# Isothermal and solution calorimetry to assess the effect of superplasticizers and mineral admixtures on cement hydration

**P. Siler · J. Kratky · N. De Belie**

**Abstract** The heat of hydration evolution of eight paste mixtures of various water to binder ratio and containing various pozzolanic (silica fume, fly ash) and latent hydraulic (granulated blast furnace slag) admixtures have been studied by means of isothermal calorimetry during the first 7 days of the hydration process and by means of solution calorimetry for up to 120 days. The results of early heat of hydration values obtained by both methods are comparable in case of the samples without mineral admixtures; the values obtained for samples containing fly ash and granulated blast furnace slag differ though. The results from isothermal calorimetry show an acceleration of the hydration process by the presence of the fine particles of silica fume and retarding action of other mineral admixtures and superplasticizer. The influence of the presence of mineral admixtures on higher heat development (expressed as joules per gram of cement in mixture) becomes apparent after 20 h in case of fly ash without superplasticizer and after 48 h for sample containing fly ash and superplasticizer. In case of samples containing slag and superplasticizer the delay observed was 40 h. The results obtained by solution calorimetry provide a good complement to the ones of isothermal calorimetry, as the solution calorimetry enables to study the contribution of the mineral admixtures to the hydration heat development at later ages of the hydration process, which is otherwise hard to obtain by different methods.

**Keywords** Isothermal calorimetry · Solution calorimetry · Superplasticizer · Mineral admixtures · Cement hydration

## Introduction

Mineral admixtures such as silica fume (SF), ground granulated blast furnace slag (GBFS) and fly ash (FA) are commonly used in concrete because they may reduce the porosity and hence increase the durability and improve the interface between cement matrix and aggregates [1, 2]. The use of mineral admixtures is also advantageous from economical and ecological point of view as the lower cement requirement leads to a reduction of $CO_2$ emissions generated by the production of cement. The necessity of increased application of secondary raw materials leads to an increased use of fly ash and granulated blast furnace slag. The influence of both mentioned admixtures on the course of setting and hardening of ordinary portland cement (OPC) depends on many factors—e.g., on the cement composition, additives composition, amount, specific surface area, combination of the additives and method of preparation of the mixture [3, 4]. In some cases, inappropriate combination of the additives or poor cement-additive compatibility can lead to the decrease of the effect of the additive, or even a serious adverse effect on the desired property. It is thus beneficial to test the influence of additives and admixtures on the properties of the mixture [3]. For a determination of the effect of additive on the course of hydration, various methods based on calorimetry proved to be useful for their fastness, simplicity of analysis and high informative value [5]. From the

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techniques suitable for the heat of hydration evaluation monitoring solution calorimetry and isothermal calorimetry has been selected. Solution calorimetry is convenient for long-term monitoring of the heat of hydration and also, e.g., for rapid determination of the components influencing the properties of the material (e.g., $SiO_2$, $SO_3$, $CaO$) and pozzolanic activity of the ashes and slag [6, 7]. The other method applied, isothermal calorimetry, which useful mainly for studying of the initial hydration process.

## Influence of the additives and admixtures on portland cement hydration

The main components of OPC are tricalciumsilicate ($3CaO \cdot SiO_2$, $C_3S$, alite), dicalciumsilicate ($2CaO \cdot SiO_2$, $C_2S$ belite), tricalcium aluminate ($3CaO \cdot Al_2O_3$, $C_3A$, Celite) and calcium aluminoferrite ($4CaO \cdot Al_2O_3 \ Fe_2O_3$, $C_4AF$, brownmilerite). During the hydration processes, up to 28% by weight of ordinary portland cement is converted to calcium hydroxide ($Ca(OH)_2$, CH, portlandite) [8]. Because of its usually macrocrystalline nature, partial water solubility ($\sim 2\%$ by weight in pure water at 25 °C [9]) and chemical reactivity with acidic environment, the presence of large amounts of portlandite have negative influence on the durability of concrete. The positive feature of portlandite in concrete is that it maintains a high pH, thus stabilizing the oxide layer, which protects steel reinforcement of concrete from corrosion [10].

An application of finely ground SF, GBFS, and FA in concrete results in the presence of a thermodynamically favorable surface for portlandite crystallization, hence resulting in "smoother" microstructure. Another effect lays in the consumption of portlandite by the mechanism of pozzolanic reaction [11]. Silica fume, GBFS and FA react with portlandite evolved during the portland cement hydration process, producing additional calcium–silicate–hydrates (C–S–H) material, which then contributes to the strength of the cement paste matrix [12, 13].

