

# Heat evolution in hydrating expansive cement systems

W. Nocuń-Wczelik · A. Stok · Z. Konik

CCTA10 Special Issue  
© Akadémiai Kiadó, Budapest, Hungary 2010

**Abstract** Calorimetry was applied to follow the hydration of special cement mixtures exhibiting expansion or shrinkage compensation. The standard, common cements show generally less or more visible shrinkage on setting and hardening but mixed with an expansive agent, usually of aluminate and sulfate nature, they can exhibit the increase of volume. The calcium aluminate cement CAC 40 was ground together with special sulfate–lime sinter to produce an expansive additive to Portland cement (CEM I 42.5R). The expansive additive in the environment of hydrating cement transforms into ettringite at “right time” to give expansion before the final setting and hardening takes place. In the experiments the proportions of components of expansive mixture and basic cement were variable. The rate of hydration versus time for common cements is commonly known and reflects the moderate setting and early hardening during the first days after mixing with water (two peaks and the induction period between them). The aim of measurements presented in this study was to show the course of heat evolution curve and the heat evolved values, equivalent to the acceleration/retardation of hydration, in case of the paste with the expansive mixture, as well as the pastes produced from Portland cement and the components of expansive additives added in variable proportions. It was possible to see how the calorimetric curve and consequently the hydration process itself declines from the controlled setting/hardening. These measurements were supplied by the examples of phase composition studies by XRD.

**Keywords** Calcium aluminate cement · Portland cement · Heat of hydration · Ettringite · Expansion

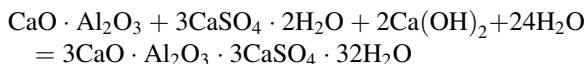
## Introduction

The kinetics and mechanism of hydration in various cementitious systems with additives can be investigated by use of calorimetry [1–3]. The heat evolution curve reflects the physical processes and reactions occurring in the hydrating system and leading to the transformation of plastic cement paste into hardened matrix. This process is known as cement setting.

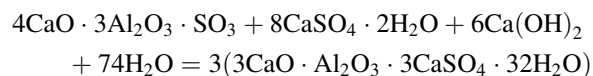
It is commonly known that the standard, common cements show generally less or more visible shrinkage on setting and hardening because the volume of formed hydrated phases is less than the sum of cement and water consumed in the hydration reaction. These volume changes are usually of little significance; however, in some conditions they cause cracks in hardened cement matrix. To avoid this, different kinds of expansive cements have been developed for almost 100 years [4, 5]. These binders are usually produced by mixing of different Portland cements with an expansive additive composed of calcium aluminate–sulfate component or the mixture of calcium aluminate cement and calcium sulfate (gypsum or anhydrite). The expansive additive in the environment of hydrating cement transforms into ettringite— $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$  with volume increase at “right time” to give expansion of paste before the setting and hardening takes place. The three types of expansive cements are designated; their classification is given in the ASTM C845-04 standard [6]. Each differs from the others in its aluminate compound from which the expansive ettringite is formed.

W. Nocuń-Wczelik (✉) · A. Stok · Z. Konik  
Faculty of Material Science and Ceramics, University of Science and Technology AGH, Al. Mickiewicza 30, 30-059 Krakow, Poland  
e-mail: wiesia@agh.edu.pl

The reaction of ettringite formation from the calcium aluminate (main component of calcium aluminate cements commercially available) follows the scheme [7, 8]:



while the transformation of the tetracalcium sulfoaluminate (special compound synthesized by Klein, corresponding to the natural mineral yeelimite), the component of some expansive cements can be written as follows:



One should note that in every case an additional calcium hydroxide is needed.

The reaction of aluminate with calcium sulfate is the process strongly affected by the chemical activity and proportions of  $\text{Al}_2\text{O}_3$  and  $\text{CaO} \cdot \text{SO}_3$  bearing compounds added usually to the Portland cement [9].

