



Chromium behavior during cement-production processes: A clinkerization, hydration, and leaching study

Suthatip Sinyoung^a, Prayoon Songsiriritthigul^{b,c}, Suwimol Asavapisit^{d,e,*}, Puangrat Kajitvichyanukul^{e,f,*}

^a Department of Environmental Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, Bangkok, 10140, Thailand

^b Synchrotron Light Research Institute, PO Box 93 Nakhon Ratchasima, 30000, Thailand

^c School of Physics, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand

^d Environmental Technology, School of Energy and Materials, King Mongkut's University of Technology Thonburi, Bangkok, 10140, Thailand

^e National Center of Excellence for Environmental and Hazardous Waste Management, Faculty of Engineering, King Mongkut's University of Technology Thonburi, Bangkok, 10140, Thailand

^f Department of Civil Engineering, Faculty of Engineering, Naresuan University, Phitsanulok, 65000, Thailand

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ABSTRACT

The behavior of chromium during the production of cement clinker, during the hydration of cement and during the leaching of cement mortars was investigated. The microstructures of clinker and mortar properties were investigated using free lime, XRD, SEM/EDS, and TG/DTA techniques. Chromium was found to be incorporated in the clinker phase. The formation of new chromium compounds such as $\text{Ca}_6\text{Al}_4\text{Cr}_2\text{O}_{15}$, $\text{Ca}_5\text{Cr}_3\text{O}_{12}$, $\text{Ca}_5\text{Cr}_2\text{SiO}_{12}$, and CaCr_2O_7 , with chromium oxidation states of +3, +4.6, +5, and +6, respectively, was detected. After the hydration process, additional chromium compounds were identified in the mortar matrix, including $\text{Ca}_5(\text{CrO}_4)_3\text{OH}$, $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Al}_2(\text{OH})_4\text{CrO}_4$, with chromium oxidation states of +4.6, +6, and +6, respectively. Additionally, some species of chromium, such as Cr^{3+} from $\text{Ca}_6\text{Al}_4\text{Cr}_2\text{O}_{15}$ and Cr^{6+} from CaCr_2O_7 , $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Al}_2(\text{OH})_4\text{CrO}_4$, were leached during leaching tests, whereas other species remained in the mortar. The concentrations of chromium that leached from the mortar following U.S. EPA Method 1311 and EA NEN 7375:2004 leaching tests were higher than limits set by the U.S. EPA and the Environment Agency of England and Wales related to hazardous waste disposal in landfills. Thus, waste containing chromium should not be allowed to mix with raw materials in the cement manufacturing process.

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1. Introduction

Low-waste or waste-free technologies are widely used in many developed countries, including Sweden, Italy, Germany, and Mexico [1,2]. These nations are continually searching for waste-treatment methods that are environmentally friendly and helpful in recovering energy from waste. Disposal of waste in a cement kiln is a technology based on waste-derived alternative fuels [3,4]. Wastes may be substituted for raw materials or fuel in the production process or may be used as an additive material if they do not pose any negative effect. Wastes often used as alternative fuels or additives include used oil, spent solvent, tires, plastic, and sludge from wastewater-treatment plants. Many types of heavy metals are often found in these wastes, including cobalt, cadmium, lead, zinc, nickel, and chromium [5,6]. The total heavy metal content of

the finished product is not significantly affected by the cofiring of waste-derived fuels unless those wastes exhibit a level of a particular metal that is much higher than the average content in the raw material [6]. However, to utilize waste in cement-manufacturing processes, the effect of each type of heavy metal on the cement product with respect to both the engineering properties of the product and environmental aspects must be known. Chromium, a heavy metal of major environmental concern, was considered in this study.

Chromium is found in limestone, clay, char, and oil, which serve as fuels in the cement production process [7]. In raw materials, chromium is normally present at low concentrations. In Thailand, many industrial wastes contaminated with this heavy metal have been used for alternative fuels or raw materials in cement production [8]. Because chromium can be found in cement products [3,9], it may have some effects on cement properties.

Previous studies have found that the presence of chromium at low concentrations, for example less than 0.5 wt.%, did not affect the properties of clinker phases or the content of free lime [10–13]. However, with increasing concentrations of chromium up to 2.5%,

* Corresponding authors at: Naresuan University, Phitsanulok, Thailand.
E-mail addresses: suwimol.s@hotmail.com (S. Asavapisit), puangratk@nu.ac.th (P. Kajitvichyanukul).

the decomposition of C_3S owing to an increased C_2S phase and residual free lime has been found [12]. Willitsch and Sturm [5] reported that during clinkerization at high temperatures, Cr^{3+} can be oxidized to Cr^{4+} , $Cr^{4.6+}$, Cr^{5+} , and Cr^{6+} . Among these species, Cr^{6+} is the most toxic. Several researchers have also reported negative effects of chromium on the formation of clinker phases [10–13]. However, to date there has been no in-depth report on the behavior of chromium and its impact on cement products during the manufacturing process. Changes in the properties of cement products from the initial process, clinkerization, through hydration and the final leaching process from the cement mortar thus require investigation.

The major purpose of this study was to determine the behavior of chromium and its effects on both the clinkerization process and cement hydration. A quantitative study of chromium leaching during the cement-leaching process was also performed. To this end, different initial concentrations of chromium were added to raw materials used in the cement-manufacturing process. Changes in the properties of the cement products were monitored by X-ray diffraction (XRD), gravimetric/differential thermal analysis (TG/DTA), and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS). Cement chemistry in the presence of chromium is comprehensively discussed in this work.

2. Research methodology

2.1. Raw materials

Raw meal was taken from Siam City Cement Co., Ltd. (Thailand), a local cement factory in Saraburi Province. Limestone, high-grade limestone, clay, and iron ore were premixed by the cement company and were present in the raw meal at a weight ratio of 88:2:9:1; the chemical composition of the raw meal, as determined by X-ray fluorescence (XRF) analysis and expressed in terms of oxides, is shown in Table 1. All reagents, chromium (Cr_2O_3), ethylene glycol, acetic acid, sulfuric acid, nitric acid, and sodium hydroxide were of analytical grade.

2.2. Sample preparation

2.2.1. Preparation of clinker samples

Raw meal (150 g) was blended with the required amounts of Cr_2O_3 to yield initial concentrations of 0.1, 0.5, 1, 2, and 5.0 wt.% chromium. The samples were thoroughly mixed and fired in an electric furnace at 1450 °C for 90 min [14,15]. A synthetic clinker was obtained as the product of this clinkerization stage. Free-lime content analysis by the ethylene glycol method was used to determine the clinkerization degree of ground clinker (particle diameter <125 μm) [16]. The crystalline phases and oxidation states of chromium present in the synthetic clinker were determined with XRD techniques using a Philips PW 3710 diffractometer with $Cu\ K\alpha$ X-radiation. SEM (JEOL JSM-5800LV Link ISIS series 300 coupled with quantitative EDS) was used to determine the phase composition of the clinker following a method described elsewhere [11]. Powder samples were embedded in epoxy resin, polished with SiC paper and carbon-coated before analysis. The composition of C_3S , C_2S , C_3A , and C_4AF phases was examined by point-counting

techniques including observations of size and shape. The arithmetic average of at least 10 points with similar Ca/Si and Ca/Al ratios was calculated.