To improve the workability of mortars and concrete and to facilitate the possibility to use less water for achieving the desired rheology of the fresh concrete mixture, the superplasticizers (SP) are widely used. The workability improvement is achieved by enhancing the dispersion of fine particles in concrete after adsorption of the molecules of superplasticizer onto the particle surface [14]. The microstructure of fresh cement paste is also affected, as presence of polymers can strongly influence shape and size of growing hydration products [15]. Also, an application of less water in the mixture has very beneficial effect on the mechanical properties and is resulting in denser and hence more durable microstructure.

The chemical reactions which take place after mixing the solid binder phases with water are influenced by aforementioned admixtures and additives to a large extent. The reaction of portland cement paste with water is accompanied by heat release, which causes a temperature rise in concrete. Monitoring of the heat development is particularly important because high temperature gradients in massive concrete blocks can lead to the development of cracks and therefore in reduction of mechanical properties and durability of concrete. The use of pozzolanic admixtures as OPC replacement in concrete reduces the amount of heat released during hydration in shorter terms (days or months) [12, 16], hence leading to "smoother" heat development and preventing thermal cracking of massive constructions.

The effect of FA on hydration reactions corresponds with a delay of hydration and reduced intensity of the heat dissipation rate as compared to OPC. Fly ash incorporation is accelerating alite hydration, which is apparent with increasing water to binder ratio. Nevertheless, increase of fly ash content and water to binder ratio is resulting in an increase of the setting times of the mixtures [17].

Wang et al. in [18] have published the following results:

(1) With the increase of FA content, the hydration degree of cement increases, the FA pozzolanic reaction degree decreases.
(2) The active effect of FA is composed of two parts: the pozzolanic activity of FA itself and the promoting role of FA to the hydration of cement.

In [16] it has been found that the use of FA as cement replacement resulted in a reduction of the maximum temperature rise under adiabatic curing condition. The higher the replacement levels of cement by FA, the lower the temperature rise. FA in amount of 10 % influences the heat evolution rate only in slight degree. Calorimetric curves of cement pastes with FA addition are almost identical to the curves of control cement paste. In case of larger amounts of FA, obtained curves of heat release are more flat and extended in time compared with calorimetric curves obtained for control cement paste. The duration of an induction period is also prolonged, which means the hydration products are formed slower [19].

Regarding silica fume, which is a highly active pozzolanic admixture, in [12] has been found that an addition of SF results in acceleration of early hydration of reactive cement phases by providing large amounts of reactive siliceous surface, which serves as a site for the early precipitation of hydration products.

The effects of GBFS on the hydration processes have been found to be similar to the ones of FA [13, 17, 18]. Mixtures containing GBFS do not generate higher heat initially, but they generate heat higher than the OPC pastes later on (in terms of Joules per gram of OPC) [13, 20, 21].

## Methods

### Solution calorimetry

The solution calorimeter (enthalpiograph) can be used to analyze the composition and other characteristics of portland cement and mineral admixtures, such as the determination of the heat of hydration of portland cement, rapid determination of $SiO_2$, $Al_2O_3$, $SO_3$, and the determination of pozzolanic activity [22, 23].

The method was used according to EN 196-8 and the ASTM C 186 standard procedures for the determination of the heat of hydration of hydraulic cements. The method is based on the measurement of the dry cement dissolution heat in the solution of nitric and hydrofluoric acids and the dissolution heat of a separate portion of the cement that has been hydrated for a selected period of time (e.g., 2, 7, 28 days or even years) [23].

The difference between these values gives the heat of hydration for the selected hydration period. A certain disadvantage of this method is its lower accuracy as the heat of hydration is relatively small in comparison to the obtained values of reaction heats. Its main advantage lays on the possibility to monitor the hydration process even for the samples which are several years old.

The main constituent of the calorimeter (Fig. 1) was a 200 mL styrofoam reaction vessel (1), about 2.5 g of weight. The vessel was placed in a styrofoam block (2), the thermoinsulating ability of which was sufficient to decrease the heat exchange with the surroundings to negligible level (thermal leakage coefficient must be less than 0.06 Kelvins per 15 min per 1 Kelvin of temperature difference) providing the reaction is fast and the temperature difference is in the order of tenths Kelvin degree (both conditions can be fulfilled in most cases). In the cover of the block a plastic funnel (3) for feeding the powder samples was installed
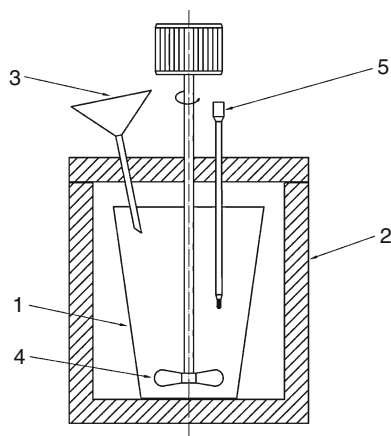


**Fig. 1** Schematic picture of solution calorimeter

and there was also a small hole for placing of a mechanical stirrer (4). The temperature changes of the solution were detected by the thermistor (5).