Not only the type and amount of aluminate proportioned into the Portland cement determine the rate and amount of ettringite formed at appropriate time to give the expansion but also the source of sulfate and calcium ions which provide an environment to stabilize the ettringite crystals [7, 9, 10]. In this process the timing becomes an important factor, because ettringite begins to form almost immediately after water is added to cement and in order to have the proper expansion effect, a large percentage of the ettringite must form after some degree of strength has been achieved.

In this study the mixtures containing various aluminate components with the sulfate and lime sinter proportioned (approximately) to give the ettringite phase were produced and used as an additive to the commercial Portland cement to obtain an expansive binder. The expansion progress versus time was investigated, as well as the heat evolution process was followed. In the next series of calorimetric experiments the proportions of expansive mixtures and cementitious materials were variable and declined from the theoretical composition giving the possibility of ettringite formation. The phase composition of hydrating pastes was studied by XRD.

## Experimental

### Materials

The standard Portland cement type CEM I 42.5R and calcium aluminate cement (CAC 40) commercially available were used in this study. Their specific surface was 3120 and 3160  $\text{cm}^2/\text{g}$  (as measured by Blaine method), respectively. The chemical composition is given in Table 1.

**Table 1** Composition of cements

Component	Percentage/wt%	
	In Portland cement	In calcium aluminate cement
$\text{SiO}_2$	19.21	1.05
$\text{Al}_2\text{O}_3$	4.96	40.68
$\text{Fe}_2\text{O}_3$	2.86	13.50
CaO	62.09	35.06
MgO	0.94	0.36
$\text{SO}_3$	2.74	0.06
Loss on ignition	3.69	4.15
Insoluble	0.76	1.48
$\text{TiO}_2$	0.36	2.07
Total	97.61	98.41

In order to produce an ettringite from monocalcium aluminate on hydration there is not only the calcium sulfate but also the CaO needed. As it results from the previous studies [10] the special anhydrite–lime sinter can be successfully used to transform the aluminates from CACs into ettringite in the hydrating paste.

The phase composition of Portland cement was as follows:  $\text{C}_3\text{S}$ —62.3%;  $\text{C}_2\text{S}$ —5.8%;  $\text{C}_3\text{A}$ —11.3%;  $\text{C}_4\text{AF}$ —8.7%, gypsum—4.7%. The estimated composition of calcium aluminate cement was:  $\text{CA} + \text{C}_{12}\text{A}_7 \approx 70\%$ ;  $\text{C}_4\text{AF} + \text{C}_2\text{AS} \approx 30\%$  ( $\text{C} = \text{CaO}$ ,  $\text{S} = \text{SiO}_2$ ,  $\text{A} = \text{Al}_2\text{O}_3$ ,  $\text{F} = \text{Fe}_2\text{O}_3$ —abbreviations commonly used in cement chemistry).

The raw mixture for the lime–sulfate sinter was proportioned using the 66.5% desulfogypsum (source of calcium sulfate) and 33.5% limestone material [10]. After the homogenization (on grinding) the heating at 1150 °C was done. After cooling the sinter was subjected to grinding to produce a fine powder. The anhydrite and CaO were found by XRD as the components of this material. The expansive mixture (abbreviation—ExM) was produced as a blend of 35% CAC 40 and 65% lime–anhydrite sinter. The proportions between the lime sulfate and aluminate correspond approximately to the stoichiometry of ettringite. In the basic series of experiments the mixture was added as an 8% (low), 12% (medium) or 16% (high percentage) cement replacement; the dosage of additive was fixed basing upon the former experiments [10, 11]. In the second series of experiments the hydrating pastes were produced using the following additives to Portland cement: 1—calcium aluminate cement only, 2—lime and sulfate sinter only ( $\text{C} + \text{Anh}$ ), 3—anhydrite and CAC with no CaO, 4—high percentage of expansive mixture (50%), and 5—additive with the excess of one component (CAC or lime + anhydrite sinter), as compared to the “basic” expansive additive. The calorimetric curve for the expansive mixture without Portland cement was also registered. In some

