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Application of calorimetry in studies of the immobilization of heavy metals in cementitious materials ☆

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Abstract

Cementitious systems based on blends of normal portland cement with different materials are used for the treatment and conditioning of toxic and hazardous wastes. The addition of waste material may interfere with the hydration reaction in the cement matrix and consequently with the setting and with hardening process. Some of the waste materials accelerate the hydration process, others act as set retarders. The progress of hydration can be monitored by heat evolution measurements and the calorimetric results are considered as indicators of the degree of hydration. In this study microcalorimetry was used to evaluate the heat output during the hydration of cement and of blends of cement and blast furnace slag treated with solutions of heavy metals.

Keywords: Blast furnace slag; Cement hydration; Cementitious materials; Hazardous waste; Heavy metals; Microcalorimetry; Waste disposal

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1. Introduction

The use of normal portland cement and blended cements to immobilize heavy metals is well documented [1, 2]. The wastes to be immobilized can be introduced as liquids, sludges or dusts to the hydrating grout. Cementitious materials react with water to yield a number of hydrate phases of low solubility, which are capable of stabilizing the heavy metal compounds by sorption, lattice incorporation or precipitation. The

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precipitation of hydroxides or other phases takes place at the high pH in the liquid phase of the hydrating paste. The solidification arises also from the physical barrier effect; the matrix is microporous but less susceptible to leaching than would be expected from its structure. To a greater or lesser extent the waste materials modify the setting and hardening process of the matrix. Most of them have no definite influence, particularly when present at low concentrations, but some act as strong set retarders. The effect depends very often upon the presence of accompanying chemical species. Generally, strong accelerators or retarders affect the microstructure and permeability of the hardened matrix giving rise to hydration products different from those occurring in cement paste without admixtures. The Cr, Pb, Cd and Zn compounds used in the study are successfully immobilized in normal portland cement matrix [3–6]. Chromium is widespread in industrial and municipal wastes. Cr(III) is very well immobilized in cement paste, owing to the $Cr(OH)_3$ precipitation mechanism, but Cr(VI) not as well. The mechanism of Cr(VI) immobilization in cement paste is not fully explained. Cr compounds are known as hydration accelerators.

Pb, Cd and Zn react with the hydrating cement constituents forming more or less insoluble compounds, hydroxides or carbonates, precipitating on cement grains and thus hindering the access of water. In the case of Zn zinc silicates can also appear. Lead and cadmium compounds generally act both as hydration and set retarders; zinc promotes rapid setting, which is not equivalent to proper hydration and hardening.

In a highly alkaline cement paste environment the elements discussed in the paper can exhibit amphoteric character and consequently an increase in solubility. On the other hand, the accompanying anions may cause positive changes of the chemical immobilization potential. The influence of heavy-metal-containing compounds can be evaluated by use of calorimetry. This method gives not only information about hydration kinetics but also can be applied to predict the development of strength, stresses and risk of early thermal cracking. The substitution of cement in whole or in part by slag reduces the heat evolved on hydration, but, on the other hand, increases the sensitivity of the matrix to the action of foreign admixtures. Calorimetric experiments on cement and cement–slag blends hydrated with Na_2CrO_4, $Zn(NO_3)_2$, $Pb(NO_3)_2$ and $CdCl_2$ solutions were carried out to evaluate differences in hydration kinetics and to discuss the predicted microstructural and permeability characteristics.

2. Experimental

Normal portland cement from the Górażdże in Poland was used in the investigations. Blends of this cement with the ground, granulated blast furnace slag from the metallurgical plant in Kraków were also prepared in the mix proportion 50:50. Solutions (1%, 3% and 6%) of Na_2CrO_4, $Zn(NO_3)_2$, $Pb(NO_3)_2$ and $CdCl_2$ were used to prepare the hydrated pastes.

Heat evolution measurements were carried out by use of a differential microcalorimeter type BMR (constructed in the Institute of Physical Chemistry, Polish Academy of Science). For this purpose the pastes of 0.5 liquid-to-solid ratio were mixed. The starting temperature was kept constant at 25°C.

3. Results and discussion

The calorimetric curves are presented in Figs. 1–6 and the heat evolved values in Table 1. The values measured for pure cement paste and the cement–slag blend are typical of cement of good quality and cement "diluted" with active slag. The admixtures introduced to the hydrating paste change the heat-evolved values and the rate of heat evolution.