2.2.2. Preparation of hydrated samples

The synthetic clinker obtained after clinkerization was mixed with gypsum at 4.5 wt.%, and the resulting mixture was blended with Ottawa sand at a binder-to-sand ratio of 1:2.75; a water-to-cement (binder plus gypsum) ratio of 0.45 was used. To study chromium behavior during the hydration process, samples containing Cr were hydrated for 7 or 28 days and then subjected to XRD, SEM/EDS, and TG/DTA analyses. Hydration was stopped by soaking the sample in acetone. The crystalline phases present in the samples were examined by XRD using a Philips PW 3710 diffractometer with $Cu\ K\alpha$ radiation. The surface morphology of the hydrated sample was analyzed by SEM using a JEOL JSM-5800LV Link ISIS series 300. The development of $Ca(OH)_2$ was investigated using TG/DTA (Netzsch-409) with four replicates for each sample. Subsamples with weights of 15 mg were ground to <150 μm and heated to 600 °C in alumina crucibles under an N_2 atmosphere at rate of 5 °C/min. The TG/DTA data were calibrated by analyzing varying amounts of $Ca(OH)_2$ (Univar) mixed with Al_2O_3 (Riedel-deHaen) [17].

Cubic specimens were prepared for compressive strength tests per American Society for Testing and Materials (ASTM) methods. The cement mortar slurry was transferred to molds ($5 \times 5 \times 5\text{ cm}^3$) following the ASTM standard. After 24 h, the cement mortar samples were removed from the molds and cured in water for 7 or 28 days. The compressive strengths of the mortar samples were measured according to standard testing protocol C109/C 109M-95 [18]. The initial and final setting times of cement paste were determined following ASTM C191-99 [19]. The samples were tested according to ASTM C191 using a Vicat apparatus consisting of a frame and a movable rod weighing 300 g with a 10 mm plunger on one end and a 1 mm removable needle on the other. The setting time was determined to be the time at which the needle could penetrate less than 1 mm into a sample prepared according to ASTM C 187 (Normal Consistency of Hydraulic Cement) [20].

2.2.3. Preparation of samples for leaching tests

Chromium leaching was assessed using the toxicity characteristic leaching procedure (TCLP) (U.S. EPA method 1311) with 0.1 M acetic acid for powder samples and the tank-test method (EA NEN 7375:2004) for monolith samples [21,22]. Chromium leaching was assessed using both methods on samples containing 0.1, 0.5, 1.0, 2.0, and 5.0 wt.% chromium with three replicates for each sample.

For TCLPs (U.S. EPA method 1311) [21], approximately 10 g portions of hydrated mortar samples were weighed into polypropylene bottles, and extraction fluid was added at a 20:1 ratio of fluid to sample (~200 mL of TCLP extraction fluid No. 2; this solution was 0.1 M acetic acid and was tested to ensure that the pH was 2.88 ± 0.1). The bottles were tumbled at 30 rpm in a rotary extractor at room temperature for 18 h. At the end of the extraction, the leachate was filtered with glass-fiber filter paper. The pH of the filtrate was measured and the leachate was acidified to pH < 2 by the addition of a small amount of concentrated nitric acid to preserve the sample before analysis.

Table 1
Composition of raw meal.

	Compound								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	LOI*
Content (wt.%)	14.33	3.26	2.17	43.13	1.14	0.47	0.03	0.17	35.31

* LOI = loss on ignition

For the tank-test method (NEN 7375:2004) [22], cylindrical specimens were prepared. Mortar slurry was transferred to cylindrical plastic molds 4 cm in diameter and 5 cm in length. After demolding, the samples were wrapped with cling film, and curing was continued under ambient conditions for 28 days. An acid solution containing H_2SO_4 and HNO_3 (80:20 by weight) and deionized water were used as leachants, with initial pH values adjusted to 3 and 7, respectively. The weight ratio of leachant to monolith sample was 10:1. Leachant was renewed after cumulative contact times of 0.29, 1, 3, 4, 9, 16, 36, and 64 days. The water leachant at pH 7 was called the natural leachate or natural solution. The acid leachant at pH 3 was called synthetic acid rain. Leachate samples were collected and filtered through membrane filters for further chromium analysis. Total chromium and Cr^{6+} in the leachate were determined using an inductively coupled plasma-optical emission spectrometer and a UV-visible spectrometer at a wavelength of 540 nm.

3. Results and discussion

3.1. Behavior of chromium in clinker

3.1.1. Speciation of chromium in clinker

The crystalline phases of the synthetic clinker in the presence of increasing concentrations of chromium from 0 up to 7.0 wt.% are shown in Fig. 1. At low concentrations of Cr (0.1%, 0.5% and 1.0%), the positions of the prominent peaks of C_3S , C_2S , C_3A , and C_4AF did

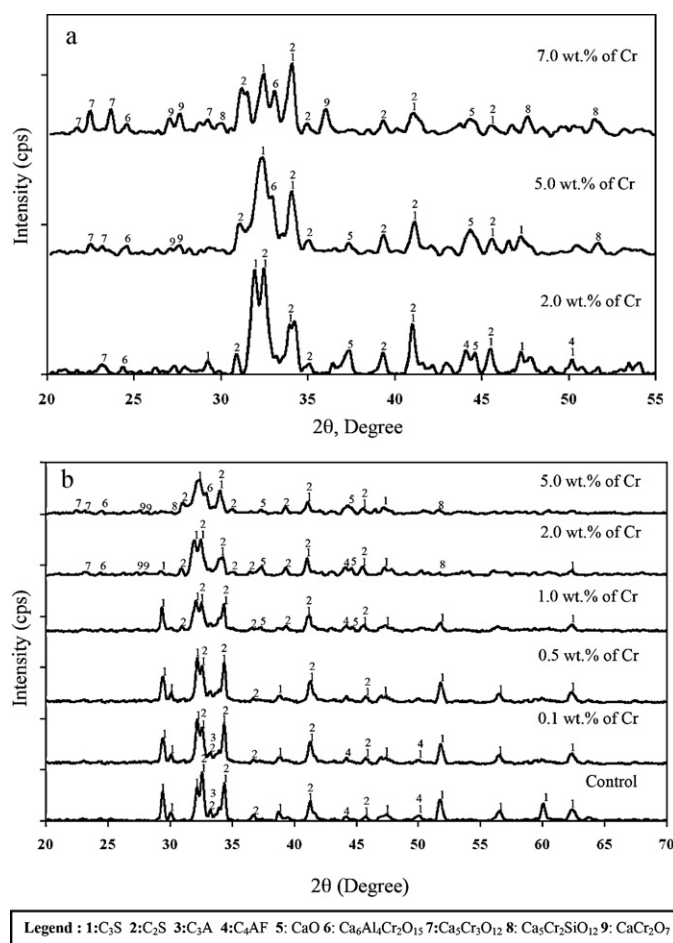


Fig. 1. XRD patterns of synthetic clinkers: (a) 2.0 wt.% of Cr, 5.0 wt.% of Cr, and 7.0 wt.% of Cr and (b) control, 0.1 wt.% of Cr, 0.5 wt.% of Cr, 1.0 wt.% of Cr, 2.0 wt.% of Cr, and 5.0 wt.% of Cr.

not differ from those of the control (Fig. 1a), while a slight decrease in the intensity of these peaks was observed.