**Table 2** Compositions of hydrating samples; methods

No	Sample	Method	
1	CEM I 42.5R	Calorimetry	XRD
2	CEM I 42.5R + 8% ExM	Calorimetry	Exp.
3	CEM I 42.5R + 12% ExM	Calorimetry	XRD, Exp.
4	CEM I 42.5R + 16% ExM	Calorimetry	Exp.
5	CEM I 42.5R + 50% ExM	Calorimetry	XRD
6	CEM I 42.5R + 3% CAC40	Calorimetry	
7	CEM I 42.5R + 7% CAC40	Calorimetry	
8	CEM I 42.5R + 12% CAC40	Calorimetry	XRD
9	ExM only (C + Anh + CAC40)	Calorimetry	
10	CEM I 42.5R + 10% (C + Anh)	Calorimetry	
11	CEM I 42.5R + 3% (C + Anh) + 9% CAC40	Calorimetry	XRD
12	CEM I 42.5R + 9% Anh + 3% CAC40	Calorimetry	
13	CEM I 42.5R + 12% Yeelimate	Calorimetry	
14	CEM I 42.5R + 20% Yeelimate	Calorimetry	

*Exp.* restrained expansion test

calorimetric experiments another expansive material was used—synthetic calcium sulfoaluminate  $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{SO}_3$  (yeelimate). In Table 2 the compositions of hydrating samples are given together with the measurements which are documented in this study (Table 3).

### Methods

The partially restrained expansion of cement-expansive additive blends was tested using a special equipment. It was the horizontal mold playing the role of restraining cage with one moving endplate touching the measuring screw. The pastes prepared at water to cement ratio 0.32 (low to avoid

bleeding), mixed in special blender to counteract the early stiffening, were placed in the molds and covered with thin polyethylene foil. The molds with pastes were put in the containers over the water and stored at constant temperature  $23 \pm 2$  °C.

The nonisothermal–nonadiabatic differential BMR microcalorimeter, constructed in the Institute of Physical Chemistry, Polish Academy of Science, was used to follow the heat evolution on hydration. Hydrating pastes were prepared by mixing of 5 g samples with 2.5 mL of water (water to solid ratio 0.5); the initial temperature was kept constant at 25 °C. The heat evolved values were measured with accuracy of  $\pm 5$  J/g (Table 2).

**Table 3** Heat evolved on hydration

Fig. no	Sample	Heat evolved value, $\text{kJ}\cdot\text{kg}^{-1}$	
2, 3, 4,5	CEM I 42.5R	Q24 h = 108	
2	CEM I 42.5R + 8% ExM	Q24 h = 121	
2	CEM I 42.5R + 12% ExM	Q24 h = 119	
2	CEM I 42.5R + 16% ExM	Q24 h = 126	
2	CEM I 42.5R + 50% ExM	Q24 h = 88	
3	CEM I 42.5R + 3% CAC40	Q24 h = 101	
3	CEM I 42.5R + 7% CAC40	Q24 h = 72	(Q48 h = 311)
3	CEM I 42.5R + 12% CAC40	Q24 h = 68	(Q72 h = 285)
4	ExM only (C + Anh + CAC40)	Q24 h = 155	
4	CEM I 42.5R + 10% (C + Anh)	Q24 h = 125	
4	CEM I 42.5R + 3% (C + Anh) + 9% CAC40	Q24 h = 105	
4	CEM I 42.5R + 9% Anh + 3% CAC40	Q24 h = 113	
5	CEM I 42.5R + 12% Yeelimate	Q24 h = 88	(Q48 h = 368)
5	CEM I 42.5R + 20% Yeelimate	Q24 h = 110	

The phase composition of selected hydrating pastes was characterized by XRD (Philips diffractometer). In order to produce the specimens for XRD the pastes hydrating for 12 h or 3 days at water to solid ratio 0.5 were finely crushed, washed several times with acetone, and carefully dried with cold air to remove the free water (to stop further hydration).