### Isothermal calorimetry

Isothermal calorimetry has been used by several researchers to quantify the hydraulic activity of portland cement, the pozzolanic activity of fly ash or the latent hydraulic properties of slag [20, 21, 24]. Calorimetry provides continuous measurements and is, therefore, a convenient method to study the early stage of hydration where the heat rate is relatively high. Pozzolanic reactions are known to take action at later stages involving low heat rate, which makes them difficult to follow by isothermal calorimetry.

The twin isothermal calorimeter has been used (Fig. 2). Calibration of isothermal calorimeters has been made using an electrical heater [25].

## Experimental part

### Materials and mixture compositions

Table 1 An ordinary portland cement CEM I 52.5N was used in all pastes mixtures. As partial cement replacement materials in some mixtures the silica fume (SF), fly ash (FA), and granulated blast furnace slag (GBFS) were used. In some cases, the commercial polycarboxylate type superplasticizer was applied.

Influence of superplasticizer, slag, fly ashes, silica fume, and water to binder ratio (w/b, ratio between water and sum of all binders, e.g., cement + slag, etc.) were studied. The mixtures composition is shown in Table 2.

### Isothermal calorimetry

First, all solid components of the mixture were homogenized in a glass ampoule, and then the water (containing the necessary amount of superplasticizer in case of samples CSP1_33, C50S50SP1_33, and C50F50SP1_33) was added. The total amount of paste placed in the glass ampoule was 14.00 g. After mixing with water the ampoule was sealed and placed into the isothermal calorimeter. As the mixing took place outside the calorimeter, the first peak, caused mainly by start of hydration of $C_3A$ phase and by reaction on the grain surface, was not recorded entirely. This was neglected as the first peak contributes only by a few percent to the total hydration heat [26]. The heat evolved per time ($dQ/dt$; $q$) was measured at 20 °C for 7 days. The total heat $Q$ was then calculated by numerical integration.

**Fig. 2** Schematic of isothermal calorimeter
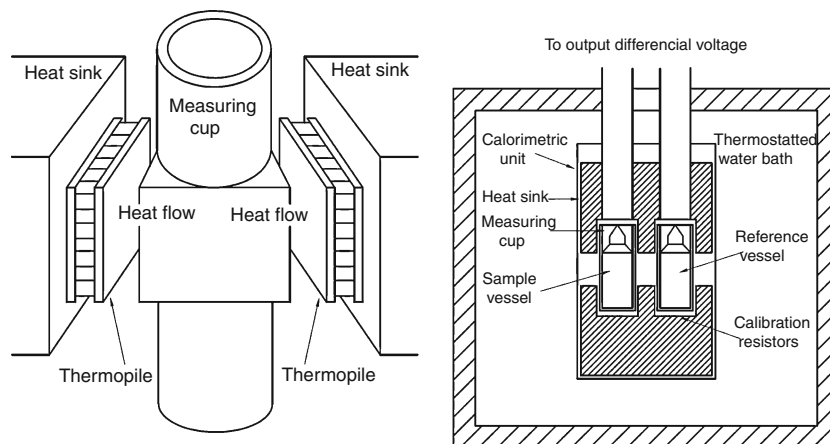


**Table 1** Chemical compositions of the components used

| % | CEM I 52.5N | GBFS | FA |
|---|---|---|---|
| LOI | 2.12 | – | 5.24 |
| 45 μm fineness | – | – | 28.75 |
| CaO | 63.12 | 40.38 | 2.47 |
| $SiO_2$ | 18.73 | 34.35 | 49.34 |
| $Al_2O_3$ | 4.94 | 11.36 | 24.55 |
| $Fe_2O_3$ | 3.99 | 0.48 | 6.23 |
| $SO_3$ | 3.07 | 1.65 | – |
| MgO | 1.02 | 7.57 | 1.73 |
| $K_2O$ | 0.77 | 0.37 | 3.84 |
| $Na_2O$ | 0.41 | 0.29 | 0.52 |
| Cl | – | 0.013 | – |
| $S^{2-}$ | – | 0.77 | – |
| Mn | – | 0.165 | – |

