

CALORIMETRIC INVESTIGATIONS OF THE INFLUENCE OF WASTE ALUMINOSILICATE ON THE HYDRATION OF DIFFERENT CEMENTS

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The aim of this work is to compare the influence of addition of waste aluminosilicate catalyst on the initial periods of hydration of different cements, i.e. calcium aluminate cements of different composition and Portland cement, basing on the calorimetric studies. Cement pastes containing up to 25 mass% of additive were studied, where the water/(cement+additive) ratio was 0.5. An attempt was undertaken to explain the mechanism of action of introduced aluminosilicate in the system of hydrating cement, particularly in the case of calcium aluminate cement pastes.

It was found that the presence of fine-grained additive caused in all studied cases the increase of the amount of released heat in the first period after the addition of water. In the case of aluminate cements with aluminosilicate addition, a significant reduction of induction time and faster precipitation of hydration products were observed compared to the reference sample (without additive). In the experimental conditions, the additive caused the acceleration of aluminate cements hydration, and the mechanism of its action is probably complex and can encompass: nucleative action of small grains and formation of new chemical compounds.

Keywords: calcium aluminate cement, calorimetry, cement hydration, spent catalyst, Portland cement

Introduction

Spent catalyst from the fluidized catalytic cracking (FCC) installation is a fine grained aluminosilicate material, porous and of well developed specific surface. Approximate chemical composition of this waste material can be presented as follows: $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 85$ mass%. Specific surface can even exceed $100 \text{ m}^2 \text{ g}^{-1}$ and average diameter of a grain is below $80 \mu\text{m}$ [1–6].

In the FCC installation two types of spent catalyst are collected: waste collected from electrostatic precipitator and catalyst removed from the process because of reduced catalytic activity [2, 6, 7]. These materials differ mainly in the size of grains and their morphology.

Physicochemical properties of spent catalyst make it an attractive material, which could be introduced into a cement composition.

Spent catalyst in the environment of hydrating Portland cement exhibits so called pozzolanic activity [1–12]. It means that, in the presence of such additive in the composition, the amount of $\text{Ca}(\text{OH})_2$, a product of hydration of Portland cement, is reduced. $\text{Ca}(\text{OH})_2$ reacts with active components of pozzolanic material, as an effect products similar to the phases formed during hydration of cement: hydrated calcium

silicates (so called C–S–H phase) and hydrated calcium aluminates and sulphoaluminates, are produced. Pozzolanic activity of spent catalyst, similarly to other pozzolanic materials, depends on the size of its grains. Higher activity is exhibited by materials of smaller grains (for example catalyst collected from electrofilters, or subjected to additional grinding) [2]. Acting as an active micro-filler, spent catalyst modifies the properties of cement compositions produced with its participation.

With the appropriate use of the waste as an additive to Portland cement composite (optimal amount of aluminosilicate and its granulometric composition, the method of additive introduction, use of plasticizers admixtures, etc.), a material (concrete, cement mortar), of improved properties, such as strength or tightness can be obtained [3–7].

Attempts are undertaken to apply spent catalyst as a component of heat resistant concretes made of aluminate cements [13], which could reduce the costs of their production. Chemical and mineralogical composition of aluminate cements is significantly different from the composition of Portland cement. That is why the mechanism of action of spent aluminosilicate catalyst in such systems has to be also different.

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The aim of this work is to compare the influence of addition of waste aluminosilicate on the initial periods of hydration of different cements, i.e. calcium aluminate cements and Portland cement, basing on the calorimetric studies. Such investigations, often carried out for different types of Portland cements, are relatively rarely found in papers referring to the processes of aluminate cements hydration.

Experimental

Materials and methods

In his work, two types of aluminate cements: Górkal 40 and Górkal 70 (produced by Górkal Cement, Poland), as well as Portland cement CEM I 32.5 R were used. Applied aluminate cements differ in chemical and phase composition. For Górkal 40 (grey cement), the content of components recalculated into oxides is: Al_2O_3 min. 40%, CaO min. 36%, SiO_2 2–4%, Fe_2O_3 max. 14 mass%, and mineralogical composition** is: CA as a primary phase and C_4AF , C_{12}A_7 and C_2AS as concurrent phases. For Górkal 70 (white cement) the composition is: Al_2O_3 69–71%, CaO 28–30%, SiO_2 less than 0.5, Fe_2O_3 less than 0.3 mass%, the mineralogical composition: fundamental phase: CA and CA_2 , concurrent phases: C_{12}A_7 and $\alpha\text{-Al}_2\text{O}_3$ (according to product description given by producer [14]).