**Results**

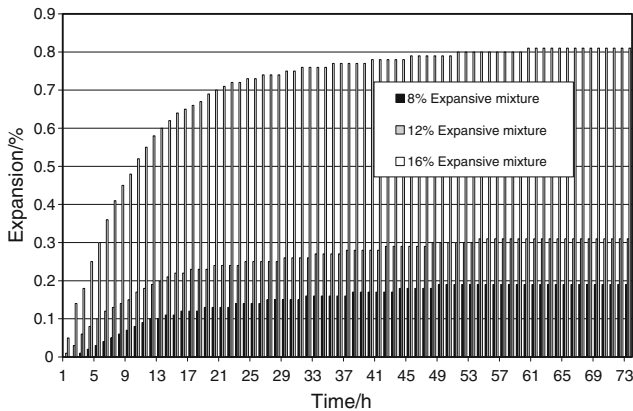
The plot illustrating the expansion of pastes versus time is shown in Fig. 1.

The heat evolution curves are shown in Figs. 2, 3, 4, 5; the heat values are listed in Table 2.

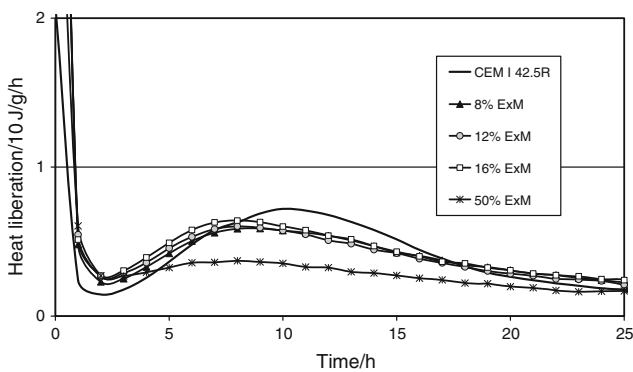
The example sets of diffraction patterns for hydrating cement; the mixtures are shown as Figs. 6, 7, 8.

**Discussion**

As one could expect, the expansion depends upon the amount and composition of expansive additive (Fig. 1). The small volume increase, slightly exceeding 0.3% was

