Stabilization of chromium salt in ordinary portland cement

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Abstract. Ordinary Portland cement (OPC) samples containing the chromium salt have been investigated using differential microcalorimetry, conductometry and Fourier transform infrared spectroscopic analysis. The effect of chromium on OPC hydration was evaluated by continuous observing of early hydration. The microcalorimetrical results show that with increasing the share of chromium salt, heat maximums assume lower values and the occurrence of the maximum registered in the earlier hydration times. Conductometrical measurements show that with increasing addition of chromium salt, curve did not show any specific shape, immediate drop in specific conductivity is noticed and the maximum is reached earlier. This coincides with microcalorimetrical results. It can be concluded that the addition of chromium does not affect the mechanism of the hydration process, but it does affect the kinetic parameters and dynamics of the cement hydration process. It was found that chromium salt addition to the cement–water system is acceptable up to 2 wt.%. According to standard EN 196-3 for OPC, the beginning of binding time should occur after 60 minutes. Increased amount of chromium over 2 wt.% significantly accelerate the beginning of binding time and for the system it is not acceptable.

Keywords. Stabilization/solidification; ordinary portland cement; ammonium dichromate; differential microcalorimetry; conductometry; Fourier transform infrared spectroscopy.

1. Introduction

The stabilization/solidification process of the chromium wastes generated from steel production, chrome plating, pigments and leather tanning industries is an important and complex issue (EPA 1994; Spence & Shi 2005). Among the various forms of chromium, Cr(VI) is the most important one because of its toxicity, solubility and mobility (Katz & Salem 1994; Bartlett 1991). Cr(VI) is a strong oxidizing agent and it is toxic to human, animals and plants and classified as a carcinogen (Wang & Vipulanandan 2000; Shi & Kan 2009).

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Portland cement (OPC) is often used as the binding agent on its own, or in combination with cement replacement materials, which may be hydraulic (cement kiln dust) or pozzolanic (pulverized fuel ash, slag, etc.) in nature (Taylor 1997). The use of cementitious materials can significantly reduce the release of toxic species by providing an environment of high alkalinity. In many cases, there are complex interactions between waste components and binders (inhibiting or accelerating the normal hydration reaction) (Giergiczny & Krol 2008).

Many studies have shown the effect of chromium on the Portland cement matrix. The study indicates that chromium is easily incorporated to the β-C_2S and common Portland cement pastes, but this affects the characteristics and the hydration products (Trezza & Scian 2007). Otomoso *et al* (1995) investigated chromium stabilization in tricalcium silicate and they concluded that addition of Cr(III) accelerates the tricalcium silicate hydration until the Cr(IV) does not have any effect. Wang & Vipulanandan (2000) concluded that addition of Cr(VI) in the form K_2CrO_4 extended the initial and final setting time and decreased the compressive strength. Zamorani *et al* (1989) discovered that low Cr(III) levels in cement system accelerated the setting time. Pera *et al* (1997) notified that the immobilization of Cr(VI) by hydraulic binders takes place by one or a combination of the following mechanisms: addition, substitution or precipitation of new components. Results show that Portland cement is the most efficient binder.

This paper has examined the effect of chromium salt on the hydration processes using different methods: differential microcalorimetry, conductometry and FTIR analysis. The main aim of this study is to determine an acceptable content of chromium salt in the cement system for its successful stabilization and solidification.

2. Materials and methods

2.1 *Materials and sample preparation*

All the measurements were carried on using ordinary Portland cement (OPC) and different content of ammonium dichromate. OPC (according to EN-197 CEM I) was obtained from CEMEX Croatia cement plant (Kaštel Sućurac, Croatia). Its chemical composition and physical properties are shown in tables 1 and 2. Ammonium dichromate, $(NH_4)_2Cr_2O_7$, p.a., was obtained from Kemika plant, Zagreb, Croatia.

Samples for microcalorimetrical measurements were prepared by mixing cement and 0, 1, 2, 3, 4 and 5 wt.% of ammonium dichromate. The total mass of the solid sample was constant and

Table 1. Chemical composition of OPC.

Composition	(%)
SiO_2	22.85
Al_2O_3	4.81
Fe_2O_3	2.79
CaO	65.23
MgO	1.61
K_2O	1.89
Na_2O	0.18
Loss of ignition	0.04

Table 2. Physical and mechanical properties of OPC.

Physical property	Value
Specific surface according to Blaine ($cm^2 g^{-1}$)	3300
Standard consistency (%)	26
Setting time – start (min)	85
Setting time – end (min)	150
Average flexural strength (MPa)	
after 3 days	6.26
after 28 days	8.44
Average compressive strength (MPa)	
after 3 days	33.5
after 28 days	50.7

it was 4 g. A water to solid ratio of 0.5 was used for all mixes and measurements were carried out at a temperature of 20°C.

