

CALORIMETRIC STUDIES OF CEMENTITIOUS MATERIALS – CHROMIUM INTERACTION

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Abstract

Cementitious systems based on portland cement are used for immobilization of toxic and hazardous wastes. The addition of waste material may impact the hydration reaction in cement matrix and consequently the setting and hardening process. The progress of reaction can be monitored by heat evolution measurements and the calorimetric results can indicate the declination from standard behaviour.

In this study the microcalorimetry was used to evaluate the heat output during the hydration of cements in the presence of different chromium containing salts, viz. CrCl_3 , $\text{Cr}_2(\text{SO}_4)_3$, Na_2CrO_4 and K_2CrO_4 .

Keywords: cement, chromium, heat of hydration, hydration, immobilization

Introduction

The use of cements in heavy metals immobilization is widely reported [1–3]. Cementitious materials react with water to yield number of hydrate phases with low solubility [4]. Some of them – so-called calcium silicate hydrates – exhibit disordered, near amorphous structure and high surface area ($> 100 \text{ m}^2 \text{ g}^{-1}$); those are capable to stabilize the heavy metal compounds by sorption and lattice incorporation. The others – calcium hydroxide and tricalcium sulfoaluminate hydrate (so-called ettringite) – show ordered structure. Some heavy metal ions enter the structure of crystalline hydration products and form stable solid solutions. The precipitation of hydroxides or other phases takes place under the high *pH* in the liquid phase of hydrating paste. The solidification arises also from the physical barrier effect; the matrix is microporous but less susceptible to leaching as it would result from its structure. The waste materials modify less or more the setting and hardening process of the matrix. Most of them has no definite influence particularly while occur in low concentration, but some of them act as set retarders or accelerators [5]. The effect depends also upon the presence of accompanying chemical species [6]. Generally, strong accelerators or retarders affect microstructure and permeability of hardened matrix giving rise to hydration products different from those occurring in cement paste without admixtures.

Chromium is widespread in industrial and municipal wastes [3]. Cr(III) is very well immobilized in cement paste owing to the $\text{Cr}(\text{OH})_3$ precipitation mechanism

but Cr(VI) which occurs in the form of relatively soluble chromates, not as well. The mechanism of Cr(VI) immobilization in cement paste is not fully explained [3, 7]. The substitution for sulfate in ettringite is one possible mechanism of chromate immobilization, however, this requires a high concentration of chromate ions present in pore liquid, being in equilibrium with solid. Fortunately, in most cases Cr(VI) is readily reduced to Cr(III) and the reducing conditions occur very often in "naturally" produced wastes. The reduced Cr(III) can be immobilized, as it has been mentioned earlier in the form of insoluble, crystalline $\text{Cr}(\text{OH})_3$. However, the $\text{Cr}(\text{OH})_3$ precipitate "in statu nascendi" is amorphous, better soluble and crystallizes slowly. The amorphous material reacts with hydrated aluminate phases and can be easily incorporated to their structure. These aluminate phases, in turn, react with chlorides, sulfates, carbonates and the other salts when exposed to the attack of solutions. Such a situation may occur in natural, disposal environment, in contact with ground water.

The accelerating effect of some chromium compounds (chromates, chromium chloride, nitrate) on the reaction of the main cement phases with water is known [6, 8]. This effect is explained in different ways. The influence of other Cr compounds is not documented. In the light of the data given briefly above, it seems worthwhile to follow the hydration of cement in the presence of CrCl_3 and $\text{Cr}_2(\text{SO}_4)_3$. The effect of chlorine and sulfate ions which interfere in the hydration of aluminate and silicate phase can be thus monitored.

The influence of heavy metal containing compounds can be preliminary evaluated by use of calorimetry [9]. This method gives not only the view on the hydration kinetics but also on the hydration mechanism. It can be applied to predict the development of strength, stresses and risk of early thermal crackings. The calorimetric experiments on cement hydrated with Na_2CrO_4 , K_2CrO_4 , $\text{Cr}_2(\text{SO}_4)_3$ and CrCl_3 solutions were carried out to evaluate the differences in the hydration kinetics and to discuss the possible mechanism of Cr immobilization, as well as cement phases - Cr compounds interaction.

Experimental

The normal portland cement class 35 was used in the investigations. The 0.5%, 1%, 3% and 6% solutions of Na_2CrO_4 , K_2CrO_4 , $\text{Cr}_2(\text{SO}_4)_3$ and CrCl_3 were used in the hydrated pastes preparation. The distilled water was used to produce the reference sample. The heat evolution measurements were carried out through the use of differential microcalorimeter type BMR (constructed in the Institute of Physical Chemistry, Polish Academy of Science). For this purpose the pastes of the liquid to solid ratio equal 0.5 were mixed. The starting temperature was kept constant at 25°C.