**Table 2** Compositions of selected mixtures

| Code of mixture | Cement/% | SF/% | GBFS/% | FA/% | SP/% | w/b |
|---|---|---|---|---|---|---|
| C_33 | 100 | 0 | 0 | 0 | 0 | 0.33 |
| C_40 | 100 | 0 | 0 | 0 | 0 | 0.40 |
| C_50 | 100 | 0 | 0 | 0 | 0 | 0.50 |
| CSP1_33 | 100 | 0 | 0 | 0 | 1 | 0.33 |
| C90SF10_40 | 90 | 10 | 0 | 0 | 0 | 0.40 |
| C50S50SP1_33 | 50 | 0 | 50 | 0 | 1 | 0.33 |
| C50F50SP1_33 | 50 | 0 | 0 | 50 | 1 | 0.33 |
| C50F50_40 | 50 | 0 | 0 | 50 | 0 | 0.40 |

*Solution calorimeter*

The method of the heat of hydration determination by means of the solution calorimetry is based on the method described in standard EN 196-8 [27]. First, the calibration constants of the solution calorimeter (thermal capacity and heat leak coefficient) were determined. To the styrofoam reaction vessel containing 180 grams of acid mixture ($HNO_3$ with concentration of 2 mol/L with 2.76 g of 40% HF on every 100 g of solution of $HNO_3$) tempered to 20 °C, the $3 \pm 0.05$ g of zinc oxide weighed with $\pm 0.0001$ g precision was added. The temperature changes were registered for longer than 47 min. The results were corrected for the amount of water contained in the sample and expressed in J/g binder. The heat leak coefficient and thermal capacity was calculated using the procedure specified in [27]. For the determination of the heat of dissolution of unhydrated and hydrated samples, $1.29 \pm 0.01$ g of unhydrated sample and $1.80 \pm 0.02$ g of hydrated sample, weighed with $\pm 0.0001$ g precision, were used. The heat of hydration of the samples expressed in joules per gram of material was calculated as the difference between the heat of dissolution of unhydrated and hydrated samples.

## Results and discussion

In the following figures the results obtained by means of isothermal calorimetry during the first 7 days of hydration and by means of solution calorimetry during the first 120 days of hydration are shown in Joule per gram of binder. Most of the measurements were performed after 1 day of hydration process in 3-day interval till 14 days, then with 7-day interval up to the age of the sample of 60 days and then after 2 months up to 120 days of the hydration process. The results obtained by means of solution calorimetry are interlaced by an exponential function $y = A(1 - e^{-Bx})$. The resulting exponential curve has a practical importance because the constant $A$ is corresponding to the maximum heat, which will be released from the measured sample after "infinite" time of reaction.

The comparison of cement pastes with different water/binder ratio is shown in Fig. 3.

On the isothermal calorimetry curves the following significant peaks/areas can be found [28]:

**Fig. 3** The heat of hydration of cement pastes with increasing water to binder ratio (0.33–0.5) by means of isothermal (*left*) and solution (*right*) calorimetry. (C_50 is difficult to see in the graph; C_33 should be the same black line for q and for Q)
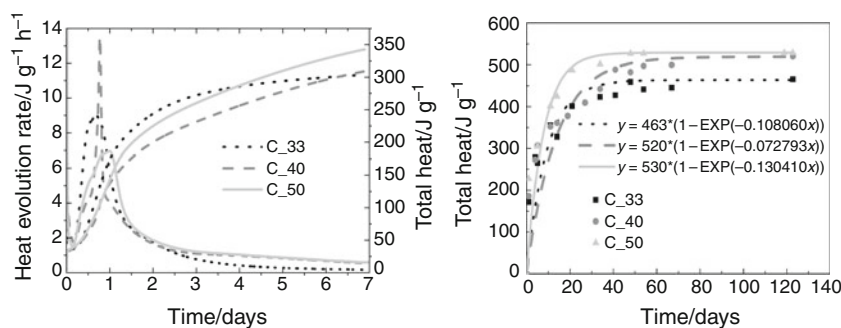


(1) Soon after the first wetting, an initial rapid exothermic reaction appears due to the surface reactions, releasing of the ions into solution and due to the initial reaction of $C_3A$ phase—this is observed as the first peak on the graph (which is not completely registered).

(2) This is then followed by deceleration of the heat evolution and the induction period during which the heat evolution is relatively low, which is characterized by an increasing saturation of the pore solution by $Ca(OH)_2$.