The studied samples were cement pastes with the addition of spent catalyst (0, 5, 10, 20 and 25 mass% of additive in the mass of dry binder). The water/(cement+additive) ratio was 0.5.

An amount of heat released during the hydration of the cements and the heat release rate were measured starting from the point when water was introduced into the binder.

The measurements were carried out during first 48 h of hydration (external temperature was 25°C), by means of the BMR calorimeter produced by the Institute of Physical Chemistry, Polish Academy of Sciences. The results were calculated using a computer software [15].

Results and discussion

The obtained results of calorimetric studies on cement pastes made of calcium aluminate cements as well as, for comparison, of Portland cement, containing addition of spent aluminosilicate catalyst, are presented in Figs 1–6.

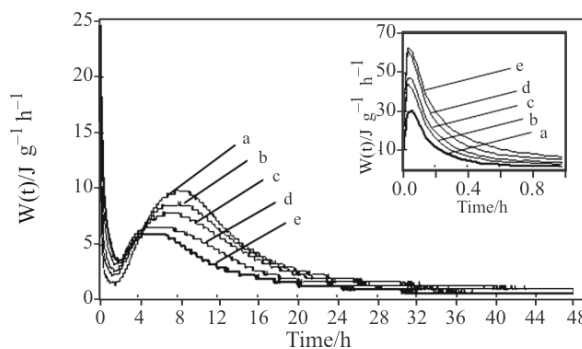


Fig. 1 The curves of heat release rate of cement pastes made of Portland cement and containing a – 0, b – 5, c – 10 d – 20 and e – 25% addition of aluminosilicate

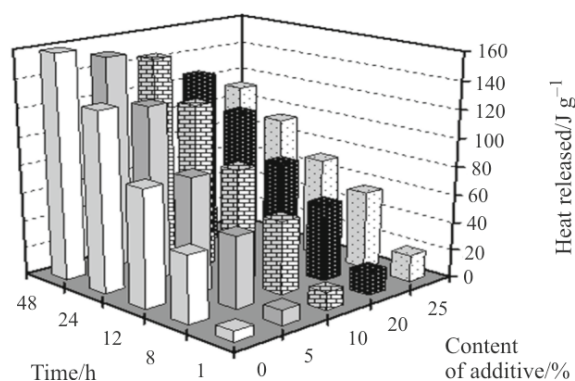


Fig. 2 The heat evolved during hydration of cement pastes made of Portland cement and containing 0, 5, 10, 20 and 25% addition of aluminosilicate

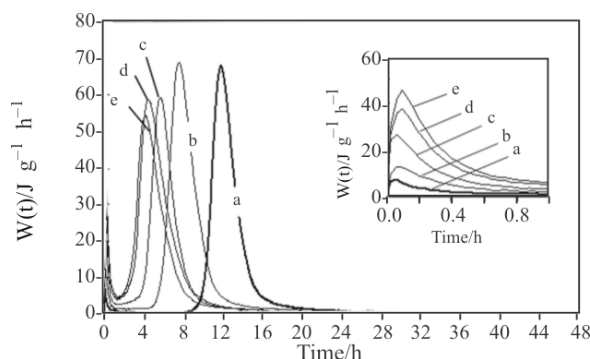


Fig. 3 The curves of heat release rate of cement pastes made of grey aluminate cement and containing a – 0, b – 5, c – 10, d – 20 and e – 25% addition of aluminosilicate

Calorimetric studies on the amount of heat released during hydration of cement and on the rate of heat release, allow the continuous observation of thermal effects of physicochemical transformations starting from first minutes from the addition of water into the cement. On a typical calorimetric curve of cement hydration, showing the changes of heat release rate, a few characteristic stages can be

