Analysis of hydration phase of cement pastes with partial replacement of cement by latent hydraulic additives

Josef Fládr and Petr Bílý
Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 7, 166 26 Prague, Czech Republic

Abstract. The paper presents a study focused on cement pastes with partial replacement of cement by metakaolin, microsilica and fly ash in different shares: 0%, 10 %, 20 %, and 50 % of cement weight. For all the additives, particle size distribution curves were obtained. Hydration phase of cement pastes was analysed by means of heat flow and hydration heat measurements. The study showed that cement replacement by 10 – 50 % wt. of an additive did not affect the hydration phase qualitatively, but some quantitative differences were found. In general, it can be stated that 20 % or lower cement replacement by any of the tested additives did not affect the hydration process of the cement paste significantly. At 50 % cement replacement, the amount of produced hydration heat and the peak value of heat flow were decreased by approximately 15 % for metakaolin, 20 % for microsilica and 35 % for fly ash.

1. Introduction
Cement is the most expensive constituent of concrete and at the same time, it is responsible for the largest part of CO₂ emissions associated with the production of concrete. Huge amounts of industrial by-products suitable for partial replacement of cement are produced every year, but their exploitation in concrete remains limited. The reason is that the properties of concrete with partial replacement of cement by latent hydraulic additive can vary substantially based on the type and amount of the additive.

Particle size distribution of the binder influences many properties of concrete. The finer is the binder, the sooner the hydration process begins and the faster is the strength growth. Watertightness of concrete produced with the use of finer binder improves. On the other hand, water consumption rises, which can lead to decrease of compressive strength, worse rheological properties and poorer durability of the material.

Therefore, it is necessary to continue with the research of the effects of partial cement replacement by latent hydraulic additives on concrete properties on both microscale and macroscale (carried out before e.g. by [1–4]). Two important aspects affecting the mechanical properties of concrete are particle size of the cementitious materials and the process of hydration of cement paste.

2. Materials
Mixture containing 1375 kg/m³ of cement and 550 kg/m³ of water (water-to-binder ratio w/b = 0.4) was selected as the reference mix. The effect of partial replacement of cement by different additives was investigated. The following materials were used (the properties given by the manufacturers are listed):
- Portland cement CEM 42.5 R from Českomoravský cement company, Mokrá plant. Material composition: 64.2 % CaO, 19.5 % SiO₂, 4.7 % Al₂O₃, 3.2 % Fe₂O₃, 3.2 % SO₃, 1.3 % MgO. Specific surface: 0.37 m²/g. Bulk density: 3050 kg/m³.
- Metakaolin Mefisto L05 from České lupkové závody company. Material composition: 54.1 % SiO₂, 40.1 % Al₂O₃, 1.8 % TiO₂, 1.1 % Fe₂O₃, 0.8 % K₂O. Specific surface: 12.69 m². Bulk density: 2300 kg/m³.
- Microsilica Stachesil S from Stachema company. Material composition: >90 % SiO₂. Specific surface: 15 m²/g. Bulk density: 2400 kg/m³.
- Fly Ash ETU EN 450 from ČEZ company, Tušimice II power plant. Material composition: 48.8 % SiO₂, 24.2 % Al₂O₃, 12.5 % Fe₂O₃, 4.2 % CaO, 1.4 % K₂O, 1.4 % TiO₂, 1.2 % SO₃, 1.0 % P₂O₅, 0.7 % MgO, 0.6 % Na₂O. Specific surface: 0.25 m²/g. Bulk density: 2000 kg/m³.

The substitution of cement by additives in particular mixes was 0 %, 10 %, 20 %, and 50 % of cement weight, while the w/b was kept constant. These particular replacement levels were selected based on the results of tests of mechanical properties of the studied cement pastes [8], that were carried out for wider range of replacements (0%, 10%, 20%, 30%, 50% and 80%). These tests have shown significant decrease of compressive strength between 20 % and 30 % replacement.

Cement has different specific surface and water absorption than additives. Therefore it was necessary to change the water amount to keep the same w/b according to formula:

\[
w/b = \frac{m_w}{m_c + k \cdot m_a}\]

(1)

where \(m_w\) is the amount of water, \(m_c\) is the amount of cement, \(m_a\) is the amount of additive and \(k\) is a correction coefficient expressing the difference between cement and additive. According to the literature, \(k = 1\) for metakaolin, \(k = 0.4\) for fly ash and \(k = 2\) for microsilica should be used. With the amount of water calculated according to standard approach, the mix with 50 % microsilica replacement was not workable. Therefore \(k = 2.5\) was used for the given mix and the amount of water was amended accordingly.

Two types of fly ash with different particle size distribution curves (denoted as fly ash 1 and fly ash 2) were mixed in the proportion of 2:1 before addition to the pastes. Compositions of studied cement pastes are given in table 1.

**Table 1. Compositions of studied cement pastes [kg/m³].**

| Compound     | Refer. mix | Metakaolin | Microsilica | Fly ash |
|--------------|------------|------------|-------------|---------|
|              | 10 %      | 20 %      | 50 %        | 10 %    | 20 %    | 50 %    |
| Cement       | 1375       | 1233       | 1118        | 874     | 1177.1  | 774.4   |
| Water        | 550        | 542.5      | 536.6       | 524.4   | 565     | 681.5   |
| Additive     | -          | 123.3      | 223.6       | 437     | 117.7   | 154.9   | 289.2   | 126     | 232     | 473     |
| k value      | -          | 1.0        | 1.0         | 1.0     | 2.0     | 2.0     | 2.5     | 0.4     | 0.4     | 0.4     |
| w/b          | 0.4        | 0.4        | 0.4         | 0.4     | 0.4     | 0.4     | 0.4     | 0.4     | 0.4     | 0.4     |

3. Experimental methods

Particle size distribution curves were measured by laser diffraction particle size analyser HELOS KR (SYMPATEC) with its classical parallel beam laser diffraction set-up. Three 4 g samples were used for each material.