(3) After the induction period, the nucleation of portlandite occurs, which initiates the second acceleration of the heat evolution due to the formation of the CSH phase. This is observed as the second peak on the graph.

Sometimes, the third peak can be also observed—this phenomenon is discussed in more detail below.

The second maximum of the isothermal calorimetric curve results is occurring first for the sample containing the least amount of water (C_33). This is probably due to the fact that the amount of water is lesser than necessary for complete hydration (theoretical amount of water necessary for complete hydration is approximately w/b = 0.4 [29], including chemically bound and gel water). When the w/b ratio is lower, the present water is faster saturated by $Ca^{2+}$ ions and hydration takes place faster. The limited amount of water can also lead to a lack of space between portland clinker particles. However, the resulting total heat of hydration is lower because the smaller amount of water decreases the maximal developed heat. C_40 has nearly the stoichiometric amount of water to insure the complete hydration of the system. We can thus observe the highest increase of the developed heat. For the sample C_50 the amount of water is higher than needed and thus part of the water remains inert, which inhibits the development of maximum temperature. Owing to the higher amount of water the particles are in better contact with it, thus the hydration is more complete and the total heat (expressed in Joules per gram of binder) is higher. Increasing retardation with increasing water content is evident from the results because of greater distances among cement grains during hydration.

After 120 days the developed heat resulting from solution calorimeter measurements has the same trends as results of total heat measured by isothermal calorimeter in the first 7 days of hydration. With increasing amount of water the amount of developed heat (expressed in Joules per gram of binder) was also increasing. The values measured for samples C_40 and C_50 (samples with sufficient amount of water) are very similar, because after 120 days the majority of cement has undergone a hydration reaction. The sample C_33 without sufficient amount of water probably is not completely hydrated after 120 days.

The total amount of released heat in the first 7 days of hydration is reduced by using superplasticizer, because the hydration process is delayed. The values measured for C_33 and CSP1_33 after 120 days are very similar because the retarding effect of superplasticizer after a long time is negligible. The comparison of the heat rate curves in Fig. 4 shows that the superplasticizer used generally causes the retardation of hydration and reduction of the maximal developed temperature. GBFS and FA also cause a decrease of the maximum of heat development rate and a retardation.

When the sample contains GBFS or FA the hydration is generally slower because these admixtures react slower then cement. In combination with SP, the third hydration peak appears. According to [24, 30] in some cements, this peak can be attributed to transformations of the aluminates hydrated phase. It can be generally attributed to some excess of tricalcium aluminate and transformation of tricalcium sulfoaluminate phase (AFt, ettringite) to monosulfoaluminate (AFm) or delayed tricalcium sulfoaluminate formation. In the pure portland cement this peak is very small, almost unnoticeable, but it is more pronounced with higher fly ash content. According to [20, 21] after the OPC hydration has liberated a sufficient amount of lime, the correct alkalinity is reached to initiate the slag reaction. This reaction appears as a third peak in the evolution of q and becomes more pronounced with increasing GBFS content.

The results obtained by means of the isothermal calorimetry show that the presence of GBFS leads to the decrease of the released heat (in J per gram of binder) in the first days of hydration, which is corresponding to the results found by other researchers [20, 21]. This decrease is probably caused by reaction of slag with $Ca^{2+}$ ions.

**Fig. 4** The comparison of
pastes with w/b = 0.33 by
means of isothermal (*left*) and
solution (*right*) calorimetry
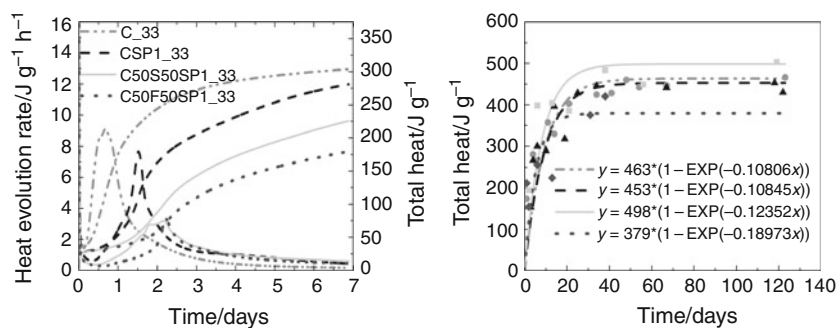