At chromium concentrations in the range of 2.0–7.0% (Fig. 1b), the intensity of the main C_3S phase decreased ($2\theta = 29.6^\circ$, 30.1° , 39.1° , 52.0° , 56.9° , and 62.8°), whereas the intensity of the C_2S phase increased ($2\theta = 31^\circ$, 35.4° and 39.7°). $\text{Ca}_6\text{Al}_4\text{Cr}_2\text{O}_{15}$, $\text{Ca}_5\text{Cr}_3\text{O}_{12}$, $\text{Ca}_5\text{Cr}_2\text{SiO}_{12}$, and CaCr_2O_7 with chromium oxidation states of +3, +4.6, +5, and +6, respectively, were detected in the doped clinkers (Fig. 1b). These compounds were formed by reactions with Ca, Si, or Al present in the raw meal. Cr^{3+} was oxidized to higher oxidation states during clinkerization at high temperature [5]. The formation of these new compounds can be considered a lime-consuming process because calcium is present within chromium compounds detected among the major clinker phases. As a result, the formation of the main cement phase was inhibited and residual free lime increased.

The composition of the C_3S and C_2S phases in the Cr-doped clinker was examined by electron microprobe and quantitative EDX. The C_3S and C_2S phases were differentiated by their shapes [23], as shown in Fig. 2. The C_3S crystals were angular and approximately 18–20 μm in average size. The C_2S crystals were rounded, and the average size was approximately 30 μm . The C_3A crystals were needle-shaped, while the C_4AF crystals exhibited no definite form. The amounts of C_3S and C_2S present in the Cr-doped clinker were determined from the average compositions of C_3S and C_2S , with Ca/Si ratios of 3 ± 0.15 and 2 ± 0.08 , respectively.

A reduction in the free lime content of a clinker indicates an improvement of the clinkerization process. In contrast, an increase in free lime content indicates a reduced degree of clinkerization. With the presence of chromium, the free lime content of the chromium-doped clinker was increased, which may result in an inhibition effect on the formation of major phases of the clinker, such as C_3S and C_2S .

The relationship between the free lime content of the clinker and the chromium concentration in the raw meal is shown in Fig. 3. The free lime content of the control sample (without chromium) was 1.06 wt.%. The free lime content of clinker did not increase with respect to the control sample when chromium was added to the raw meal at 0.1%. A significant increase in free lime was detected when the addition of chromium was equal to or greater than 2.0%; free lime content increased to 2.81% and 3.01% with chromium additions of 2.0% and 5.0%, respectively.

The relationship between the formation of the main clinker phases C_3S and C_2S and the chromium concentration in the raw meal is shown in Fig. 3. The C_3S and C_2S phase contents of the control sample were 62.31% and 18.76%, respectively. The content of C_3S decreased from 62.31% in the control clinker to 61.95%, 58.81%, 56.89%, 41.02%, and 32.84% when the chromium concentration was increased from 0% to 0.1%, 0.5%, 1.0%, 2.0%, and 5.0%, respectively, whereas the content of C_2S increased from 18.76% to 18.91%, 22.29%, 26.43%, 52.64%, and 61.40%. The increase in C_2S followed a trend similar to that of the free lime content but opposite to that of the C_3S phase; the free lime content and C_2S phase both increased with increasing chromium concentration while the C_3S phase decreased. Based on these results, it is concluded that chromium tends to exert a negative effect on clinker properties. Chromium inhibits reactions between CaO, SiO_2 , and Al_2O_3 in the raw meal to form the main phases of the clinker. The content of free lime increased sharply with the addition of chromium at a concentration of 1.5% of Cr_2O_3 in the sample. Our results are in agreement with those of Malozhon et al. [24]. Stephan et al. [12] also found that clinker doping with Cr in the range of 0.5–2.5% resulted in a higher concentration of free lime, perhaps due to the decomposition of C_3S .

To illustrate the chromium chemistry in cement and its effect on free lime, C_3S and C_2S contents, the main reactions occurring

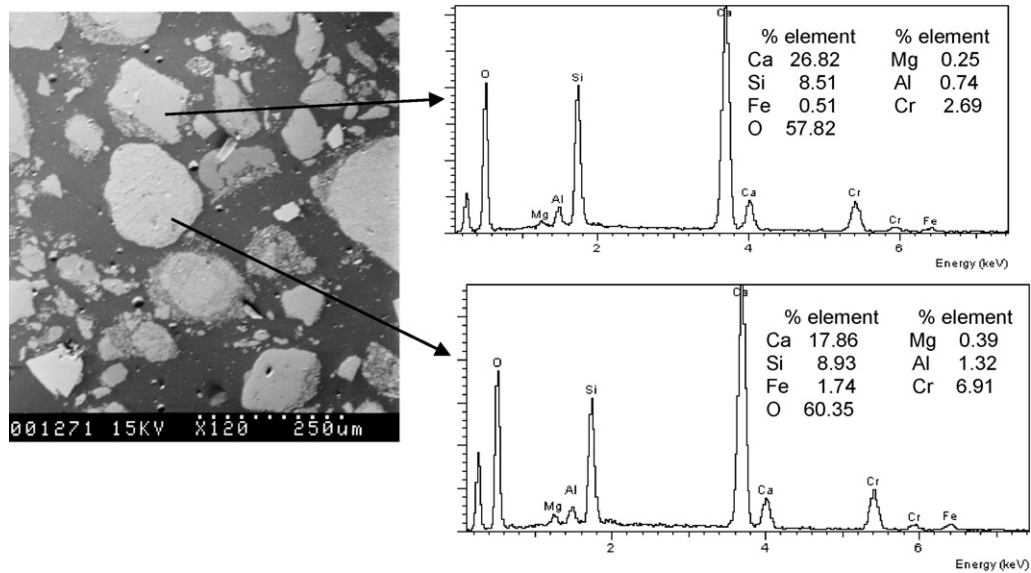


Fig. 2. Surface morphology of clinkers containing chromium at 5.0 wt.%.

in the clinkerization process are presented below Eqs. (1)–(3) [25]. As seen in Eq. (1), within the temperature range 700–900 °C, all calcium carbonate (CaCO_3) decomposes and free CaO reaches a maximum. From 900 to 1200 °C, C_2S forms Eq. (2). Above 1250 °C, and especially above 1300 °C, the liquid phase appears, and this promotes the reaction between C_2S and free lime to form C_3S Eq. (3). During the cooling step, C_3A and C_4AF are formed.

Due to the increase of the working temperature during clinkerization, physico-chemical processes take place in the raw materials, and chromium originally present as Cr^{3+} can be oxidized to higher oxidation states. With the addition of chromium to the process, both free lime and C_2S are increased while C_3S is decreased. The proposed chromium chemistry during clinkerization is shown below Eqs. (4) and (5).

