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CALORIMETRY IN THE STUDIES OF CEMENT–Pb COMPOUNDS INTERACTION

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The effect of PbO on cement hydration kinetics by calorimetric method was evaluated as a first step in this project. Substantial retardation of reaction with water at early stages with subsequent intensification of the process was found. As the next step, the model systems covering pure cement minerals and their mixtures of various composition as well as soluble Pb salts were taken into account to elucidate the mechanism of delayed, by quite good formation of products in the so-called post-induction period. The precipitation of sulphate, forming very thin impermeable layer seems to be responsible for this delaying effect in case of cement, however the other reactions of Pb compounds in alkaline environment of hydrating calcium silicate are not out of importance. In order to prove this, the studies of chemical composition in small areas were also carried out.

Keywords: *calorimetry, cement, hydration, immobilization, lead*

Introduction

The interaction of cement paste/concrete mixture with heavy metals containing compounds have been investigated for a long time in several aspects [1–5]. The detailed studies focused mainly on immobilization of these materials in cement matrix [2–5]. They are introduced with waste materials used in cement/concrete production, for example with fly ash of different origin (municipal wastes combustion or other residues after burning). Among the heavy metals found in these materials the lead(II) oxide (PbO) most frequently appear, but the other compounds, such as sulfates, chlorides and nitrates are also evidenced. As it is well known, the latter ones show better solubility in water than PbO.

However, heavy metal compounds affects strongly setting, hardening as well as durability of cement paste/hardened material. As it has been reported over 30 years ago, small amounts of solid PbO or ZnO added to cement paste retard strongly the hydration process [1]. This effect has been attributed to the formation of impermeable layer of products – heavy metal hydroxides or amphoteric salts produced in the reaction between the oxides and C_3S. The calorimetric studies revealed prolonged dormant period with many hours shift of the second heat evolution peak [1]. The author did not found full explanation of this serious retarding effect. The retarding effect of Pb or heavy metal compounds (salts) on cement hydration was also proved in some later works [6–8].

Further on the effect of heavy metals was studied from the point of view of their immobilization in hardened cement matrix [2–5]. The researchers focused on the studies of stabilization mechanism and leaching of heavy metals from different cement based materials. A very high degree of Pb immobilization was reported as well as the formation of highly disordered C–S–H in the presence of heavy metal compounds was found [6, 9].

As it results from our earlier work [9], PbO gives neither the effect on the so-called water demand (standard water to cement ratio) at the beginning of hydration nor produces the expansive products (volume changes determination). The setting process is clearly disturbed with PbO additive above 0.5% PbO. Further on PbO additive up to 0.5% gives generally no retarding effect on strength development. One can even notice a slight strength increase as compared to the control sample. At higher amount a delayed hardening at early age is observed (at 1% and more PbO it is impossible to de-cast the standard bars after 24 h).

It seems that the effect of PbO on cement/concrete hardening deals generally with alite hydration but there are also some other aspects. The studies presented in this paper, carried out initially on cement samples and continued further on using alite samples or the other mixtures with alite as a main component, put some new light on the problem.

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Experimental

Materials

Two cements: ‘Cement 1’ and ‘Cement 2’ were produced in laboratory ball mill from two clinkers from different cement plants in Poland. The clinkers were ground with gypsum (in proportions 95% clinker+5% gypsum) to the specific surface of 3000±50 $cm^2\ g^{-1}$ (Blaine). The characteristics of cement clinkers is given in Table 1 (chemical composition and phase composition calculated using Bogue’s formulas). The analytical grade PbO was used in cement pastes preparation, added as 0.1, 0.25, 0.5, 0.75, 1, 2 and 5 mass% of cement.

