Influence of Amount of Calcareous Fly Ash on Heat of Hydration of Portland Cement

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Abstract. For the reason a common strategy to reduce the emitted CO₂ the clinker in the cement is oft replace by supplementary cementitious materials, like blast furnace slag or fly ash. Therefore, it is important to investigate the influence of these materials to the hydration in blended cements. This study is dedicated to the contribution of a calcareous fly ash to the hydration of a blended cement. To assess this contribution five calcareous fly ashes were chosen. The hydration of samples of Portland cement and Portland cement with 10% mass of cement (mc), 20% mc and 30% mc of calcareous fly ash was investigated by means of isothermal heat flow calorimetry. Calorimetric investigations were carried out with a TAM Air heat-flow calorimeter. Tests were conducted in 20°C. Water-binder ratio of cement pastes for hydration heat examinations was equal 0,5. Research had shown that the addition of calcareous fly ash showed a retardation of the hydration reactions and increasing the initial heat period. The induction period of samples of Portland cement with 10%, 20% and 30% mc of calcareous fly ash is retarded compared to the samples of Portland cement. There is no difference in the cumulative heat normalized to the amount of Portland cement with 10% mc of calcareous fly ash compared to the Portland cement after 72 h. When amount of calcareous fly ash increases above 10% mc the cumulative heat is lower.

1. Introduction

During the last two decades, fly ashes produced in power plants have been commonly used in the construction sector as additives either to ordinary cement or to ready-mixed. By using the fly ashes additives numerous effects can be obtained for example pro - ecological, such as: reduction of energy consumption (due to reduction of clinker content in cement) and lowering the CO₂ emission. However, not all ashes they can be used in concrete technology, unless they meet chemical and physical requirements in relevant standards, such as ASTM C 618, EN 197-1, and EN 450-1. High – calcium fly ash (HCFA) has not been used to a significant extend as an additive to concrete or cement. This is mainly due to: significant changeability of chemical composition and physical properties of HCFA over time, high content of potentially detrimental to the durability of concrete components in HCFA (free calcium and sulphur compounds), high water demandness of HCFA and in consequence its negative influence on workability [1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11]. The use of HCFA is additionally hampered by the lack of research into the effects of HCFA in concrete or cement [5], [12]. For this reason the main objectives of this research was to explore the influence of different HCFA on the heat of hydration of pastes with cement and HCFA.
2. Experimental

2.1. Raw materials
Portland cement, high-calcium fly ashes (HCFA) were used in this research. The oxide components and the physical properties of cement and fly ashes are listed in table 1, table 2 and table 3, respectively. The research was conducted for 5 batches of HCFA. In general, HCFA was added as a substitute for 10%, 20% and 30% of cement mass (table 4).

Table 1. Properties of cement CEM I 42,5 R.

| SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | SO$_3$ | C$_3$S | C$_2$S | C$_3$A | C$_4$AF | Spec.surf. [cm$^2$/g] |
|--------|-------------|-------------|------|--------|--------|--------|--------|--------|---------------------|
| 20,5   | 4,89        | 2,85        | 63,3 | 0,73   | 65     | 10     | 8,1    | 8,7    | 3500                |

Table 2. Chemical compositions of HCFA.

|        | PLW1-0’, % by mass | PLW2-0’, % by mass | PLW3-0’, % by mass | PLW4-0’, % by mass | PLW5-0’, % by mass |
|--------|--------------------|--------------------|--------------------|--------------------|--------------------|
| LOI    | 2,56               | 3,43               | 1,85               | 2,67               | 2,12               |
| SiO$_2$| 33,62              | 35,41              | 40,17              | 45,17              | 40,88              |
| Al$_2$O$_3$ | 19,27              | 21,86              | 24,02              | 20,79              | 19,00              |
| Fe$_2$O$_3$ | 5,39               | 6,11               | 5,93               | 4,58               | 4,25               |
| CaO    | 31,32              | 25,58              | 22,37              | 20,60              | 25,97              |
| MgO    | 1,85               | 1,49               | 1,27               | 1,49               | 1,73               |
| SO$_3$ | 4,50               | 4,22               | 3,07               | 2,96               | 3,94               |
| CaO$_w$| 2,87               | 1,24               | 1,46               | 1,18               | 1,07               |
| K$_2$O | 0,11               | 0,13               | 0,20               | 0,19               | 0,14               |
| Na$_2$O| 0,31               | 0,16               | 0,15               | 0,23               | 0,13               |
| TiO$_2$| 1,21               | 1,22               | 1,01               | 1,37               | 1,52               |
| Mn$_2$O$_3$| 0,07               | 0,06               | 0,06               | 0,06               | 0,04               |
| SrO    | 0,20               | 0,17               | 0,16               | 0,13               | 0,17               |
| ZnO    | 0,02               | 0,02               | 0,02               | 0,02               | 0,01               |
| P$_2$O$_5$ | 0,17               | 0,16               | 0,33               | 0,14               | 0,10               |

Table 3. Physical properties of all the raw materials.

| HCFA            | Gęstość nasypowa, g/m$^3$ | Fineness, > 45 μm % | Blaine specific surface, cm$^2$/g |
|-----------------|----------------------------|---------------------|----------------------------------|
| PLW1-0’         | 2,62                       | 38,0                | 2860                             |
| PLW2-0’         | 2,58                       | 35,4                | 4400                             |
| PLW3-0’         | 2,64                       | 55,6                | 1900                             |
| PLW4-0’         | 2,60                       | 57,2                | 1900                             |
| PLW5-0’         | 2,60                       | 46,3                | 2370                             |
Table 4. Research plan – amount of HCFA in pastes.