Decomposition of calcium carbonate:



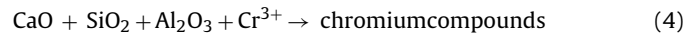
Formation of C_2S :



Formation of C_3S :



Formation of chromium compounds by lime consuming process:



Chromium compounds – $\text{Ca}_6\text{Al}_4\text{Cr}_2\text{O}_{15}$, $\text{Ca}_5\text{Cr}_3\text{O}_{12}$, $\text{Ca}_5\text{Cr}_2\text{SiO}_{12}$, and CaCr_2O_7 .

Decomposition of C_3S :



Our results clearly demonstrate that chromium inhibits the transformation of C_2S and CaO to C_3S . Chromium may react with Ca, Si, or Al present in the raw meal and form new compounds as detected by XRD Eq. (4). The reaction inhibition due to the chromium addition has been reported previously [12,24]. Usually, the occurrence of clinker phases results from the appropriate ratios of Ca:Si and a suitable temperature for each phase, as described by Eqs. (2) and (3). With the substitution of CaO, SiO_2 , Al_2O_3 , and Fe_2O_3 by chromium, the required ratio of Ca:Si is not appropriate for the formation of the major phases of clinker. The decomposition of C_3S in the presence of chromium is likely a reason for the reaction inhibition, as reported by previous works [12,24] and as shown in Eq. (5). However, this reaction was not detected in this work.

3.2. Behavior of chromium in hydrated cement

3.2.1. Speciation of chromium in hydrated cement

The XRD patterns of cement mortars with and without chromium after 28 days of hydration are shown in Fig. 4. The intensities of the C_3S and C_2S peaks were reduced due to the transformation of these phases into calcium silicate hydrate (CSH) and $\text{Ca}(\text{OH})_2$ phases.

$\text{Cr}^{4.6+}$ and Cr^{5+} in the form of $\text{Ca}_5\text{Cr}_3\text{O}_{12}$ and $\text{Ca}_5\text{Cr}_2\text{SiO}_{12}$, respectively, were the only two species in both doped clinkers and mortars. The new species $\text{Ca}_5(\text{CrO}_4)_3\text{OH}$, $\text{CaCrO}_4\cdot 2\text{H}_2\text{O}$, and $\text{Al}_2(\text{OH})_4\text{CrO}_4$ (Cr^{6+}) were also detected. These new compounds may be the result of reactions between chromium compounds in the clinker with water (H_2O) in the hydration process. However, Cr^{3+} in the form of $\text{Ca}_6\text{Al}_4\text{Cr}_2\text{O}_{15}$ and Cr^{6+} in the form of CaCr_2O_7 were not detected in the XRD patterns of Fig. 4, probably because

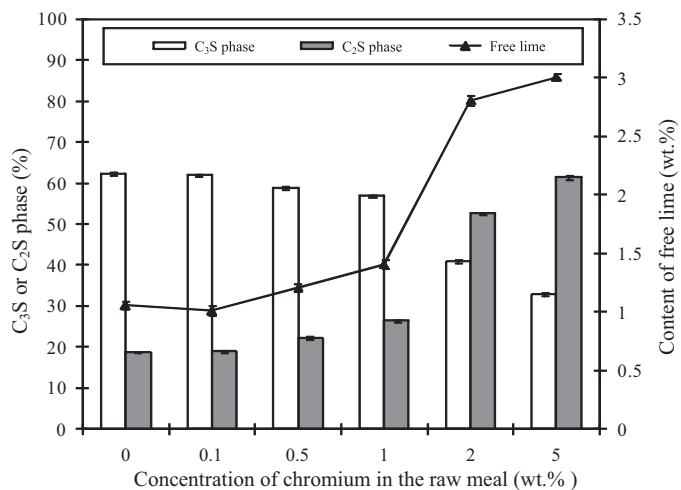


Fig. 3. Content of C_3S phases, C_2S phases and free lime of synthetic clinkers in the presence of various concentrations of chromium.

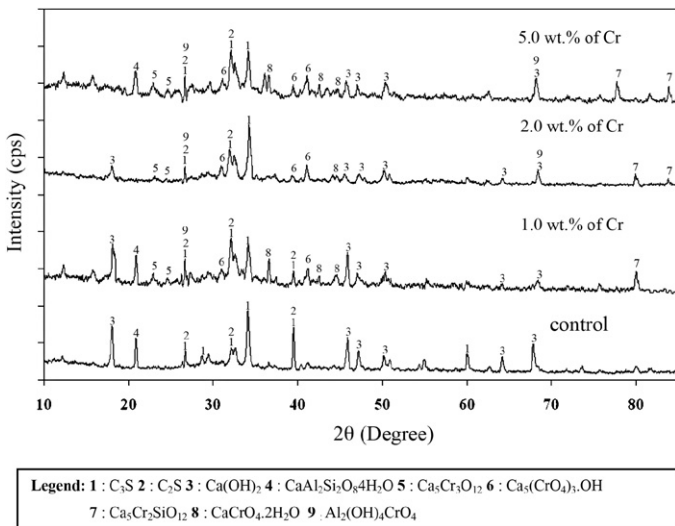


Fig. 4. XRD patterns of doped mortars at the age of 28 days: control, 0.1 wt.% of Cr, 0.5 wt.% of Cr, 1.0 wt.% of Cr, 2.0 wt.% of Cr, 5.0 wt.% of Cr.

their concentrations in the hydrated cement mortars were below the detection limit of the XRD technique.

3.2.2. Effect of chromium on hydrated cement

Typically, calcium hydroxide ($\text{Ca}(\text{OH})_2$) and calcium silicate hydrate (CSH) are the major compounds in hardened ordinary Portland cement. TG/DTA and SEM are the most commonly used methods for measuring the various phases in cementitious materials [26,27]. The $\text{Ca}(\text{OH})_2$ content of cement mortars was determined by the thermal analysis. The data obtained from DTA over the range of 450–510 °C were calibrated by analyzing varying amounts of $\text{Ca}(\text{OH})_2$ mixed with Al_2O_3 , which gave a linear relationship between the area under the DTA peak and the percentage of $\text{Ca}(\text{OH})_2$ within the mixes. In all cement samples, the peak corresponding to $\text{Ca}(\text{OH})_2$ was seen, as shown in Fig. 5. The area of each peak, which is related to the heat involved in the reaction, is shown in Table 2. The generation of $\text{Ca}(\text{OH})_2$ in hydrated cement with chromium additions of 0%, 0.1%, 0.5%, 1.0%, 2.0%, and 5.0% is shown. The percentages of $\text{Ca}(\text{OH})_2$ in hydrated cement without chromium were 4.63% and 18.86% at 7 and 28 days of hydration, respectively. The percentage of $\text{Ca}(\text{OH})_2$ in hydrated cement with chromium

Table 2

The percentage of $\text{Ca}(\text{OH})_2$ in hydrated cement containing chromium at 7 and 28 days of hydration.