Samples for conductometrical measurements were prepared in the same way as the samples for microcalorimetrical measurements, exept the total mass of the solid sample was 100 g.

Cement pastes for FTIR analysis were hydrated 28 days in a thermostat at a temperature of 20°C. After this curing time they were ground and sieved through a standard 4900 mesh/cm^2 sieve.

2.2 *Methods*

2.2a *Differential microcalorimetry*:   The microcalorimetrical measurements used to examine the interferences with a waste stabilization process were conducted by means of a differential microcalorimeter of the conduction-isoperibolic type (Krstulović *et al* 1989). An ALMEMO 2290-8 data logger was used to register heat effects of the hydration processes in the microcalorimeter, monitoring the change of voltage d$U = f(t)$. The recorded values were processed by a computer program on a computer, obtaining the values of the hydration heat, the relative reaction degree, and the heat release rate for the given hydration conditions.

2.2b *Conductivity*:   The conductometrical measurements were conducted by means of an ISKRA MA 5964 microprocessor conductometer connected to a computer via a RS 232 C digital output. The conductometrical cell electrode was made of stainless steel with a constant C = 0.285 cm^{-1}.

2.2c *Fourier-transform infrared spectroscopy (FTIR)*:   FTIR was performed with a Perkin Elmer Spectrum One spectrometer. Optically transparent discs were prepared in the mini-press from powdered samples mixed with KBr. The scanning range was from 4000 to 450 cm^{-1} and the number of scans were 10 at a resolution of 4 cm^{-1}.

3. Results and discussion

In this study, the effect of Cr(VI) on OPC hydration was evaluated by continuous observing of early hydration. For these measurements microcalorimetry was applied, which monitors
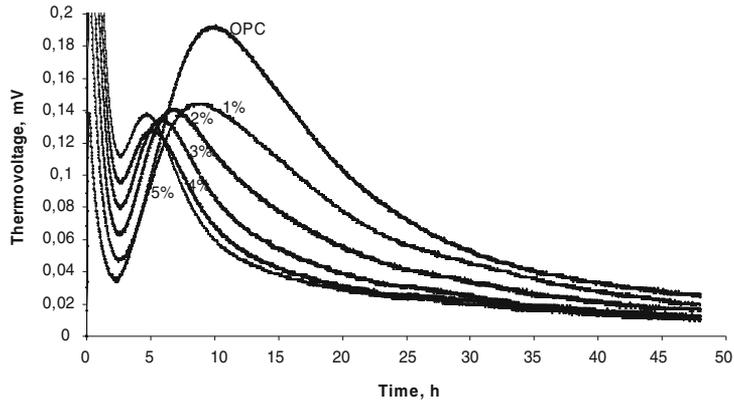
Figure 1. Thermovoltage curves for cement samples with different addition of chromium salt.

heat released during hydration. The released heat causes the operating cell of a differential microcalorimeter for a difference of temperatures between the operating and the referent cell, measured as voltage difference, dU, by thermocouples.

Figure 1 shows the thermovoltage curves for cement samples with different addition of chromium salt. The curves obtained on thermovoltage are very pronounced second maximum. Increasing the content of chromium salt maximums assume lower values and the occurrence of the maximum registered in the earlier hydration times.

As can be seen, the basic shapes of the termovoltage curves with the additions are very similar to the curve for the sample of OPC without addition. This indicates that the chromium salt does not affect the hydration mechanisms and processes of stabilization. The OPC pastes without addition show the highest values for heat of hydration ($Q = 192$ J/g) after 48 h of hydration and reaches its maximum after 10.63 h. Cement composites with maximum content of chromium salt show the lowest values for heat of hydration ($Q = 115.91$ J/g) and the maximum is reached after 4.97 h of hydration.
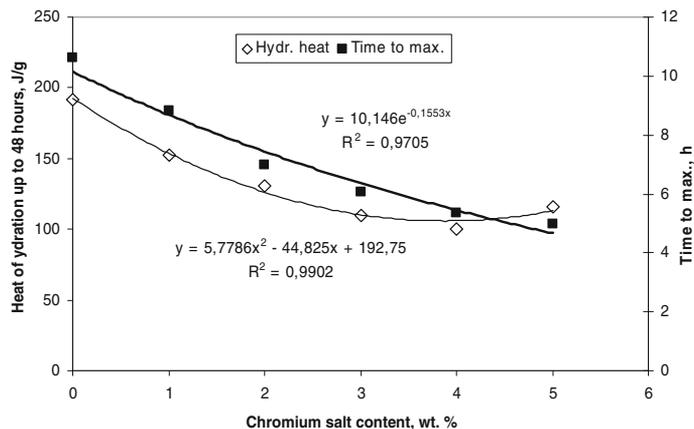
Figure 2. Heat of hydration up to 48 h and time to maximum relative to the content of chromium salt.
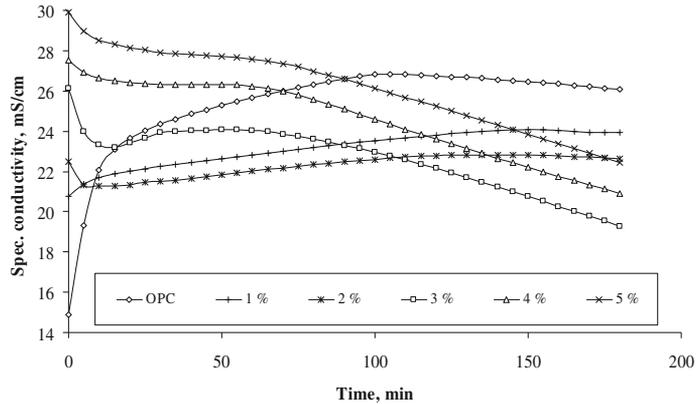
Figure 3. Dependence of conductivity on the hydration time of cement pastes with addition of chromium salt.