** Abbreviations used in the chemistry of cement: A – Al_2O_3 , C – CaO, S – SiO_2 , F – Fe_2O_3 , H – H_2O

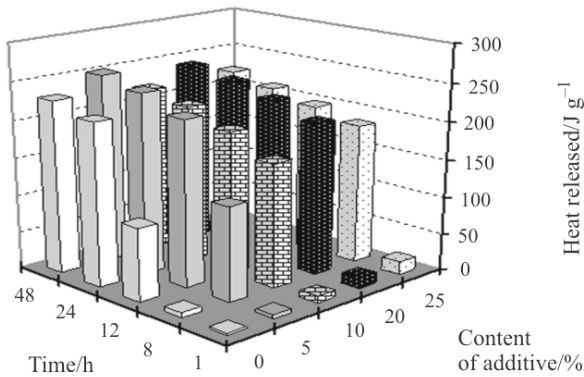


Fig. 4 The heat evolved during hydration of cement pastes made of grey aluminate cement and containing 0, 5, 10, 20 and 25% addition of aluminosilicate

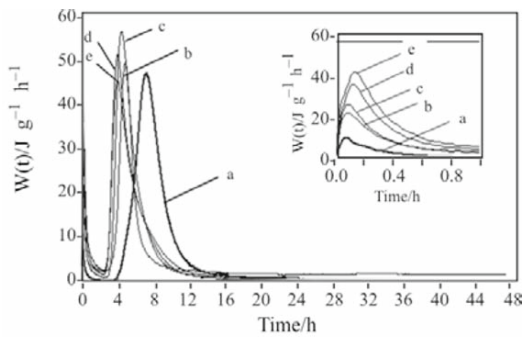


Fig. 5 The curves of heat release rate of cement pastes made of white aluminate cement and containing a – 0, b – 5, c – 10, d – 20 and e – 25% addition of aluminosilicate

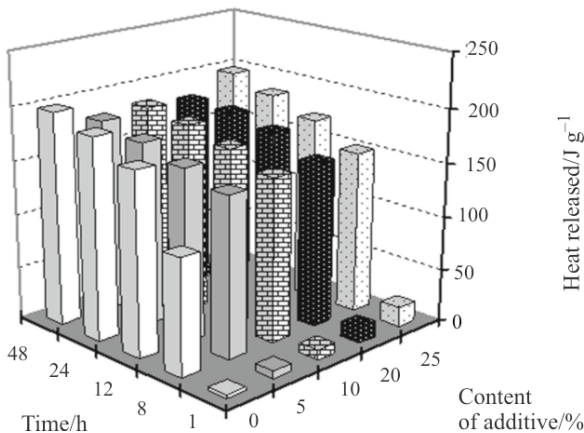


Fig. 6 The heat evolved during hydration of cement pastes made of white aluminate cement and containing 0, 5, 10, 20 and 25% addition of aluminosilicate

distinguished. After the addition of water into the cement a fast release of small amount of heat occurs. This effect can be attributed to the wetting of cement grains, their surface dissolving and the beginning of hydration processes. The next stage is a so called induction stage in which the heat release is inhibited. The increase of heat release rate occurring again after the induction period is related to fast crystallization of

hydration products. The shape of calorimetric curves is closely related to the composition of cement, which is confirmed by the results presented in this work.

As it is presented by the obtained results (Figs 1–6), the intensity of first thermal effect (wetting period) depends on the amount of spent catalyst introduced into the system. The higher is the amount of additive, the bigger amount of heat is released in the first stage of hydration, which occurs both in the Portland cement pastes and aluminate cement pastes.

For all studied pastes a shortening of the induction period after introduction of spent catalyst into the system is observed – small for the Portland cement pastes and distinct for the samples made of aluminate cements. In the case of pastes made of aluminate cements, and particularly in the case of grey cement (Fig. 3), the reduction of the induction period occurs after the introduction of first batches of spent catalyst. On the other hand, the increase of additive content above 10 mass% does not cause significant influence.

After the end of the induction period, a release of heat starts again. In the case of Portland cement pastes, this period starts earlier than in the aluminate cement pastes, and its course is more moderate and stretched in time. In the case of aluminate cements, the heat release after the induction period, contrary to the Portland cement pastes, is a fast and intensive process. Practically the whole amount of heat released in the studied period of hydration of aluminate cements is liberated before the 24th hour of hydration, while for the Portland cement pastes still further heat release occurs. It confirms a well known fact related to the differences in exothermicity and intensity of chemical transformations during the hydration of aluminate and Portland cements.