Initial concentration of chromium in raw meal (wt.%)	% of $\text{Ca}(\text{OH})_2$ in hydrated cement	
	7 days	28 days
Control	4.63	18.86
0.1	4.72	18.64
0.5	4.03	17.69
1.0	3.57	15.78
2.0	2.41	14.13
5.0	0.96	10.06

was lower than that in hydrated cement without chromium. The shift of the peak temperatures towards lower temperature values may arise from the change of cement microstructure. With 5.0% chromium, the reaction occurred to a slight degree, and a very small amount of $\text{Ca}(\text{OH})_2$ was obtained. The endothermic reaction to occurred to a lesser degree, with a reduced amount of $\text{Ca}(\text{OH})_2$ formed.

Qualitative information on CSH gels was obtained from SEM micrographs of the surface morphology of hydrated cements with and without chromium at 7 and 28 days, which are presented in Figs. 6 and 7, respectively. Amorphous CSH gel (light color), which is the main hydration product, was observed in hydrated mortar without chromium at 7 and 28 days. With increasing chromium concentrations, decreasing amounts of amorphous CSH gel were observed in the SEM micrographs. This finding agrees with the DTA results showing that the formation of hydration products decreased with an increasing amount of chromium (Table 2).

In addition, when using EDS to examine the mortar samples, chromium was found in the CSH gel, as shown in Fig. 7e and f. Chromium in the clinker was mainly found in the silicate phase, as reported previously by Stephan et al. [12]. Chromium caused changes not only in the clinker phase but also in the contents of $\text{Ca}(\text{OH})_2$ and CSH in the hydrated cement, consequently altering the cement properties.

3.2.3. Effects of chromium on compressive strength and setting time

After curing for 7 or 28 days, cubic samples (with and without chromium) were tested for compressive strength according to ASTM C109. The averages of six tests for each cured sample are presented in Fig. 8. The compressive strength was dependent on

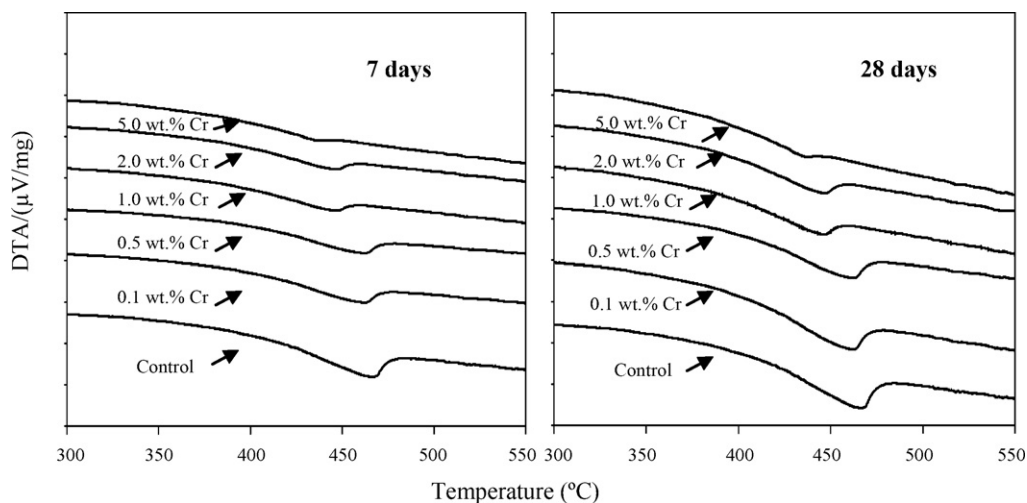


Fig. 5. DTA curve of hydrated cement without and with various concentrations of chromium at 7 and 28 days.

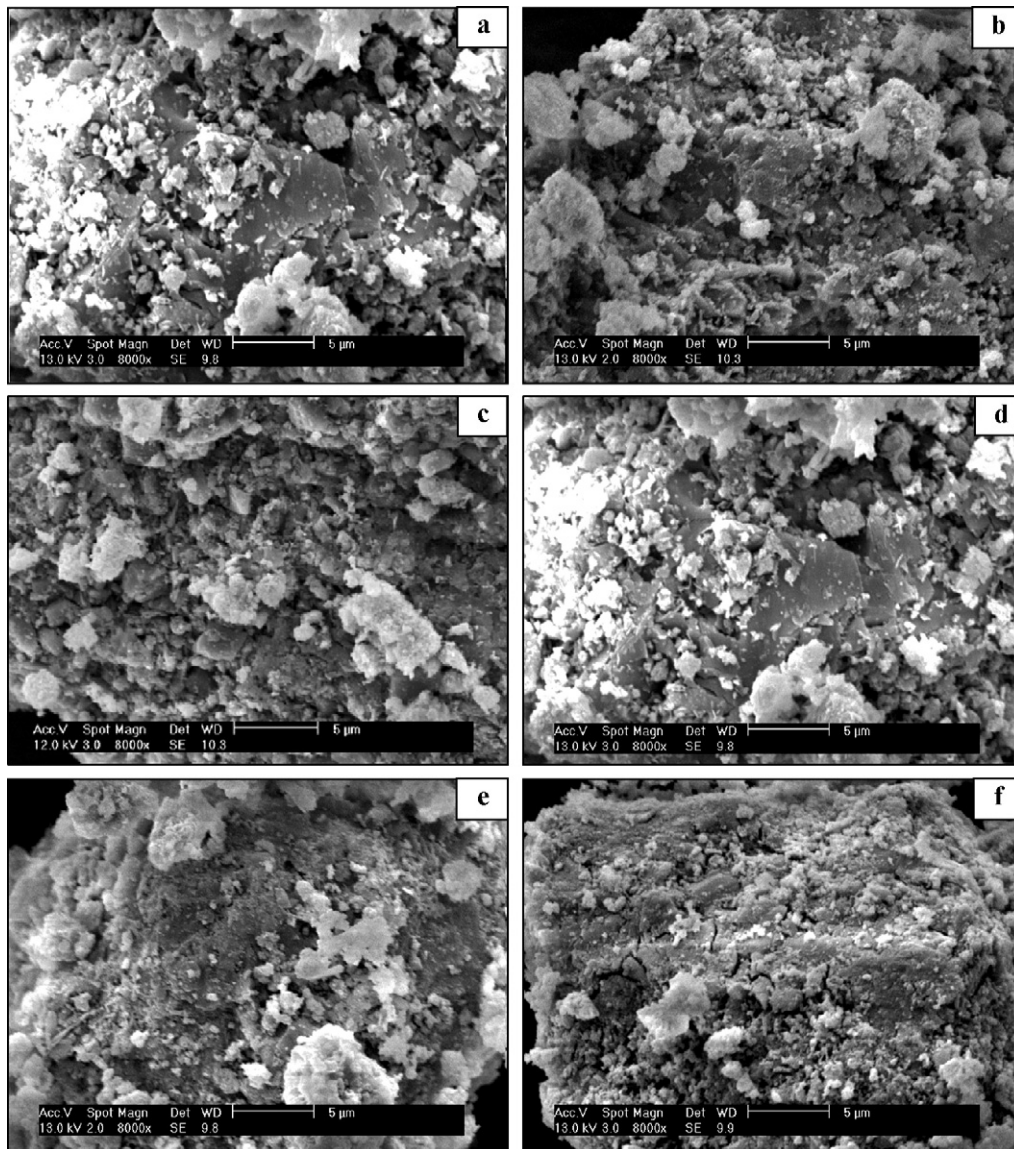


Fig. 6. Surface morphology of hydrated cement at the age of 7 days: (a) control, (b) 0.1 wt.% of Cr, (c) 0.5 wt.% of Cr, (d) 1.0 wt.% of Cr, (e) 2.0 wt.% of Cr, and (f) 5.0 wt.% of Cr.