**Fig. 5** The comparison of
samples with w/b = 0.40 by
means of isothermal (*left*) and
solution (*right*) calorimetry
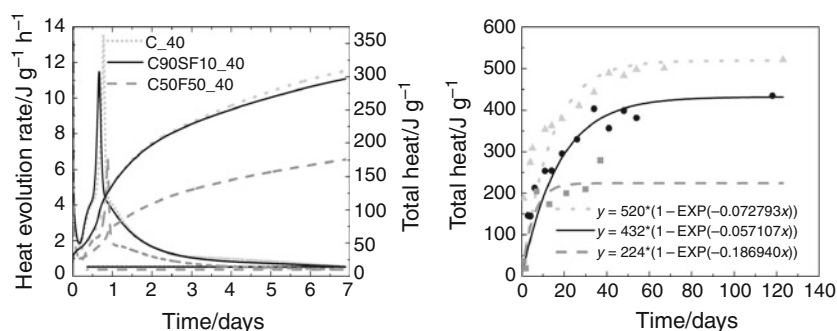


There is obvious reduction of developed heat (in both kinds of measurements) at all stages of hydration when fly ash is present in the mixture (50% by weight). When the fly ash is used, the developed heat is reduced throughout the hydration period. The reason for this reduction in the early days is reaction with $Ca^{2+}$ ions. The reason for the reduction of developed heat in the later days of hydration is the effect of "dilution" because the reactive portland cement is replaced by less reactive fly ash, which is unable to release the comparable amount of heat. This heat cannot be released through pozzolanic reaction even in the later stages of hydration.

After 120 days the total hydration heat of C50S50SP1_33 is even higher than of CSP1_33. This is caused by the heat generated later on, which is higher than for OPC pastes. Such a difference may be attributed to the slag reaction. These results are also consistent with observations made by other researchers [13].

Figure 5 shows the decrease of maximal developed temperature when fly ash or silica fume is used. Fly ash retards the hydration, while in the sample containing silica fume the maximum occurs sooner than in the case of sample C_40. The acceleration of hydration occurs probably because SF is providing a large reactive siliceous surface, which serves as a site for the early C–S–H precipitation, which influences the heat development rate significantly [12].

When SF is added, the course of hydration obtained from the isothermal calorimeter during the first days is

**Table 3** Evaluated values of the maximum released heat

| Code | Released heat/J $g^{-1}$ |
|---|---|
| C_33 | 463 |
| C_40 | 520 |
| C_50 | 530 |
| CSP1_33 | 453 |
| C90SF10_40 | 432 |
| C50S50SP1_33 | 498 |
| C50F50SP1_33 | 379 |
| C50F50_40 | 224 |

similar to the hydration of cement paste with the same water to binder ratio.

The results of the solution calorimetry measurements (also see Table 3) of the samples containing FA show a larger scatter of the values obtained. This was probably due to the segregation of the components of the mixture, which makes it harder to prepare a homogeneous sample for measurement. Owing to the unreliability of the results obtained, the data collection was ended after 38 days.

The total amount of cumulative heat for the sample with silica fume is lower than for plain cement paste. This is probably because the pozzolanic reaction of SF is generating less heat than the reaction of portland cement and thanks to the reaction with $Ca^{2+}$.

For the sample containing FA the total amount of cumulative heat is very low especially in the presence of the SP.

The values of the maximum released heat (obtained from constant A from the equation $y = A(1 - e^{-Bx})$ which corresponds to the total theoretical heat evolved after "infinite" time of reaction) are listed in Table 3.

## Conclusions

For the pure cement pastes with increasing w/b ratio (see Fig. 3), the total heat development expressed in Joules per gram of cement is increasing because components are in better contact with water and hydration is more completed. This effect becomes apparent after certain age (starting approximately 6 days) of the samples and is apparent on both isothermal calorimetry and solution calorimetry results trends.

Total amount of released heat in the first 7 days of hydration is reduced by using of superplasticizer, because the hydration process is retarded. After several days, the values of the total heat are comparable, which is in agreement with the results published by other researchers [31].

When SF is added, the course of hydration obtained by means of isothermal calorimeter during the first days is similar to the hydration of cement paste with the same w/b ratio. The heat effect of this admixture after several days of hydration is lower than the heat effect of cement. The total amount of cumulative heat is lower than for plain cement paste. This is because the reaction of SF is generating less heat than the portland cement hydration. From the comparison of the differential curves an acceleration of hydration has been found, which is in agreement with previously published results [12, 32]. The acceleration of hydration occurs probably because SF is providing large reactive siliceous surface, which serves as a site for the early C–S–H precipitation, which influences the heat development rate [12].