It is clearly seen that, among the heavy metals compounds used in this study, only sodium chromate accelerates the heat evolution output, both for the pure cement and cement–slag blend. As the percentage of admixture increases, a change of hydration mechanism takes place—the two main peaks corresponding to aluminate and silicate hydration tend to interfere. This means that the secondary hydration of aluminate compound can start earlier and proceeds simultaneously with the accelerated reaction of the silicate phase with water. The presence of chromates does not disturb the slag activation process. Zinc generally promotes rapid setting which is not equivalent to the proper, moderate setting and strength development. The heat evolution curve in the presence of zinc nitrate consists of the high and broad effect corresponding to an early stage exothermic reaction. The formation of zinc-containing hydration products on takes place cement grains and these products cut off the access of water to the interior of the material. Because of the impermeability of this product layer, heat liberation stops within a few hours. Consequently the degree of hydration and strength become low.

This topochemical process occurs both in cement and in cement–slag paste. Lead and cadmium compounds reduce the rate of heat evolution but hydration is not

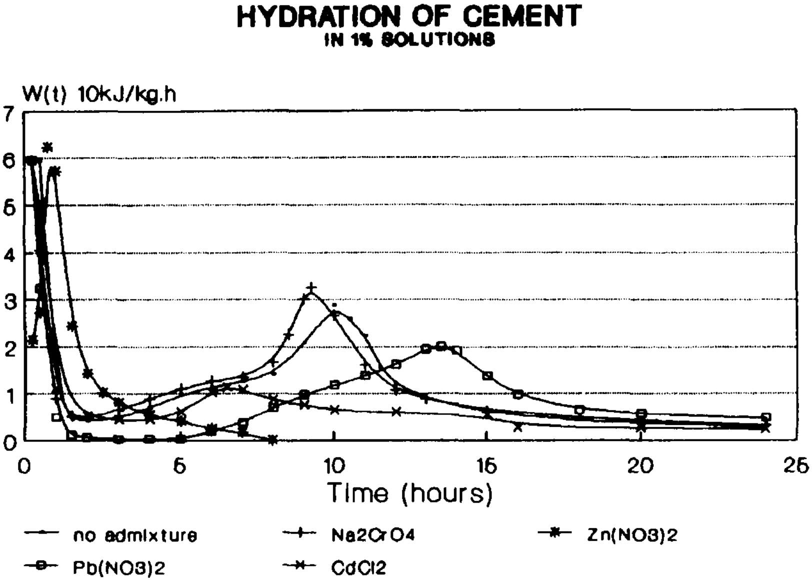

Fig. 1. Calorimetric curves of cement containing 1% solutions of Cr, Zn, Pb and Cd compounds.

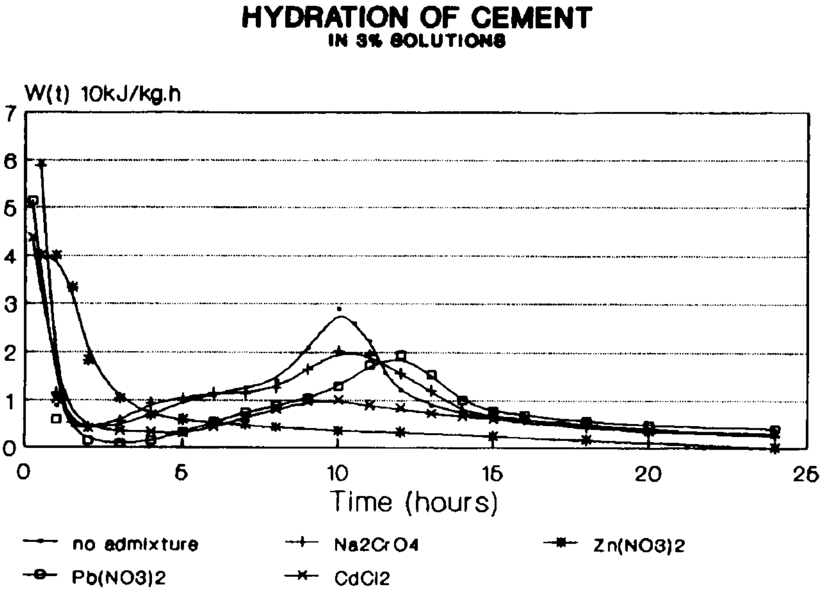

Fig. 2. Calorimetric curves of cement containing 3% solutions of Cr, Zn, Pb and Cd compounds.