| Symbol of pastes                                      | Amount of cement, % | Amount of fly ash, % |
|-------------------------------------------------------|---------------------|----------------------|
| CEM I                                                 | 100                 | 0                    |
| PLW1-0’/ PLW2-0’/ PLW3-0’/ PLW4-0’/ PLW5-0’          | 0                   | 100                  |
| PLW1-0’-10/ PLW2-0’-10/ PLW3-0’-10/ PLW4-0’-10/ PLW5-0’-10 | 90                  | 10                   |
| PLW1-0’-20/ PLW2-0’-20/ PLW3-0’-20/ PLW4-0’-20/ PLW5-0’-20 | 80                  | 20                   |
| PLW1-0’-30/ PLW2-0’-30/ PLW3-0’-30/ PLW4-0’-30/ PLW5-0’-30 | 70                  | 30                   |

2.2. Test method
The heat of hydration of cements was measured with help of isothermal microcalorimeter. All tests were carried out on cement pastes with water-binder ratio 0.5 at 20 °C. The cements were weighed out into 20ml ampoules and mixed with water. Next the ampoules were capped and placed into isothermal calorimeter about 10 min after cement was first mixed with water and then monitored for up to 72 h. The heat release and rate of heat release between 1 h and 72 h after mixing were determined.

3. Results and discussions
3.1. Rate of heat evolutions of pastes
The results of heat of hydration cement pastes with fly ash are presented in Figure 1-5. The curves of hydration rates of pure HCFA vary from each other. HCFA PLW1-0’ has no significant main peak on its curve, while the remaining HCFA tested has the main peak. For the HCFA PLW2-0’ and PLW3-0’ the maximum occurs after about 10 hours and for HCFA PLW4-0’ and PLW5-0’ the maximum occurs much later after 56 hours and after 47 hours respectively. For pastes composed of CEM I and HCFA the curves of heat of hydration are similarly to curve of CEM I. For all the samples, after the first period of fast hydration, the overall hydration rate slows down (induction or dormant period). The sample with cement CEM I has a dormant period after the initial peak until a sample age of about three hours. For pastes with HCFA a dormant period starts later, and for pastes with 30% HCFA it lasts until the sixth hour after mixing the binder with water. The main peak in the hydration curve of pastes with 30% HCFA occurs about one hour later then in paste only with CEM I, and it is lower 0,75 mW/g. Generally, addition of the HCFA decreases the peak assigned to the silicate reaction, indicating reduced hydration of the clinker phases C3S and C2S. There is one except.

![Figure 1. Rate of heat evolutions of pastes PLW1-0’ during 72 hours of hydration](image-url)
In paste with 30% HCFA PLW2-0’ the peak commonly assigned to the conversion of AFt to AFm has disappeared. Instead, a very pronounced peak is observed which possibly subsumes both the late silicate reaction and the AFt to AFm conversion (figure 2). In pastes with HCFA there is increased significantly the second peak of hydration. The period of maximum heat evolution occurs typically between about 10 and 20 hours after mixing and then gradually falls off. The maximum heat release period usually lasts about 22 hours and then gradually disappears. In pastes with HCFA PLW1-0’, PLW4-0’ and PLW5-0’ this period also lasts 22 hours. However, in pastes with HCFA PLW3-0’ and PLW2-0’ this period is reduced to 18 hours and 12 hours respectively.

![Figure 2. Rate of heat evolutions of pastes PLW2-0’ during 72 hours of hydration](image)

![Figure 3. Rate of heat evolutions of pastes PLW3-0’ during 72 hours of hydration](image)
3.2. Total heat of hydration of pastes

The total heat after 72 hours is shown in figures 6-10. In all cement pastes with HCFA the total heat release is reduced with respect to the references. The total heat released by cement pastes is dependent on the presence of the type of HCFA. The most reduced is observed in pastes PLW4-0'-30 and PLW3-0'-30 and cumulative heat was about 200 J/g. Moreover, a reduction in the total released heat with the increasing dosage of HCFA was observed. It is noted that the cumulative hydration heat of blended cement containing HCFA PLW1-0'-10 was almost as much as that of Portland cement within 72 h. The total heat of hydration of pure HCFA were about 50 and 80 J/g within 72 h.
**Figure 6.** Heat of hydration of pastes PLW1-0’ up to 72h of hydration

**Figure 7.** Heat of hydration of pastes PLW2-0’ up to 72h of hydration

**Figure 8.** Heat of hydration of pastes PLW3-0’ up to 72h of hydration
Figure 9. Heat of hydration of pastes PLW4-0' up to 72h of hydration

Figure 10. Heat of hydration of pastes PLW5-0’ up to 72h of hydration

4. Conclusions
The hydration of samples of Portland cement and Portland cement with five vary batches of calcareous fly ash was investigated by means of isothermal heat flow calorimetry. Based on the tests carried out, the following conclusions were reached:

- Dosage of HCFA in cement pastes leads to retardation which is indicated by delaying of the onset of the main hydration peak with increasing amount of HCFA;
- In pastes with HCFA there is increased significantly the second peak of hydration in proportion to the amount of HCFA;
- The total heat of hydration of cement paste with HCFA were between 200 and 250 J/g within 72 h;
- The heat of hydration of cement pastes with HCFA is influenced not only by the amount of HCFA but also by its chemical composition and physical properties.
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