The analysis of data from figure 2 yielded a mathematical relation of maximum heat of hydration relative to the addition of content.

For the addition of chromium salt, the function of heat of hydration has the form $y = 5.7786x^2 - 44.825x + 192.75$, where y is the maximum heat released (J/g) and x represents addition of chromium salt in wt.%. Time to heat maximum can be calculated by the equation $z = 10.146e^{-0.1553x}$, where z is the time in hours, and x is the addition of content.

The results show that the chromium salt has a strong effect on the hydration processes and reactions. The main reason is the slow nucleation of hydration products in the outer, preliminary dissolved layer, and low, gradually growing up concentration of ions in the surrounding liquid phase. Subsequently, the induction period is followed by the acceleration of hydration due to the crystallization of hydrates and further decomposition of anhydrous substance.

Conductometrical measurements were carried out to determine the initial bonding time of the cement composites, as a parameter for judging the success solidification and stabilization of chromium salt (EN 196-3), which is reflected by the appearance of a maximum in specific conductivity curves (figure 3). According to standard EN 196-3 for OPC, the beginning of binding

Table 3. Time to occurrence of maximum conductivity for various addition of chromium salt.

Addition of chromium (wt.%)	Time to occurrence of maximum conductivity (min)
0	105
1	150
2	145
3	50
4	50
5	45

Figure 4. FTIR spectra of cement pastes with addition of chromium salt.

time should occur after 60 minutes. For the practical application, the end of binding time should happen in time below 200 minutes.

It can be seen that with increasing addition of chromium salt, no peaks are observed in the curve, specific conductivity immediately drops and the maximum is reached soon. Microcalori-metrical results show that addition of chromium salt in the cement–water system is acceptable up to 2 wt.% (table 3). Increased contents of chromium over 2 wt.% significantly accelerate the beginning of binding time and for the system which is not acceptable.

FTIR data show that changes in the silicate and carbonate phases when chromium salt is mixed with OPC (figure 4).

The results show very sharp peak at 3645 cm^{-1}. This is attributed to the O–H stretching of Ca(OH)$_2$ (Bensted & Varna 1974). The band of 3450 cm^{-1} is caused by the symmetric and asymmetric stretching of the water molecules. The band at 1645 cm^{-1} corresponds to the defor-mation mode of the molecular water. Additional bands at approximately 1425, 1497, 875 and 732 cm^{-1} correspond to υ_3, υ_2 and υ_4 CO$_3^{2-}$. Comparing the bands of silicate in the range 969–987 cm^{-1} for samples with and without addition of chromium salt it shows that υ_3 SiO$_4^{4-}$ bands shifted to higher frequencies suggesting a slightly higher degree of polymerization of the silicate units in the presence of chromium. But, it is difficult to draw conclusions from the FTIR results.

4. Conclusions

In this study, the effect of Cr(VI) on OPC hydration was evaluated by continuous observing of early hydration. The microcalorimetrical results show that with increasing the content of chromium salt, heat maximums assume lower values and they are registered in the earlier hydra-tion times. Conductometrical measurements show that with increasing addition of chromium salt, curve did not show a specific shape, specific conductivity immediately drops and the maxi-mum is reached soon. This coincides with microcalorimetrical results. The addition of chromium does not affect the mechanism of the hydration process, but it does affect the kinetic parameters and dynamics of the cement hydration process. It was found that chromium salt addition to the

cement–water system is acceptable up to 2 wt.%. Increased shares of chromium over 2 wt.% significantly accelerate the beginning of binding time and it is not acceptable for the system.

Acknowledgements

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