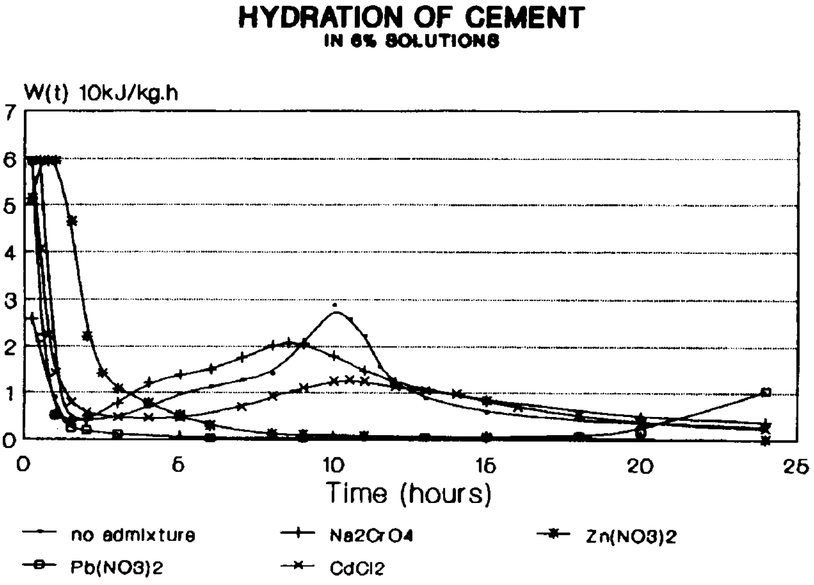

Fig. 3. Calorimetric curves of cement containing 6% solutions of Cr, Zn, Pb and Cd compounds.

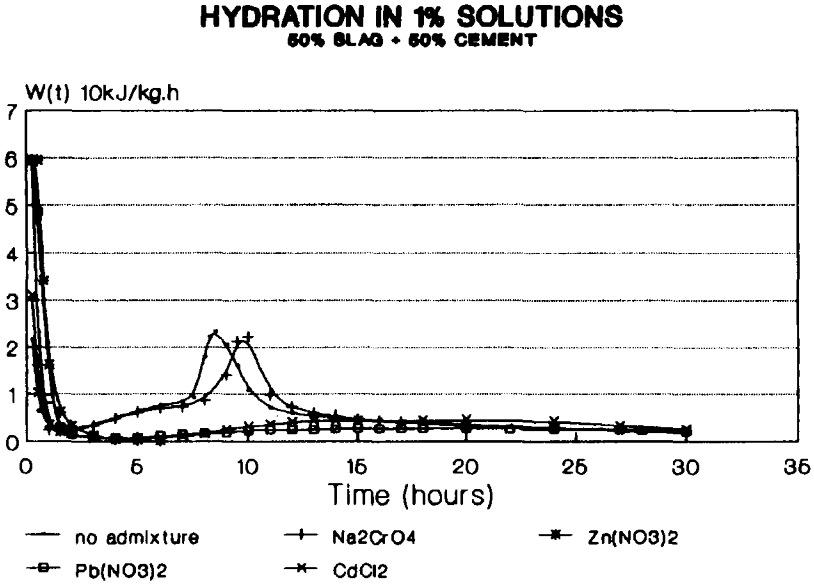

Fig. 4. Calorimetric curves of slag+cement blends containing 1% solutions of Cr, Zn, Pb and Cd compounds.