When GBFS is used, a retardation of hydration is observed in the first hours and the total generated heat is also lower. This is because GBFS reacts more slowly compared to SF. After 120 days the cumulative heat of C50S50SP1_33 is slightly higher than for CSP1_33. This may be caused by the long-term hydration heat released later on as GBFS needs longer time to complete the hydration process. These results are also consistent with the results of [13].

There is a third peak apparent on the differential calorimetric curves when the GBFS or FA is used simultaneously with SP (see Fig. 4). According to [20, 21] it is because the start of GBFS hydration accelerated after the OPC hydration has liberated a sufficient amount of lime and the suitable alkalinity is reached to initiate the slag reaction. This reaction appears as a third peak in the evolution of $q$ and becomes more pronounced with increasing GBFS content.

According to [24] for the pure portland cement this peak is a very small, barely noticeable, but it increases with higher fly ash content. It can be generally attributed to some excess of tricalcium aluminate and transformation of tricalcium sulfoaluminate phase (AFt, ettringite) to monosulfoaluminate (AFm) or delayed ettringite formation. When FA is used there is also retardation in the first hours of hydration [13, 17, 18]. This is explained by the slower formation of the hydration products [19].

The total heat measured during the first 7 days of hydration by both isothermal and solution calorimetry for the samples without the presence of mineral admixtures are similar. The results observed for the samples containing portland cement together with other admixtures (silica fume, fly ash and granulated blast furnace slag) do not show the same level of similarity—generally the results obtained by solution calorimetry shows higher total heat in comparison to isothermal calorimetry (with exception of mixture containing silica fume).

The probable reason for this phenomenon can be seen in experimental conditions—the isothermal calorimeter system is constantly cooling, whereas the reaction of pozzolans is very susceptible to temperature [33–35]. At 20 °C the reactions that become apparent at elevated temperature (which may be reached under normal curing conditions of the samples measured by means of solution calorimetry) may proceed slower. This explains the different values when samples were measured by different methods.

From the results of the experiments it can be seen that isothermal calorimetry is more suitable for measurements during the first days of hydration, while the solution calorimetry is more suitable for the measurement of hydrated samples after several days of hydration. After a few days of hydration, changes in hydration heat are already very small. For isothermal calorimetry some inaccuracies may arise resulting from the measuring equipment itself or by changes in ambient temperature. For solution calorimetry it is difficult to monitor the course of hydration in the first days because there are big changes in values. For measurements over a long period of hydration, the changes of hydration heat are small and the resulting value should be obtained by averaging the values of several measurements.

## References

1. Khatib JM. Metakaolin concrete at a low water to binder ratio. Constr Build Mater. 2008;22:1691–700.
2. Vessalas K, et al. Pozzolanic reactivity of the supplementary cementitious material pitchstone fines by thermogravimetric analysis. J Therm Anal Calorim. 2009;97:71–6.

3. Erdem TK, Kirca Ö. Use of binary and ternary blends in high strength concrete. Constr Build Mater. 2008;22:1477–83.

4. Habert G, et al. Effects of the secondary minerals of the natural pozzolans on their pozzolanic activity. Cem Concr Res. 2008;38: 963–75.

5. Ježo L, Palou M, Kozánková J, Ifka T. Determination of activation effect of $Ca(OH)_2$ upon the hydration of BFS and related heat by isothermal calorimeter. J Therm Anal Calorim. 2010; 101:585–93.

6. Brandštetr J, Polcer J, Krátký J, Holešinský R, Havlica J. Possibilities of the use of isoperibolic calorimetry for assessing the hydration behavior of cementitious systems. Cem Concr Res. 2001;3:941–7.

7. Krátký J, Havlica J, Brandštetr J. Contribution of calorimetric methods for the assessing the reactivity of components of cementitious systems. In: Non-traditional cements & concrete, Brno: Brno University of Technology. 2002;162–6.

8. Wild S, Khatib JM. Portlandite consumption in metakaolin cement pastes and mortars. Cem Concr Res. 1997;27:137–46.

9. Duchesne J, Reardon EJ. Measurement and prediction of portlandite solubility in alkali solutions. Cem Concr Res. 1995;25: 1043–53.

10. Glasser FP, Marchand J, Samson E. Durability of concrete—degradation phenomena involving detrimental chemical reactions. Cem Concr Res. 2008;38:226–46.

11. Oner A, Akyuz S. An experimental study on optimum usage of GGBS for the compressive strength of concrete. Cem Concr Comp. 2007;29:505–14.