the hydration period and the concentration of chromium added to the raw meal. The compressive strength of the control sample was higher than that of chromium-containing samples of the same age. The highest strength, 30 MPa, was observed for the control sample at 28 days of hydration, whereas the compressive strengths of the other samples markedly decreased as the concentration of chromium was increased. The average compressive strengths of samples with 0.1%, 0.5%, 1.0%, 2.0%, and 5.0% chromium at 7 days of curing were 18.2, 16.1, 14.4, 11.8, and 5.6 MPa, respectively. After curing for 28 days, the average compressive strength values obtained with 0.1%, 0.5%, 1.0%, 2.0%, and 5.0% chromium were 29.2, 27.1, 25.5, 16.8, and 11.2 MPa, respectively. Increasing the chromium content in the raw meal significantly reduced the compressive strength.

This experimental result can be explained by two mechanisms: the replacement of chromium in the raw meal and the inhibition of chromium on hydration reactions, causing lower $\text{Ca}(\text{OH})_2$ and CSH gel contents. As shown earlier (Section 3.1.1), the replacement of raw meal by chromium (dilution effect) leads to a lower content of C_3S and a higher content of free lime and C_2S . Usually, for a cement rich in C_2S , the strength of the cement increases more slowly if there is a high amount of free lime in the cement, which leads

to the expansion of small cracks and a decrease in compressive strength.

For the second mechanism, the inhibition of chromium on hydration reactions, our previous results from DTA and SEM showed that the $\text{Ca}(\text{OH})_2$ and CSH gel contents were decreased in samples containing chromium. Normally, the hardening of cement is supported by these compounds.

The results presented in Fig. 9 show that the control cement reached initial setting time in 50 min and final setting time in 78 min. In the presence of 0.1% chromium in the raw meal, the initial and final setting times were 55 and 85 min, respectively. With 5% chromium present in the raw meal, the initial setting time was 980 min and final setting time was 1189 min. Changes in initial and final setting times are dependent on initial chromium concentrations. With an increased chromium concentration in the samples, longer setting times were required; chromium retards the setting process of cement. This retarding effect observed for the initial and final setting times of chromium-doped cement mixes can be related to a reduction in the hydration kinetics of C_3S and aluminates, as discussed in a previous work [27]. As described previously, the replacement of chromium in the raw meal leads to a low C_3S content and high free lime and C_2S contents. Thus, the presence

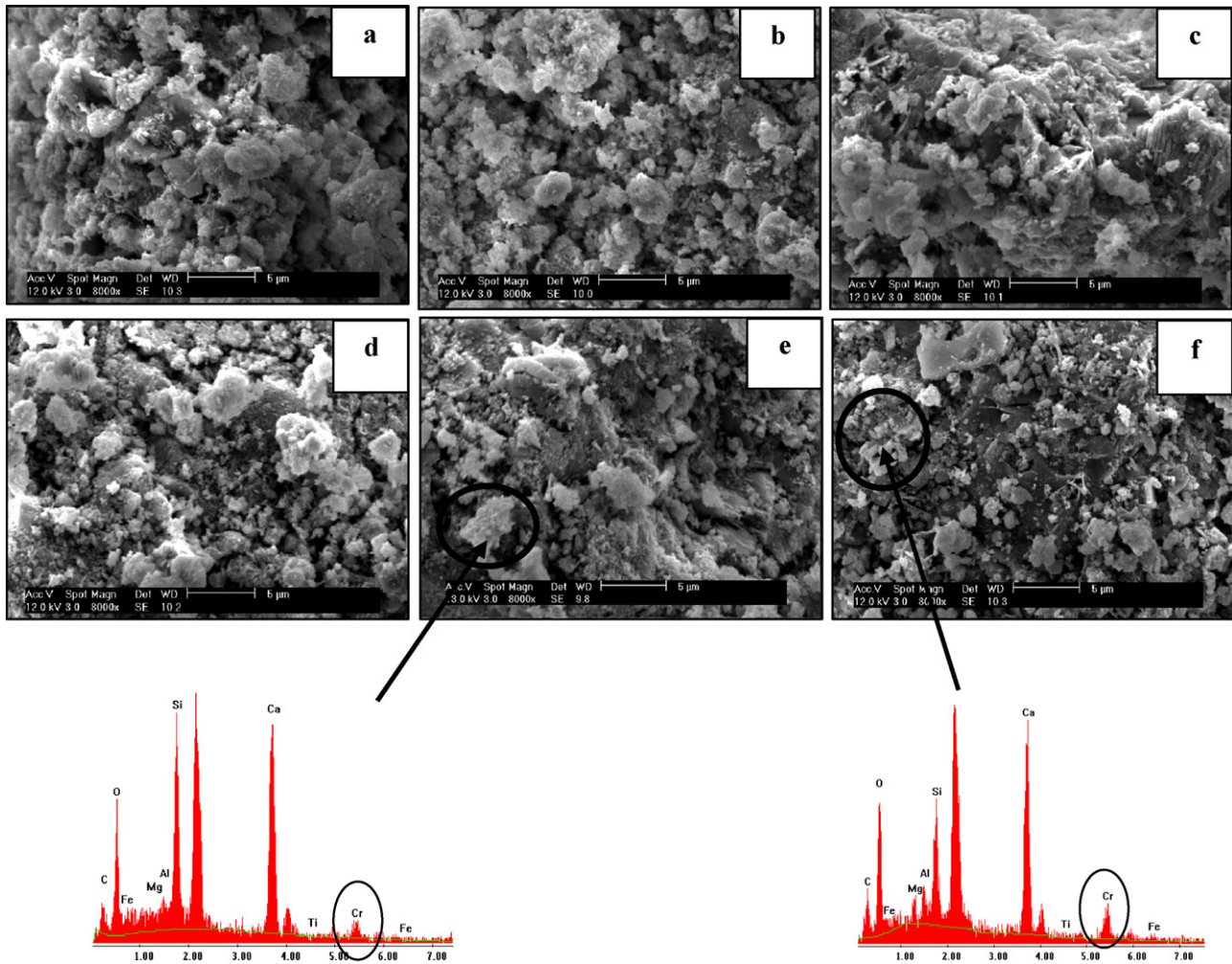


Fig. 7. Surface morphology of hydrated cement at the age of 28 days: (a) control, (b) 0.1 wt.% of Cr, (c) 0.5 wt.% of Cr, (d) 1.0 wt.% of Cr, (e) 2.0 wt.% of Cr, and (f) 5.0 wt.% of Cr, EDS-CHS.

of chromium decreases the compressive strength and retards the setting time of cement. Our results are in agreement with those of Wang and Vipulanandan [28], who added K_2CrO_4 (at concentrations ranging from 0.5% to 5%) to a Portland cement matrix (Type I). They observed that the addition of chromium lengthened the initial and final setting times and that when the Cr^{6+} content was increased in cement, the compressive strength decreased.