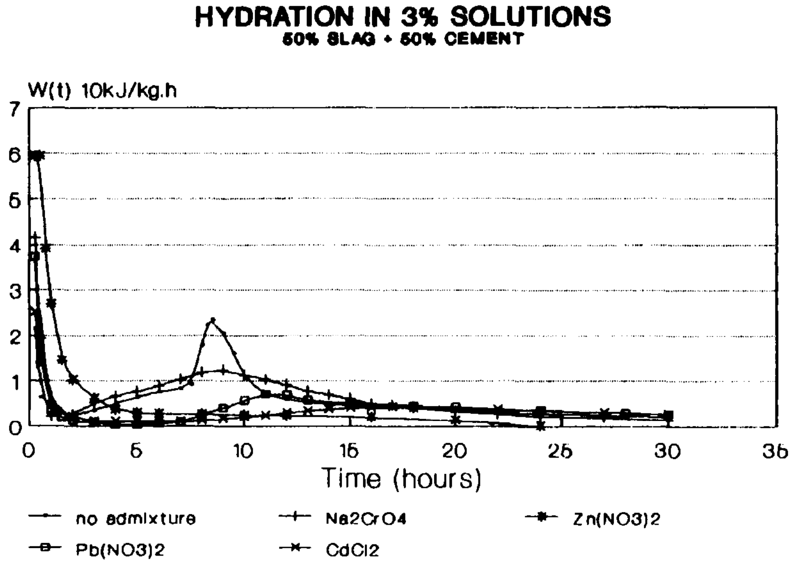

Fig. 5. Calorimetric curves of slag+cement blends containing 3% solutions of Cr, Zn, Pb and Cd compounds.

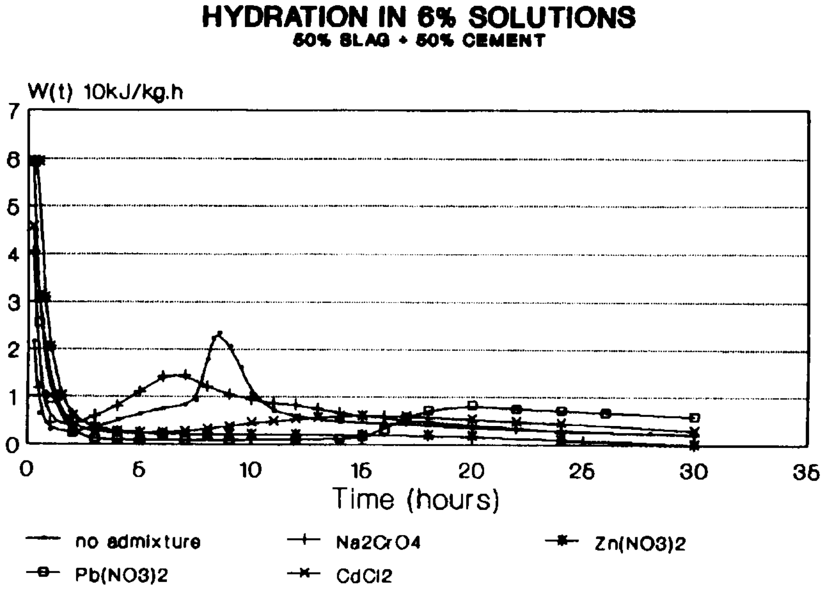

Fig. 6. Calorimetric curves of slag + cement blends containing 6% solutions of Cr, Zn, Pb and Cd compounds.

Table 1
Calculated heat evolved during 24 h hydration of cement and cement + blast furnace slag pastes containing solutions of heavy metals compounds

Admixture	[%]	Heat evolved during 24 h hydration in kJ kg^{-1}	
		Cement paste	Cement + slag paste
Reference samples		242	155
	1	257	163
Na_2CrO_4	3	238	165
	6	253	184
	1	94	50
$Zn(NO_3)_2$	3	151	115
	6	149	106
	1	206	104
$Pb(NO_3)_2$	3	200	103
	6	164	110
	1	160	87
$CdCl_2$	3	158	79
	6	196	136

interrupted. A very slow reaction takes place for a long time. The rate of diffusion through a thin layer of insoluble hydroxides is a hydration progress controlling agent.

Cadmium seems to act as a stronger set retarder than lead though the chloride ions express their accelerating action at higher concentrations. In both cases the slag activation process is decelerated. These results correspond well with reports on compressive strength reduction and fairly good immobilization of Cd and Pb in cement pastes.

4. Conclusions

1) Sodium chromate immobilized in cement or in slag–cement pastes accelerates the hydration of aluminate and silicate phases in the cement.
2) Zinc nitrate reacts rapidly with cementitious materials with the formation of an impermeable layer of hydration products.
3) Soluble lead and cadmium salts bring about a substantial reduction in the hydration rate.

Acknowledgement

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