Results and discussion

The calorimetric curves are presented in Figs 1-4 and the heat evolved values in Table 1. The values measured for cement paste are typical for cement of good quality. The admixtures introduced to the hydrating paste accelerate generally the heat

Table 1 Calculated heat evolved during 24 and 72 h hydration of cement in the solutions of chromium compounds

Admixture	%	Heat evolved in kJ kg ⁻¹	
		after 24 h	after 72 h
Reference sample		223	322
Na ₂ CrO ₄	0.5	233	318
	1	232	318
	3	257	343
	6	274	373
K ₂ CrO ₄	0.5	222	364
	1	254	398
	3	260	381
	6	289	360
Cr ₂ (SO ₄) ₃	0.5	242	367
	1	235	347
	3	242	315
	6	167	318
CrCl ₃	0.5	275	405
	1	276	400
	3	258	347
	6	267	389

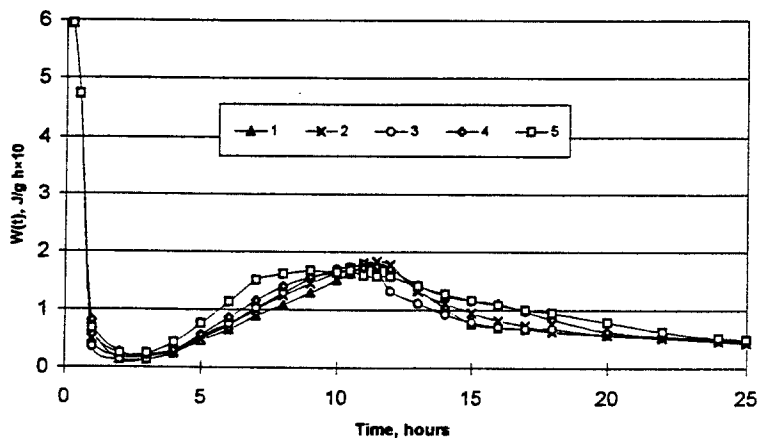


Fig. 1 Calorimetric curves of cement in Na₂CrO₄ solutions of varying concentrations: 1 – reference, 2 – 0.5%, 3 – 1%, 4 – 3%, 5 – 6%

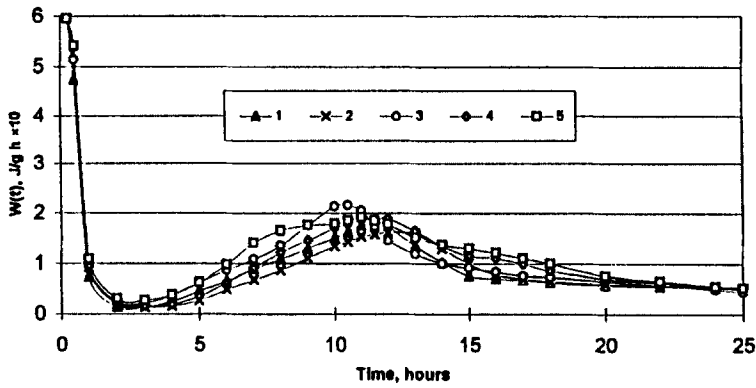


Fig. 2 Calorimetric curves of cement in K_2CrO_4 solutions of varying concentrations: 1 – reference, 2 – 0.5%, 3 – 1%, 4 – 3%, 5 – 6%

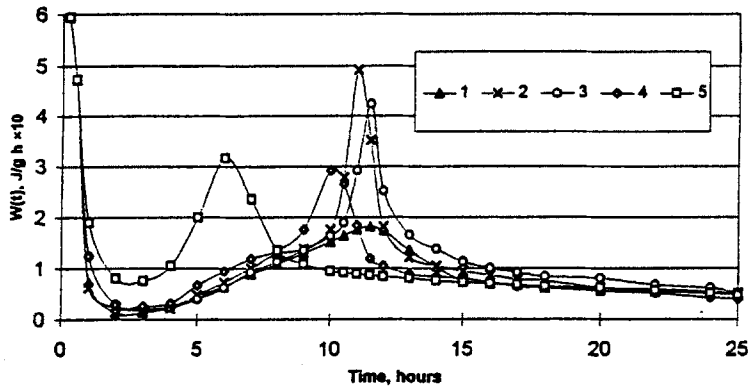


Fig. 3 Calorimetric curves of cement in $Cr_2(SO_4)_3$ solutions of varying concentrations: 1 – reference, 2 – 0.5%, 3 – 1%, 4 – 3%, 5 – 6%