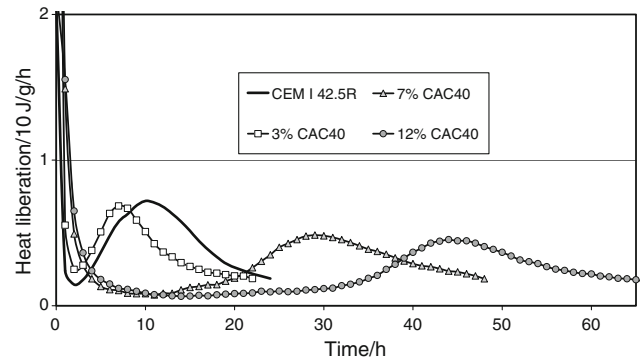


**Fig. 1** Restrained expansion of pastes versus time, growing with the percentage of expansive mixture

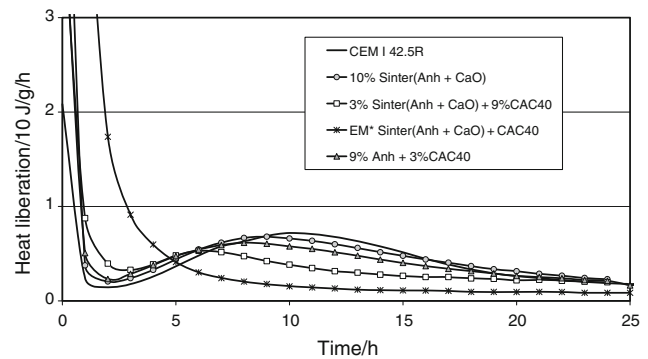


**Fig. 2** Heat evolution of cement with expansive mixture

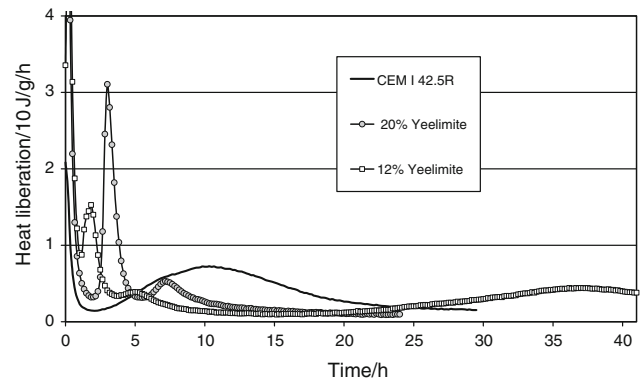
found for the 8 and 12% content (these binders can be considered as shrinkage compensating ones). At 16% expansive additive the volume increase is 0.8% (this is the consequence of the highest content of aluminate phases promoting the formation of expansive product—ettringite) and this result is approximately in the range attributed in the ASTM 845-96 standard to the expansive material. Expansion commences soon after mixing of cementitious



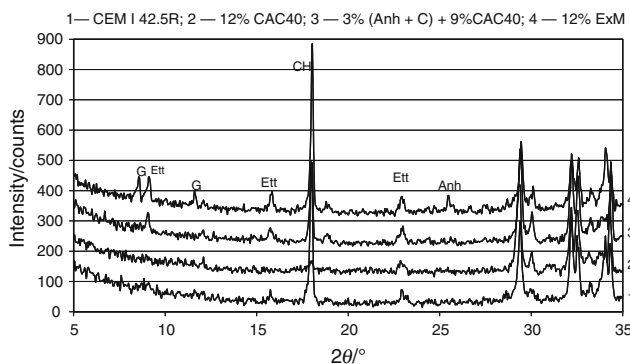
**Fig. 3** Heat evolution of Portland cement with calcium aluminate cement used as additive



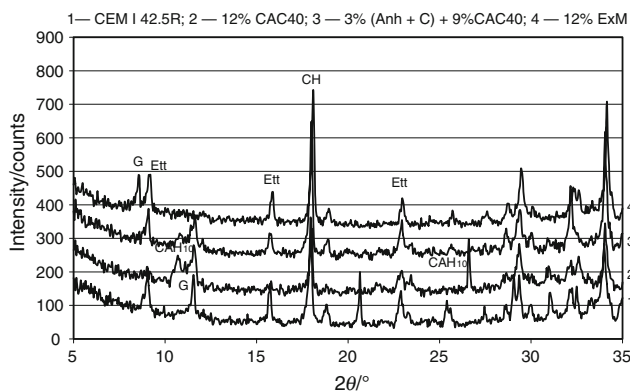
**Fig. 4** Heat evolution of Portland cement with varied amounts of components of expansive mixture; EM\*—expansive mixture only



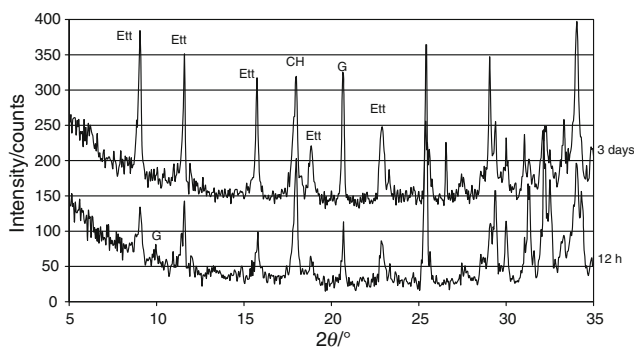
**Fig. 5** Heat evolution of Portland cement with varied amounts of another expansive additive—calcium sulfoaluminate (yeelimit)



**Fig. 6** XRD. Phase composition of pastes after 12-h hydration. The peaks on the right side of the patterns ( $28\text{--}35^\circ 2\theta$ ) are attributed to the unhydrated Portland cement constituents. (1) reference sample; (2)–(4) cement pastes containing expansive additives (see the legend)



**Fig. 7** XRD. Phase composition of pastes after 3-day hydration. The peaks on the right side of the patterns ( $28\text{--}35^\circ 2\theta$ ) are attributed to the unhydrated Portland cement constituents. (1) reference sample; (2)–(4) cement pastes containing expansive additives (see the legend)