12. Korpa A, Kowald T, Trettin R. Hydration behaviour, structure and morphology of hydration phases in advanced cement-based systems containing micro and nanoscale pozzolanic additives. Cem Concr Res. 2008;38:955–62.

13. Pane I, Hansen W. Investigation of blended cement hydration by isothermal calorimetry and thermal analysis. Cem Concr Res. 2005;35:1155–64.

14. Plank J, et al. Synthesis and performance of methacrylic ester based polycarboxylate superplasticizers possessing hydroxy terminated poly(ethylene glycol) side chains. Cem Concr Res. 2008; 38:1210–6.

15. Zingg A, et al. The microstructure of dispersed and non-dispersed fresh cement pastes—new insight by cryo microscopy. Cem Concr Res. 2008;38:522–9.

16. Atiş CD. Heat evolution of high-volume fly ash concrete. Cem Concr Res. 2002;32:751–6.

17. Rahhal V, Talero R. Influence of two different fly ashes on the hydration of portland cements. J Therm Anal Calorim. 2004;78: 191–205.

18. Wang A, Zhang Ch, Sun W. Fly ash effects II. The active effect of fly ash. Cem Concr Res. 2004;34:2057–60.

19. Pacewska B, Blonkowski G, Wilinska I. Investigations of the influence of different fly ashes on cement hydration. J Therm Anal Calorim. 2006;86:179–86.

20. Gruyaert E, Robeyst N, De Belie N. Modelling the hydration heat of Portland cement blended with blastfurnace slag. In: Non-traditional cement and concrete III, Brno: Brno University of technology. 2008;302–11.

21. Gruyaert E, Robeyst N, De Belie N. Study of the hydration of Portland cement blended with blast-furnace slag by calorimetry and thermogravimetry. J Therm Anal Calorim. 2010;102:941–51.

22. Krátký J, Havlica J, Brandštetr J, Krátký J. The use of calorimetry in the analysis and rapid quality tests of fly ashes, binders and mixes. In: Chemické listy, Proceedings of the 2nd Meeting of Chemistry and Life, Brno, 2002;215–18.

23. Brandštetr J, Krátký J, Havlova J, Pospíšil O. Použití roztokové kalorimetrie (entalpimetrie) při anlýze a zkouškách reaktivity surovin a výrobků maltovinářského průmyslu, (The use of solution calorimetry (entalpimetri) in analysis and tests of reactivity of raw materials and products of mortary industry). Silika. 2002;5–6:177–80.

24. Baert G, Hoste S, De Schutter G, De Belie N. Reactivity of fly ash in cement paste studied by means of thermogravimetry and isothermal calorimetry. J Therm Anal Calorim. 2008;94:485–92.

25. Haines PJ. Principles of thermal analysis and calorimetry. Royal Society of Chemistry, 2002;145–7.

26. De Schutter G. Hydration and temperature development of concrete made with blast-furnace slag cement. Cem Concr Res. 1999;29:143–9.

27. NBN_EN 196-8:2003 (E). Methods of testing cement—Part 8: heat of hydration—solution method.

28. Stephan D, Dikoundou SN, Raudaschl-Sieber G. Hydration characteristics and hydration products of tricalcium silicate doped with a combination of MgO, $Al_2O_3$ and $Fe_2O_3$. Thermochim Acta. 2008;472:64–73.

29. Aitcin PC. Vysokohodnotný beton, (High performance concrete), Praha, ČKAIT, 2005.

30. Rahhal V, Talero R. Fast physics-chemical and calorimetric characterization of natural pozzolans and other aspects. J Therm Anal Calorim. 2010;99:479–86.

31. Sakai E, Kasuga T, Sugiyama T, Asaga K, Daimon M. Influence of superplasticizers on the hydration of cement and the pore structure of hardened cement. Cem Concr Res. 2006;36:2049–53.

32. Rahhal V, Cabrera O, Talero R, Delgado A. Calorimetry of portland cement with silica fume and gypsum additions. J Therm Anal Calorim. 2007;87:331–6.

33. Escalante JI. Reactivity of blast-furnace slag in Portland cement blends hydrated under different conditions. Cem Concr Res. 2001;31:1403–9.

34. Hanehara S, Tomosawa F, Kobayakawa M, Hwang KR. Effects of water/powder ratio, mixing ratio of fly ash, and curing temperature on pozzolanic reaction of fly ash in cement paste. Cem Concr Res. 2001;31:31–9.

35. Mostafa NY, EL-Hemaly SAS, Al-Wakeel EI, El-Korashy SA. Activity of silica fume and dealuminated kaolin at different temperatures. Cem Concr Res. 2001;31:905–11.