₂CrO₅·3H₂O in the leached residue which still has some unleached Cr. The same reaction occurs in the low-concentration Cr^{VI} pastes, the difference being in the rate of formation of CH and the condensation of C–S–H which increases with increasing Cr^{VI} content.

4. Conclusions

1. Depending on the concentration of Cr^{VI} in the doped paste, soluble CaCrO₄·2H₂O formed within a few minutes of hydration when the Cr-to-Ca ratio was greater than unity. Increasing the concentration of Ca²⁺ in the pore solution results in the formation of a more stable and partially soluble Ca₂CrO₅·3H₂O phase, which persisted throughout the period of hydration.
2. Ca₂CrO₅·3H₂O concentration was found to decrease with age. Small amounts of the residual Cr^{VI} possibly occupy tetrahedral sites in the C–S–H.
3. The rate of C₃S consumption increases with increasing Cr^{VI} concentration.

Acknowledgements

The authors wish to thank the Department of Natural Resources Canada (CANMET), and the Natural Sciences and Engineering Research Council of Canada for funding this research.

References

1. F. P. GLASSER, in "Proceedings of the Chemistry and Microstructure of Solidified Waste Forms", edited by R. D. Spence (Lewis Publishers, Boca Raton, Florida, 1993) p. 1.
2. J. L. MEANS, L. A. SMITH, K. L. W. NEHRIG, S. E. BRAUNING, A. R. GAVASKAR, B. M. SASS, C. C. WILES and C. I. MASHNI, "The application of solidification/stabilization to waste materials" (Lewis, Boca Raton, Florida, 1995).
3. C. TASHIRO, H. TAKAHASHI, M. KANAYA, I. HIROKIDA and I. YOSHIDA, *Cem. Concr. Res.* **7** (1977) 288.
4. N. L. THOMAS, D. A. SAMESON and D. D. DOUBLE, *ibid.* **11** (1981) 143.
5. C. S. POON, A. I. CLARK, C. J. PETERS and R. PERRY, *Waste Manag. Res.* **3** (1985) 127.
6. C. S. POON, A. I. CLARK, R. PERRY, A. P. BARKER and P. BARNES, *Cem. Concr. Res.* **16** (1986) 161.
7. P. L. BISHOP, *Hazardous Waste Hazardous Mater.* **5** (1988) 129.
8. R. B. HEIMANN, D. CONRAD, L. Z. FLORENCE, M. NEUWIRTH, D. G. IVEY, R. J. MIKULA and W. W. LAM, *J. Hazardous Mater.* **31** (1991) 39.
9. D. G. IVEY, R. J. MIKULA, W. W. LAM, M. NEUWIRTH, D. J. CONRAD and R. B. HEIMANN, in "Proceedings of the Chemistry and Microstructure of Solidified Waste Forms", edited by R. D. Spence (Lewis, Boca Raton, Florida, 1993) p. 123.
10. A. KINDNESS, S. A. MACIA and F. P., GLASSER, *Waste Manage.* **14** (1994) 3.
11. H. POELLMAN, ST. AUER, H. J. KUZEL and R. WENDA, *Cem. Concr. Res.* **23** (1993) 315.
12. H. F. W. TAYLOR, "Cement chemistry" (Academic Press, London, 1990).

13. J. BENSTED and S. P. VARMA, *Silicates Industriels* **37** (1972) 315.
14. K. B. WILBERG, "Oxidation in organic chemistry", Part IV (Academic Press, New York, 1965).
15. R. KELLER, "Basic tables in chemistry" (McGraw-Hill, New York, 1967).
16. E. E. PRESSLER, S. BRUNAUER, D. L. KANTRO and C. H. WEISE, *Anal. Chem.* **33** (1961) 877.
17. W. A. GUTTERIDGE, *Brit. Ceram. Proc.* **35** (1984) 11.
18. H. P. KLUG and L. E. ALEXANDER, "X-ray diffraction procedures for polycrystalline and amorphous materials" (Wiley, New York, 1974).
19. Environmental Protection Agency, *Federal Register* **51** (1986) 21685.

*Received 19 April
and accepted 19 December 1996*