**Fig. 8** XRD. Phase composition of Portland cement mixed with 50% expansive mixture; pastes after 12-h and 3-day hydration. The peaks on the right side of the patterns ( $28\text{--}35^\circ 2\theta$ ) are attributed mainly to the unhydrated constituents

material with water, and the most evident, steady growth takes place during the first 24 h. It means that the ettringite formation occurs at moderate rate, and it is not limited by

setting process and precipitation of the other hydration products. The volume increase becomes slower and slower during the next 24 h; the volume stabilizes up to 60–70 h from the beginning of the processing with water.

The calorimetric curves for those samples which exhibit proper “standard” expansion do not decline especially from the commonly known heat evolution plots for Portland cement (Fig. 2). Of course they reflect the shortage of “basic” cement; however, the formation of some more ettringite, being highly exothermic (high, broadened first peak, shorter induction period, lower second peak) is proved. The amount of ettringite seems not to be too high at the beginning and during the induction period; however, it is sufficient to produce the effect of shrinkage compensation or expansion as it is observed (Fig. 1). Further ettringite formation coincides well with the formation of the other hydration products, after the induction period. Therefore, the total heat evolved becomes a little higher (see Table 2).

As it can be easily seen in Fig. 3 the heat evolution process in Portland cement mixed with some percentage of alumina cement (3–12%) is intensively modified. One must find once again [12] that the CAC additions hinder generally the reaction of PC with water and consequently the heat evolution process. Only at 3% CAC the hydration is accelerated; however, with growing CAC content the latent period becomes longer and longer and there is a significant delay in the appearance of the main hydration peak. It seems that the formation of calcium aluminate hydrated phases, covering the cement grains and cutting off the access of water takes place, thus hindering the Portland cement hydration. However, the diffusion of water through the impermeable layer of hydrates results in swelling of hydrated calcium silicates from Portland cement component and this barrier collapses after a time; therefore, the hydration is continued and the total heat effect after 2 or 3 days is significant (see Table 2). As it has been suggested by the other authors [13], gypsum from Portland cement can be consumed by the CAC phases during the first hours and the impermeable layer of initially amorphous ettringite is also responsible for retarding effect. This process cannot be excluded as well.

In Fig. 4 the heat evolution versus time is plotted for various compositions of CAC, sulfate, and CaO mixtures. Generally, the course of heat evolution curves is disturbed as the composition of additive declines from that for expansive mixture giving ettringite on hydration. The excess of anhydrite (9%) retards a little the hydration in the presence of 3% CAC only, while at the presence of 3% lime–sulfate sinter and 9% CAC the hydration is not especially disturbed. This problem needs further studies, and presumably the role of CaO in the process of ettringite formation should be better documented. When the heat



evolution accompanying the hydration of Portland cement mixed with yeelimite is considered, this declination from the course of calorimetric curve for cement is clearly visible (Fig. 5). In this case, there is also the shortage of lime component.

The XRD plots showing the phase composition of pastes with different additives (CAC, expansive mixture, mixture with deficient lime and anhydrite component) are presented as Figs. 6, 7, 8. The ettringite phase is present in all the samples after 12 h hydration except of the sample with CAC only. This would suggest the presence of amorphous hydration products (rather calcium aluminate hydrate, see the data for 3-day hydrated sample) surrounding the hydrating Portland cement grains. The amount of ettringite is slightly growing with the percentage of expansion giving components, there is also some anhydrite residue (visible mainly in the sample with 12% expansive mixture), some gypsum (product of anhydrite hydration), and  $\text{Ca}(\text{OH})_2$ . The latter phase originates both from CaO and from calcium silicates (main constituents of Portland cement) hydration. The peaks in the range  $29^\circ\text{--}35^\circ 2\theta$  are attributed to the residue of anhydrous cement phases (calcium silicates). After 3 days hydration, the growth of ettringite, the better consumption of anhydrite, the peaks of calcium hydroxide increase, as well as the peaks of anhydrous cement phases decrease can be noticed. It means that the hydration of Portland cement constituents is continued. However, in the sample with CAC as an additive the calcium aluminate hydrate is well visible and the crystallization of ettringite is very poor. The growth of ettringite is clearly seen in the pastes with 50% expansive mixture (Fig. 8); the XRD pattern reveals the presence of ettringite strong peaks, as well as the residual gypsum.