Table 1 Chemical and phase composition of cement clinkers

Component	Content/mass%	
	Cement clinker 1	Cement clinker 2
CaO	65.55	68.11
SiO_2	21.33	22.57
Al_2O_3	5.46	4.97
Fe_2O_3	2.65	2.13
MgO	1.06	0.82
SO_3	0.71	0.40
Alkalis	1.05	0.37
L.O.I.		0.25
C_3S	64.2	68.05
C_2S	12.6	13.23
C_3A	9.9	6.79
C_4AF	8.1	7.28
CaO_{free}	1.2	0.68

The two model cements were produced for further experiments: pure synthetic alite and alite with 5% gypsum of analytical purity. PbO and $Pb(NO_3)_2$ were used as lead bearing compounds in the form either of water suspension (PbO) in process water or as water solution (nitrate). This latter was added in concentrations giving the same Pb content as in PbO doped samples (the $Pb(NO_3)_2$ water solutions of corresponding concentrations were produced). Basing on the previous results [8] the dosages of PbO were fixed on the level of 0.5 and 2%; the references without PbO were also tested. The calorimetric experiments were also done using NaOH solution as ‘process water’ for alite+PbO samples.

Methods

In our studies the calorimetry was used as a basic method to investigate directly the hydration process, very sensitive for any changes involved by the presence of Pb compounds. Heat evolution measurements were carried out by use of differential microcalorimeter BMR (non-isothermal – non-adiabatic; constructed in the Institute of Physical Chemistry, Polish Academy of Science) on pastes produced at *w*/*c* ratio 0.5. The starting temperature was kept constant at 25°C. This method has been used many times in the studies of the other cementitious systems; recently reported are [10, 11].

Results and discussion

Calorimetric measurements

The calorimetric curves are presented as Figs 1–6.

The calorimetric studies, documented as sets of total heat evolved curves *vs.* time in Figs 1 and 2, prove the systematic retardation of cement hydration with growing PbO addition. We can observe a longer and longer shift of the growing part of these heat curves along the time axis, but the values of total heat effect (showed by the flat part of the curve after the growth) remains little changed, particularly in case of cement 2. The initial some hours lasting ‘dormant period’ would indicate the formation of a physical ‘barrier’ which is effective at early age, augments with PbO additive and becomes withdrawn after a shorter or longer time, depending on PbO content. This barrier (impermeable layer of Pb containing material?) is

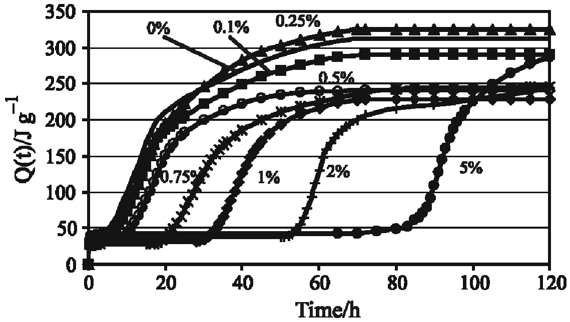

Fig. 1 Heat evolved *vs.* time for hydration of cement 1 doped with PbO(%)

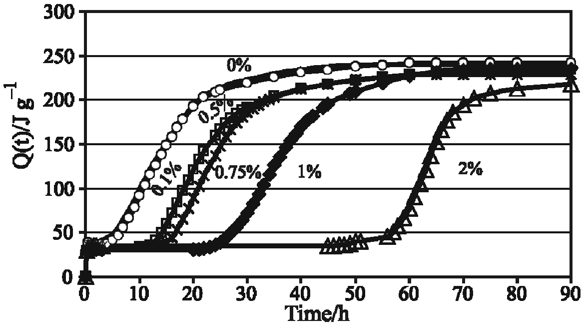

Fig. 2 Heat evolved *vs.* time for hydration of cement 2 doped with PbO(%)

presumably thicker and more stable at higher PbO content and really must be once destroyed; after this, further heat evolution – it means the hydration process (the formation of products) takes place.