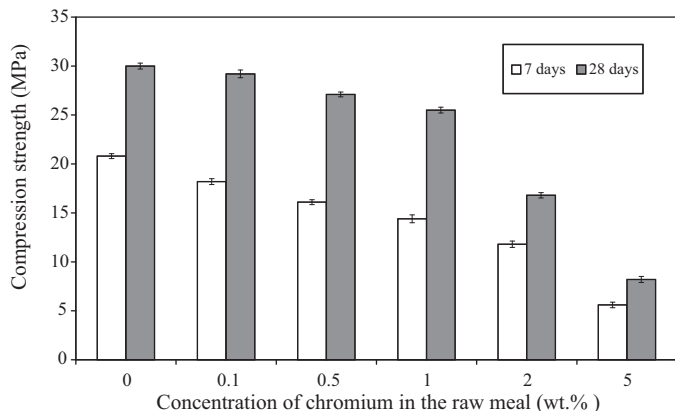


Fig. 8. Compression strength of hydrated cement at 7 and 28 days.

3.3. Behavior of chromium in the leaching process

3.3.1. Speciation of chromium after the leaching process

Mortars were taken after 28 days of curing for the EA NEN 7375:2004 leaching test. Fig. 10 shows the XRD patterns of all mortars investigated after leaching tests. The leached chromium-doped mortars contained calcium silicate hydrates with traces amounts

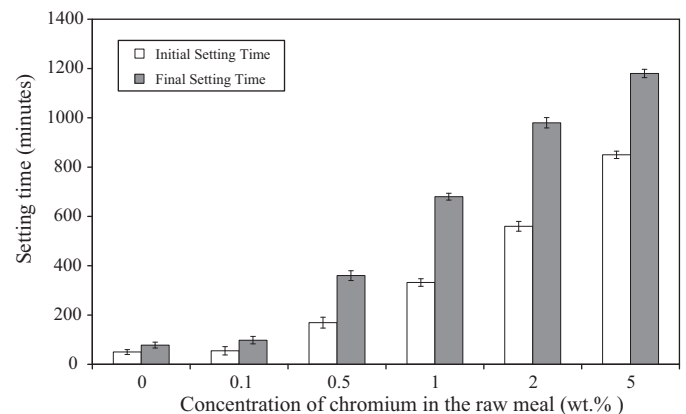


Fig. 9. Effect of chromium on the cement setting time determined using the Vicat needle.

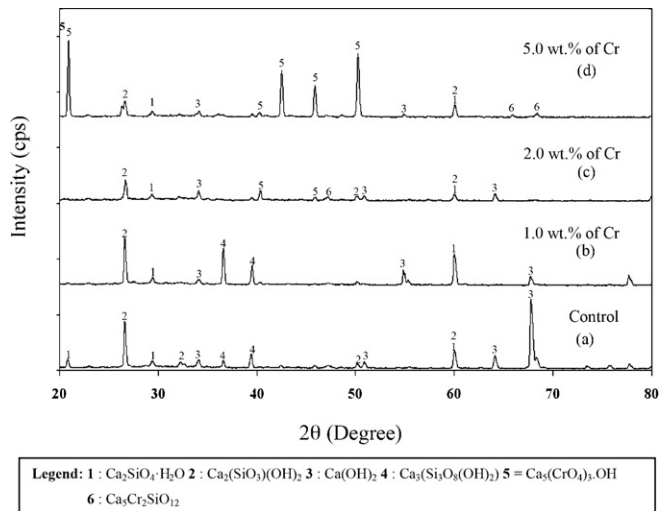


Fig. 10. XRD patterns of the leached mortars at the age of 28 days: control, 1.0 wt.% of Cr, 2.0 wt.% of Cr, 5.0 wt.% of Cr.

of chromium compounds with +4.6 and +5 oxidation states. $\text{Cr}^{4.6+}$ and Cr^{5+} were detected in the form of $\text{Ca}_5(\text{CrO}_4)_3\text{OH}$ and $\text{Ca}_5\text{Cr}_2\text{SiO}_{12}$, respectively. Other compounds such as $\text{Ca}_2\text{SiO}_4\cdot\text{H}_2\text{O}$, $\text{Ca}_2(\text{SiO}_3)(\text{OH})_2$, and $\text{Ca}_3(\text{Si}_3\text{O}_8)(\text{OH})_2$ were also detected in the leached mortar. Chromium species with +3 and +6 oxidation states were found in the leachate, as shown in Table 3. Cr^{6+} was the predominant species, and the amount leached was close to that of the total chromium content. Cr^{3+} and other species of chromium were leached from the cement at lower levels than Cr^{6+} . This behavior can be explained by the different solubilities of the various chromium species; Cr^{6+} is highly soluble compared to Cr^{3+} [28]. It is known that Cr^{3+} is slightly soluble, whereas $\text{Cr}^{4.6+}$ and Cr^{5+} are insoluble; therefore, only Cr^{6+} was found in the leachate at a fraction of approximately 80–90% of the total Cr (Table 3). The low solubility of Cr^{3+} and the other species in the clinker phases was likely the major reason for their low percentage of the total chromium concentration in the control and doped solutions.

3.3.2. Leaching of chromium from mortar

Leaching tests were performed to determine the chromium concentration in the leachant, which can cause environmental problems when the cement product is in use. For chromium-contaminated cement to be used as a construction material, the constituent mortar should not exhibit a leaching behavior typical of a hazardous waste. Because of this consideration, the EA NEN 7375:2004 and TCLP method 1311 (U.S. EPA) leaching tests were used. The leaching results obtained from these tests were compared with U.S. EPA regulations applied to monolithic and powder wastes acceptable at hazardous-waste landfills.

3.3.2.1. TCLP method 1311 (U.S. EPA). The cement mortars were ground to $<125\ \mu\text{m}$ before use in the TCLP tests. This method is

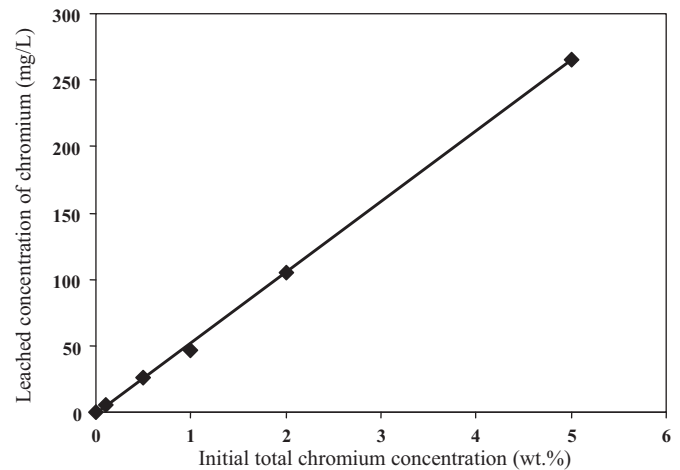


Fig. 11. Average concentration of chromium leached from TCLP.

the U.S. EPA-mandated method for classifying wastes as hazardous or nonhazardous based on toxicity. If the TCLP extract contains any one of the characteristic toxic constituents in an amount equal to or greater than the concentrations specified in 40 CFR 261.24, the waste possesses the characteristics of toxicity and is therefore considered a hazardous waste. The results of the TCLP tests are shown in Fig. 11.