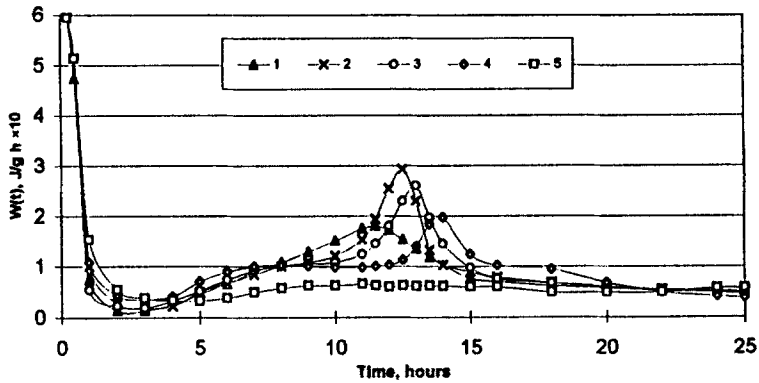


Fig. 4 Calorimetric curves of cement in $CrCl_3$ solutions of varying concentrations: 1 – reference, 2 – 0.5%, 3 – 1%, 4 – 3%, 5 – 6%

evolved on hydration. The shape of calorimetric curves is not specially affected by the presence of chromates. After a high first peak, responsible for initial sorption of liquid and dissolution of anhydrous material, a few hours so-called induction or dormant period occurs, in which the rate of heat evolution is very low. This is because of 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, accompanied by the rate of heat evolution increase. After a maximum the heat evolution curves fall down – the process becomes diffusion controlled and the rates of particular reactions decrease.

As one can notice, the highest 6% concentrations of chromates clearly accelerate the hydration of cement in the post-induction period but simultaneously a thick layer of hydration products covers the hydrated grains – the peaks are lower and broadened. In the presence of alkaline chromates not only the solid solution of sulfoaluminate with chromate ions is produced but also the calcium silicate hydration is accelerated.

The heat evolution process on cement hydration is significantly affected by the presence of chromium chloride and chromium sulfate. It is evident that the mechanism of CrCl_3 and $\text{Cr}_2(\text{SO}_4)_3$ interaction show some similarity and differences.

The sulfate anions from $\text{Cr}_2(\text{SO}_4)_3$, while occur at small concentrations, accelerate the hydration of aluminate phase with gypsum in cement, as it can be visualized by a sharp third peak on the heat evolution curves. However, the formation of $\text{Cr}(\text{OH})_3$ takes place simultaneously and the insoluble hydroxide layer cuts off the access of water to the anhydrous material. At higher concentration, the sulfate ions do not promote the hydration process, but probably favourize the growth of impermeable coating, producing gypsum crystals in reaction with calcium ions, originating from hydrolysis of silicates. At 6% $\text{Cr}_2(\text{SO}_4)_3$ addition the hydration is significantly retarded – the second heat evolution peak is flattened, the third one does not appear. The total heat evolved after 24 h is low. However, further diffusion is rather intense, resulting in fairly high heat evolved after 3 days of reaction. It seems that the chromium hydroxide produced in strongly basic cement paste environment is relatively stable and does not react readily with the aluminate hydration products. This is one important reason that Cr(III) is effectively immobilized in cement grout.

The “competition” mechanism between the cationic and anionic part is also observed in the case of CrCl_3 addition. It is clearly seen that the reaction of aluminate and sulfate phase from cement is strongly accelerated by Cl ions from the solution as it has been reported for CaCl_2 , and the chloride analogues of ettringite must be subsequently formed. At 6% CrCl_3 the second and third peak interfere and only the second rather high and sharp peak is seen on the heat evolution curve, after a shortened induction period in which the rate of heat evolution is relatively high. It means that at 6% CrCl_3 the silicate components of cement are easily dissolved and Cr ions enter the calcium silicate hydrate structure.

Conclusion

1 The chromium containing inorganic salts accelerate generally the hydration of cement.

2 As it results from the course of heat evolution curves, the chromates accelerate the hydration process without significant changes in the hydration mechanism.

3 Cr(III) containing salts affect the mechanism of cement hydration depending on the type of accompanying anion:

– Cr₂(SO₄)₃ at low concentrations accelerate the hydration of aluminate phase, at higher concentration acts as a retarder;

– CrCl₃ accelerate the hydration of aluminates and silicates.

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