It seems reasonable that the Pb containing compounds, if they are formed affect in some extend the mechanism and rate of hydration after the initial prolonged dormant period, when they are present in the paste. The dissolution of PbO in alkaline liquid phase, formation of some insoluble products as well as the incorporation of some Pb ions to the structure of hydration products (C–S–H) is possible.

According to the suggestion given in one previous work [1] the retarding effect of PbO should be attributed to the blocking up the alite surface by the formation of impermeable layer of product. Therefore the retardation would depend on alite content. However it is difficult to adapt this explanation to the data for cement 1 and 2. The setting and hydration kinetics of cement 1, that is of lower alite content is more retarded. There must be other processes involved. Anyway, the authors of this first study cited here [1] clearly point out that there is not satisfactory explanation dealing with PbO influence on cement hydration and there some points unclear (e.g. there was no defined products detected).

To elucidate some aspect of PbO retarding mechanism the authors carried out some further experiments. Therefore the calorimetric studies to follow the hydration of alite with PbO were carried out as a next step. In this case the measurements of alite+PbO heat effect were followed by the measurements produced with NaOH solution used as process water. The heat evolved *vs.* time is plotted in Figs 3 and 4.

When PbO is introduced to the neat alite hydrating samples the elongation of the so-called dormant period is not observed, as it is in case of cements. Additionally, the heat evolution significantly increases with PbO content. It seems quite reasonable that in case of pure alite PbO plays a role of nucleating agent prior to retard the process. The formation of any Pb containing compound deposited on the surface of hydrating grains by a through solution mechanism is then impossible or very slow.

What is more: in the experiments with NaOH solution (Fig. 4) the effect of 'excess' of easily soluble alkalis and other ions, which might strongly accelerate PbO dissolution and promote the formation of e.g. insoluble $Pb(OH)_2$ or any other insoluble salt with Pb in anion has not been found. The acceleration of alite hydration was practically the same.

The next series of calorimetric experiments, as shown in Fig. 5, shows that there is another change of heat effect in the presence of Pb additive in soluble form of $Pb(NO_3)_2$. At lower concentration, that is corresponding to 0.5% PbO, the heat evolution is intensified without any delaying effect. At higher $Pb(NO_3)_2$, that is corresponding to 2% PbO, the induction period is very long; it means that the early hydration is hindered up to about 8 h. After this, a very intensive reac-