## Conclusions

- The mixtures composed of the calcium aluminate cement and the lime–anhydrite sinter play successfully the role of expansive agent when used as an additive to Portland cement. The mixtures added as ca. 8% Portland cement replacement give a slight expansive effect; at the 12 or 16% cement replacement, the controlled expansion occurs. The volume changes are stabilized within the first 72 h.
- Heat evolution at the presence of expansive mixture giving the controlled shrinkage compensation or expansion effect, corresponding to ettringite, is well compatible with the heat evolution for matrix cement.
- The shortage of particular components of expansive mixture to give ettringite formation is reflected by the retardation/acceleration of heat evolution process; this is particularly seen in the presence of CAC without sulfate. In the presence of calcium aluminosulfate (yeelimite), a substantial modification of the heat evolution occurs.
- The hydration products formed in cement paste with expansive mixture are: ettringite, calcium hydroxide, and gypsum. The early hydration is hampered when only CAC without CaO and anhydrite, or yeelimite without CaO is added to cement.

**Acknowledgements** The experimental support of Łukasz Nowak and Karolina Leżuch is appreciated. The financial support from the Ministry of Education and Science in Poland (grant No: N N507 450934; AGH - 18.18.160.692) is acknowledged.

## References

1. Pacewska B, Błonkowski G, Wilińska I. Studies on the pozzolanic and hydraulic properties of fly ashes in model systems. *J Therm Anal Cal.* 2008;94:469.
2. Nocuń-Wczelik W. Calorimetry in the studies of cement–Pb compounds interaction. *J Therm Anal Cal.* 2007;88:291.
3. Talero R, Rahhal V. Calorimetric comparison of portland cements containing silica fume and metakaolin. Is silica fume, like metakaolin, characterized by pozzolanic activity that is more specific than generic? *J Therm Anal Cal.* 2009;96:383.
4. Odler I. *Special inorganic cements.* London, New York: Taylor & Francis; 2000. p. 316.
5. Mehta PK, Polivka M. Expansive cements. *Proc of the Sixth Int Congr Chem Cem.* Moscow; 1974; 3: p.158.
6. ASTM C845 standard specification for expansive hydraulic cement. ASTM International, West Conshohocken; 2004.
7. Kurdowski W. *Chemistry of cement.* Warsaw: PWN editor; 1991. p. 415 (in Polish).
8. Odler I, Subauste CJ. Stresses generated in expansive reactions of cementitious systems. *Cem Concr Res.* 2002;32:117.
9. Szeląg H. Factors governing the stresses appearing in the mortars of expansive cement. Part 1 and 2. *Cement - Wapno - Beton* 2008;13/75:315. 2009;14/76:11.
10. Konik Z, Małolepszy J, Roszczynialski W, Stok A. Production of expansive additive to portland cement. *J Eur Ceram Soc.* 2007; 27:605.
11. Nocuń-Wczelik W, Konik Z, Stok A. Blended systems with calcium aluminate and calcium sulphate expansive additives. 11th International Conference and Exhibition of the European Ceramic Society ECERS 2009. Book of abstracts. p. 206. to be published.
12. Gawlicki M, Nocuń-Wczelik W, Bąk Ł. Calorimetry in the studies of cement hydration. Setting and hardening of Portland cement–calcium aluminate cement mixtures. *J Therm Anal Cal.* 2009. on-line.
13. Gu P, Beaudoin JJ, Quinn EG, Myers RE. Early strength development and hydration of ordinary Portland cement/calcium aluminate cement pastes. *Adv Cem Bas Mat.* 1997;6:53.