The presence of spent catalyst in the cement pastes causes the calorimetric curves recorded for pastes made of Portland cement in the post-induction period (Fig. 1) to be flatter, similarly as it was observed in the earlier works [2, 3]. It is possible that, particularly for the additive content above 10 mass%, the effect of cement attenuation starts to predominate over the influence of aluminosilicate activity, which is also indicated by smaller amount of total released heat. The shift of the calorimetric curve maximum towards earlier hours of hydration indicates effective promoting action.

In the case of pastes made of calcium aluminate cements (Figs 3–6), earlier release of main amount of heat is observed, and on the calorimetric curve the maximum related to the fast formation of hydration products is observed earlier, compared to the result obtained for the reference sample without additive.

Similar acceleration of aluminate cement hydration in the presence of spent catalyst was also observed by the authors of [13], where exothermic effects were recorded in the samples of concrete.

Calcium aluminate cements used in this work differ in their composition, mainly in the content of particular components. On the other hand they are significantly different from the Portland cement. While the main components of Portland cement are calcium silicates (C_3S+C_2S), aluminate cements are composed of mainly aluminates, such as CA, CA_2 , and C_2S can occur only in very small concentration. As an effect, the products formed during hydration of these cements are different. For example, in the case of pastes made of aluminate cements $Ca(OH)_2$ practically is not formed as a product of hydration. Small amount of formed $Ca(OH)_2$ in an environment rich in aluminate compounds rapidly reacts forming other products [16]. So it can be assumed that the mechanism of action of spent aluminosilicate catalyst in such systems is also different. However, some elements of its action can be similar for the pastes made of calcium aluminate cements and paste made of Portland cement.

In a broad scope, it can be ascertained that the spent catalyst causes in all studied pastes and particularly in the pastes made of aluminate cements, acceleration of physicochemical processes. It is observable already in the first minutes of hydration, when the increase of released heat and heat release rate is observed, more intensive with higher amount of introduced additive. In the further hours of hydration, the accelerating influence is evidenced by shorter induction periods and faster attainment of the second thermal effect maximum. Several mechanisms can contribute to such behavior of aluminosilicate additive, i.e. nucleative action and formation of new chemical compounds.

Influence of aluminosilicate additive on the initial period of cements hydration can be related to the increase of total specific surface of the binder, caused by the introduction of highly porous additive, acceleration of cement hydration (nucleative action) or start of reaction between aluminosilicate and cement components. A known fact is the accelerating action on the hydration of Portland cement and aluminate cements by finely comminuted materials, introduced into the system and acting as nucleation centers. Moreover, in the pores of catalyst grains, can adsorb ions being transferred into the solution as an effect of cement hydration, which can result in an acceleration of hydration processes. Such theory, related to the pastes made of Portland cement with the addition of waste aluminosilicate, was presented by the authors of [10], who also observed the increase of

heat released in the initial stage of hydration of cement paste containing spent catalyst. In their opinion, Ca^{2+} ions can adsorb on the surface of the catalyst, and their removal from the solution results in the acceleration of alite (C_3S) hydration. In the first hours of hydration the influence of pozzolanic reaction taking place with aluminosilicate, predominates over the effect of cement 'dilution'. Moreover, in [10] it was demonstrated that spent catalyst in saturated lime solutions already in the first hours can exhibit pozzolanic activity comparable to the activity of silica fume and much higher than the pozzolanic activity of fly ash. Additives of strong pozzolanic activity can cause the increase of the amount of heat released during the hydration of cement, because of exothermic effect of pozzolanic reaction between $Ca(OH)_2$ and active components of the additive.

It is possible that similar process with the participation of Ca^{2+} ions, takes place in the pastes made of calcium aluminate cement. According to often accepted theory referring to the mechanism of early hydration of aluminate cements, after addition of water into the binder, congruent dissolving of anhydrous phases occurs, and Ca^{2+} and $Al(OH)_4^-$ ions are transferred to the solution, which quickly becomes saturated. Subsequently, nuclei of hydrates appear and grow (in the induction period), and after the end of the induction period, massive precipitation of hydrates occurs, which is accompanied by significant release of heat [17, 18]. Therefore it can be expected that the first products of reaction between the additive and the solution are formed by the saturation of grains with Ca^{2+} ions. This process, along with nucleative action of small grains of additive, can accelerate hydration, resulting in the reduction of induction time and faster precipitation of hydration products. It is possible that, for the higher amounts of introduced additive, with simultaneous reduction of cement content, the lack of easily available Ca^{2+} ions starts to arise, and problems with diffusion start as an effect of consumption of significant amount of water by the process of grains wetting. It can explain the observed relationship between the length of induction period and the amount of additive (Fig. 3).