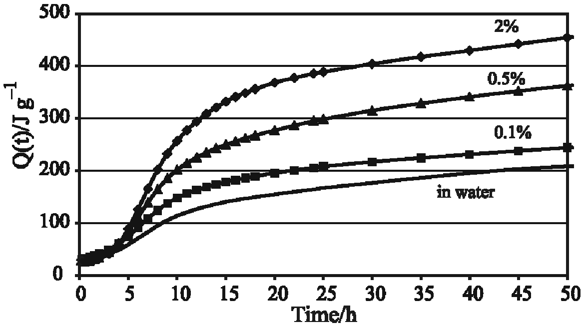

Fig. 3 Heat evolved *vs.* time for hydration of alite with PbO

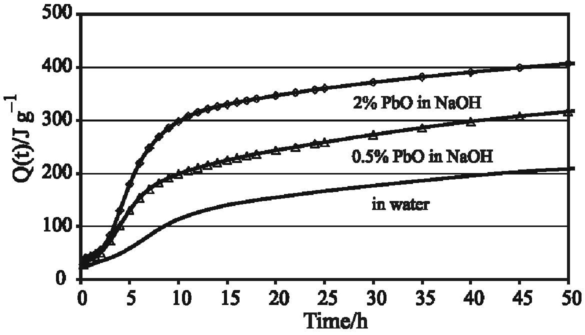

Fig. 4 Heat evolved *vs.* time for hydration of alite with PbO in NaOH solution

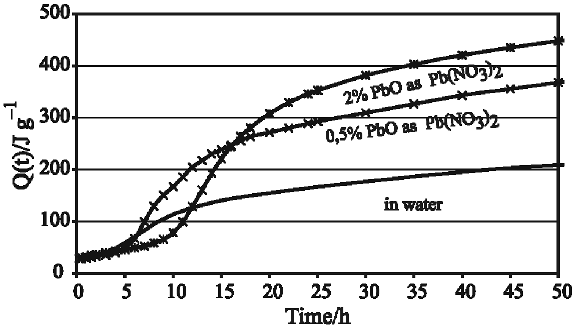

Fig. 5 Heat evolved *vs.* time for hydration of alite in $Pb(NO_3)_2$ solutions of different concentrations

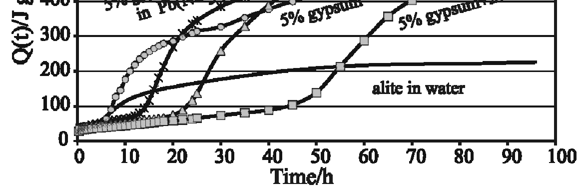

Fig. 6 Heat evolved *vs.* time for hydration of alite+gypsum mixture, doped with PbO or in $Pb(NO_3)_2$ solution

tion with high heat effect takes place. In this case the presence of nitrate anions in the liquid phase may disturb the precipitation of calcium hydroxide and C–S–H at early age but further on the hydration products, presumably with Pb ions are easily formed.

Therefore, as a further step, the interaction alite – PbO–$CaSO_4$ – was taken into account. The rapid total heat effect increase is evident as in case of alite+gypsum only. But further on the calorimetric measurements visualise the retarding effect of gypsum on alite+PbO hydrating mixture (Fig. 6). The heat evolution on hydration of alite with 5% gypsum and growing PbO percentage show significant variations. At the lowest 0.5% PbO addition to hydrated paste dormant period is about 10 times longer, while at 2% PbO – almost 20 times. When Pb is added in soluble form this retarding effect – elongation of the induction period – is reduced. From these data it results that the hydration/setting process in the presence of gypsum is significantly disturbed and alite–gypsum mixture behaves like cement systems. We can presume that the insoluble $PbSO_4$ layer is formed; its thickness is in some extend the function of Pb content. In the presence of nitrate anions this effect is weaker. After a time the insoluble and impermeable layer collapses, probably destroyed by osmotic pressure of hydrating silicate and further on the Pb ions can be consumed by poorly ordered C–S–H and/or intensify the process in other way.

Conclusions

- Heat evolution in the presence of fine grained PbO or soluble Pb – bearing compounds added to hydrated cement or alite paste is strongly affected proportionally to the content of additive in hydrating materials.
- Effect of retardation by PbO is observed in case of cements – at 2–5% PbO the induction period becomes many times longer, but after this the reaction starts again with some modification of the heat effect.
- Solid PbO powder does not hinder the heat evolution process of alite; PbO gives a significant growth of heat output – presumably there is no sufficiently strong barrier in the absence of other cement components (calcium aluminate and sulphate), hardly soluble fine-grained PbO plays effectively the role of nucleating agent.
- The heat effect in case of alite+PbO mixture hydrated in NaOH solution remains the same as on hydration in water.
- In the presence of Pb additive in soluble form of $Pb(NO_3)_2$ at lower concentration (corresponding to 0.5% PbO), the heat evolution in hydrating alite sample is intensified; at higher $Pb(NO_3)_2$, concentration (as 2% PbO), the induction becomes long; it means that the early hydration is hindered.
- Alite hydration is strongly hindered in the presence of gypsum – $PbSO_4$ seems to be the main factor responsible for retarding effect.
- The mechanism of Pb compounds interaction with hydrating cement/alite is complex. It seems that there is no one hypothesis which should be operative. This is not only the question of physical barrier on cement/alite grains surface; the reason of this relates to the other phenomena/factors affecting the hydration process, for example the equilibrium in the liquid phase.

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