The leached concentrations of chromium exhibited a direct relation to the initial concentrations of chromium. After 18 h of leaching, the amounts of leached chromium detected from concrete prepared with the initial (raw meal) chromium concentrations of 0.1%, 0.5%, 1.0%, 2.0%, and 5.0% were 5.8, 26.3, 46.7, 105.5, and 265.9 mg/L, respectively. According to the U.S. EPA, the allowable concentration of chromium in leachate is less than 5 mg/L. It is evident that chromium concentrations in the extraction fluid (0.1 M acetic acid) were higher than the allowable value in all tests.

3.3.2.2. The tank-test method (EA NEN 7375:2004). The tank-test method (EA NEN 7375:2004) was used to study the release of chromium from monolithic cementitious matrices. This method simulates the leaching of chromium compounds from molded and monolithic materials under aerobic conditions as a function of time. Leaching was investigated over 64 days.

The leaching behavior of chromium under both acidic (pH 3) and neutral (pH 7) conditions is shown in Fig. 12a and b. The leaching of chromium occurred as a two-stage process. The chromium leaching rate was high during the first 7 days of exposure to the simulated acid rain solution. The leaching of chromium in the first stage may occur through a diffusion mechanism that controls the release of the loosely bonded chromium compounds present near the surface of the solid phases. The decrease in the concentration gradient between the liquid and solid phase may cause a small increase of chromium in the leachate in the second stage [28].

Table 3

Leachable fraction of chromium from cement mortar.

Initial concentration of chromium in raw meal (wt.%)	Natural solution				
	Total Cr (mg/L)	Cr^{6+} (mg/L)	% of Cr^{6+} in leachate	Cr^{3+} (mg/L)	% of Cr^{3+} in leachate
Control	–	–	–	–	–
0.1	1.02	0.82	80.39	0.20	19.61
0.5	3.90	3.20	82.05	0.70	17.95
1.0	6.21	5.41	87.12	0.80	12.88
2.0	12.82	11.14	86.90	1.68	13.10
5.0	26.90	24.39	90.67	2.51	9.33

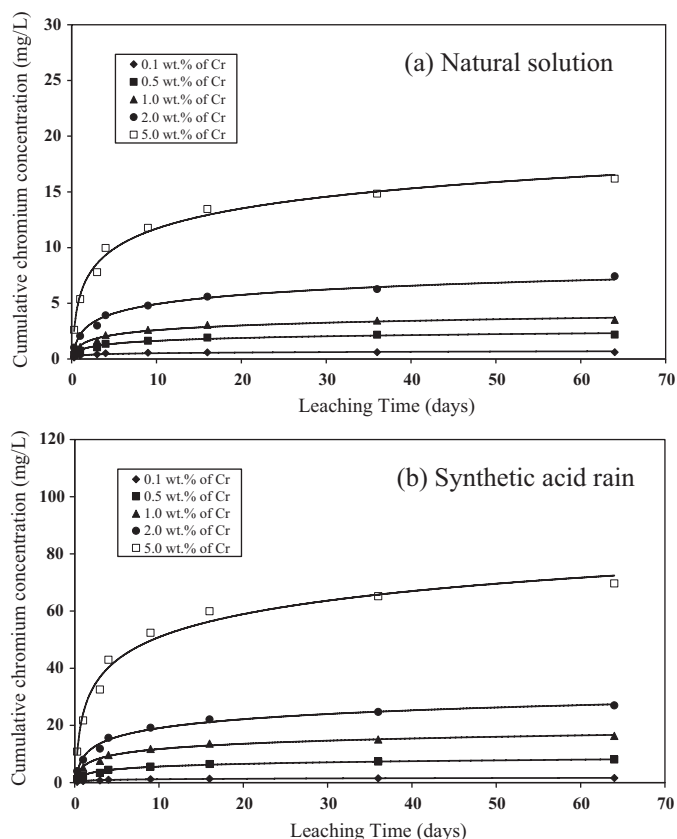


Fig. 12. Cumulative concentration of chromium leached from the hydrated cement with different concentrations of chromium in synthetic acid rain and natural solution.

The leaching rate of both conditions decreased thereafter as exposure time increased. In addition, the cumulative concentration of chromium after 64 days of contact with samples containing 0.1%, 0.5%, 1.0%, 2.0%, and 5.0% chromium was 0.6, 2.2, 3.5, 7.9, and 16.6 mg/L, respectively, in the natural leachate and 1.6, 8.1, 16.4, 27.0, and 69.7 mg/L in the synthetic acid rain leachate (Fig. 12a and b).

EA NEN 7375:2004 was used to determine leaching from the monolithic samples as the criteria for waste acceptance at hazardous waste landfills. According to the Environment Agency of England and Wales, the allowable chromium level in leachate is less than 25 mg/m² [29]. In our experiments, the cumulative leaching of total chromium in the natural leachate was 7, 24, 39, 88, and 184 mg/m², and the leaching in synthetic acid rain leachate was 20, 101, 204, 338, and 871 mg/m² after contact with samples containing 0.1%, 0.5%, 1.0%, 2.0%, and 5.0% of chromium, respectively. The cumulative leaching of chromium in the synthetic acid rain for the cement with chromium higher than 0.1% was higher than the allowable value. In the natural solution, the cumulative leaching of chromium for the samples with chromium higher than 0.5% was higher than the allowable value. From TCLP and the EA NEN 7375:2004 test, it is concluded that waste containing chromium should not be allowed to mix with raw material in cement manufacturing processes.

4. Conclusions

The results of this study show that the addition of chromium with an oxidation state of +3 to typical raw meal for cement production affects not only the composition of the clinker phases produced but also the setting time and the development of the com-

pressive strength of hydrated mixes. The formation of chromium compounds with different chromium oxidation states and the variation of the contents of tricalcium silicate, bicalcium silicate and free lime occur during clinkerization, with lower contents of C₃S compared to levels produced with undoped clinker. As a consequence, changes in the contents of Ca(OH)₂ and CSH are observed for hydrated mortars prepared with chromium-doped cements. The changes in the compressive strength are proportional to the chromium content in the raw meal. The leaching behavior of both the powdered and the monolithic mortars containing chromium, when assessed by the U.S. EPA method 1311 and EA NEN 7375:2004 test methods and judged according to the U.S. EPA and the Environment Agency of England and Wales Standards, indicates that wastes containing chromium should not be mixed with raw materials in the cement manufacturing process.

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