In the later stages of hydration of cement paste, the reactions involving silicate and aluminate ions formed by dissolving of aluminosilicate surface can occur. It seems probable that used spent catalyst, in a cement paste, can behave as a natural zeolite having pozzolanic properties. In a high pH environment, aluminosilicate matrix of the zeolite depolymerizes, $[SiO(OH)_3]^-$ and $[Al(OH)_4]^-$ ions are transferred into the solution, where they react with Ca^{2+} ions, forming

hydrated calcium silicates and aluminates [19]. According to what was presented in [20], the pozzolanic activity of zeolites can encompass the following subsequent stages: exchange of cations, dissolving, possible formation of aluminosilicate gel, precipitation of hydrated calcium silicates and aluminates from the solution. It is possible that in the case of aluminate cement pastes, in the initial stage of reaction involving the added aluminosilicate, compounds analogous to the products of pozzolanic reaction, i.e. hydrated calcium silicates (C–S–H phase) and calcium aluminates are formed. Subsequently, in an aluminate-rich environment they can undergo further transformations towards aluminosilicates. Another mechanism of these transformations can be the reaction between silicate ions originating from the aluminosilicate, and hydrated calcium aluminates. Such mechanism is proposed in the case of hydration of calcium aluminate cement in the presence of silica fume [21]. According to what was presented by the authors of [22], silica reacts with the phases of calcium aluminate in the cement and with water, forming various crystalline hydrates of variable Ca, Al and Si proportions, as well as complex phases of zeolite type and C–S–H type calcium silicates, depending inter alia on the temperature. C_2ASH_8 type aluminosilicates were identified in later periods in the systems in which aluminate cement was hydrated in the presence of silica fume [21, 23], zeolites [24, 25], as well as granulated slags [26, 27].

Introduction of aluminosilicate additive into the pastes made of calcium aluminate cement, changes the chemical and phase composition of the system, particularly in the area of overall content of silicates, because compounds of this type occur in aluminate cements in very small amounts. Addition of spent catalyst increases therefore the participation of silicates and aluminosilicates in the system. In the case of grey cement, it is possible that also new phases are formed as a result of the hydration of ferrite phase in the presence of aluminosilicate additive, similar to the phases of hydrated aluminates and aluminosilicates.

It has to be accentuated that calorimetric studies of cement hydration, despite allowing continuous observation of processes occurring in the initial periods of hydration and being very useful in comparative studies, do not give answers relating to the type of formed compounds. That is why, the hypotheses presented above need to be confirmed using other experimental methods.

Conclusions

Spent catalyst introduced into the system of hydrating cement modifies the kinetics of hydration of both calcium aluminate and Portland cements. The presence of aluminosilicate additive causes in all studied pastes, and particularly in aluminate cement pastes, action accelerating physicochemical processes. In the first period after the addition of water into the cement, the higher is the amount of introduced additive, the bigger amount of heat is released. In the case of Portland cement the catalyst slightly accelerates the hydration process but in later hours the effect of cement 'dilution' starts to predominate. However, in the case of pastes made of aluminate cements with the addition of spent catalyst, a significant reduction of induction time is observed and faster precipitation of hydration products compared to respective reference samples prepared without additive. Because aluminate cements are significantly different from Portland cement in their composition and properties, the mechanism of interaction of spent catalyst in such systems also has to be different. Some processes can be however similar for both types of cements, for instance the nucleation action of fine grains of additive. The action of aluminosilicate additive can encompass several mechanisms, i.e. nucleative action of small grains, formation of new chemical compounds. The definition of the direction of chemical transformations occurring on the presence of spent catalyst requires however additional, detailed studies, allowing to identify the phases formed during particular stages of hydration.

The results presented in this work constitute the introduction into wider studies on the influence of the addition of spent catalyst on the hydration of calcium aluminate cements.

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