Hydration of cement can be monitored by two methods – solution calorimetry or isothermal calorimetry. Solution calorimetry is based on comparison of hydration heat released by non-hydrated cement and partially hydrated cement in a mixture of acids. The difference of the two values corresponds to the amount of heat released by partially hydrated cement. This first method is mostly used for long-time measurements. Isothermal method, which is based on direct measurement of hydration heat in a sample, is more suitable for very precise short-time measurements [6,7]. To
measure the heat flow and hydration heat development during the hydration phase of studied cement pastes, 8-channel isothermal microcalorimeter TAM Air (TA Instruments) was used. Hydration of samples weighing 2 g placed in glass ampules at 25°C was monitored for 48 hours.

4. Results and discussion

Results of particle size measurements are summarized in figure 1 and table 2. Values of $x_{50}$ (median particle size, 50% of particles are finer than this size) and $x_{90}$ (90% of particles are finer than this size) were used for comparison. As expected, metakaolin and microsilica were significantly finer than Portland cement. Fly ash 2 was comparable with metakaolin and microsilica, but as the fly ash was used as a mixture of fly ash 1 and fly ash 2 in the proportion of 2:1 in the samples, the resulting fly ash mix was coarser that Portland cement. On the whole, the particle sizes of particular materials correspond to specific surface areas given by the manufacturers (see section 1).

![Particle size distribution of particular materials](image)

**Figure 1.** Particle size distribution of particular materials.

**Table 2.** Main characteristics of particle size distribution curves.

| Material       | $x_{50}$ [μm] | $x_{90}$ [μm] |
|----------------|--------------|--------------|
| Cement         | 9.11         | 34.06        |
| Metakaolin     | 2.15         | 7.50         |
| Microsilica    | 2.92         | 6.74         |
| Fly ash 1      | 40.41        | 183.84       |
| Fly ash 2      | 2.10         | 6.82         |
| Fly ash 1+2 2:1| 5.89         | 124.35       |

Results of heat flow and hydration heat measurements are reported in figures 2 – 7 and table 3. The hydration process was similar for all studied cement pastes. The presence of additives and the cement replacement ratio affected the process quantitatively, but not qualitatively. Discussion is provided after the figures and table.
Figure 2. Heat flow and hydration heat of metakaolin – 48 hours.

Figure 3. Heat flow and hydration heat of microsilica – 48 hours.

Figure 4. Heat flow and hydration heat of fly ash – 48 hours.
Figure 5. Heat flow and hydration heat of metakaolin – initial 1 hour.

Figure 6. Heat flow and hydration heat of microsilica – initial 1 hour.

Figure 7. Heat flow and hydration heat of fly ash – initial 1 hour.
In all cases, maximum heat flow was recorded 4 – 5 minutes after homogenization, reaching ca. 15 – 20 mW/g. This was caused by wetting of cement grains and dissolving of aluminates and sulphates resulting in creation of portlandite and ettringite in the pre-induction period of hydration [5]. In the dormant induction period when nuclei of CSH crystals are formed, the heat flow rapidly decreased to ca. 0.25 – 0.6 mW/g at 2 – 5 hours after homogenization. Acceleration period characterized by formation of CSH and portlandite followed, reaching the second peak of heat flow of ca. 2 – 3 mW/g at ca. 10 – 12 (in rare cases 15 – 17) hours from homogenization. After that, heat flow slowly decreased during the deceleration period, reaching ca. 0.5 mW/g at the age of 48 hours when the pastes entered the steady state period [5].

The amount of hydration heat released after 1 hour varied approximately between 12 – 14 J/g for all the mixes. Total hydration heat after 48 hours was found to be ca. 200 – 250 J/g in most cases.

Heat flow in the induction period compared to reference sample was virtually unaffected in case of fly ash samples. Microsilica addition decreased heat flow, probably due to low contents of aluminates and sulphates in microsilica. Significant decrease was observed in case of 20 % replacement by metakaolin, but this tendency was not confirmed by the sample with 50 % replacement.

Hydration heat released after 1 hour decreased negligibly (by less than 10 % compared to reference sample) for all the samples except 20 % replacement by metakaolin (15 % difference). In the acceleration period, peak value of heat flow increased slightly with increasing cement substitution in case of metakaolin (by 11 % for 50 % replacement compared to reference paste) and decreased quite substantially in case of microsilica (by 25 %) and fly ash (by 37 %).

Total hydration heat measured at 48 hours decreased with increasing replacement ratio for all the additives. No substantial differences were found for 10 % and 20 % replacement by metakaolin and microsilica. In case of fly ash, replacement became notable at 20 % when the hydration heat decreased by 14 % compared to reference sample. 50 % replacement was significant for all the additives, the reductions being 15 % for metakaolin, 20 % for microsilica and 32 % for fly ash. The hydration heat released by pastes containing fly ash was generally the lowest, corresponding with the fact that fly ash was by far the coarsest material used in the study.

5. Conclusions

Based on the aforementioned results, following conclusions can be drawn for the studied cement pastes with partial replacement of cement by latent hydraulic additives:

- Cement replacement by 10 – 50 % wt. of metakaolin, microsilica or fly ash did not affect the general course of hydration phase from the point of view of hydration heat development. However, some quantitative differences were observed.

### Table 3. Main characteristics of hydration phase.

| Additive in the paste | Substitution [%] | Heat flow | Hydration heat |
|-----------------------|------------------|-----------|---------------|
|                       |                  | Peak 1 [mW/g] | Time 1 [h] | Peak 2 [mW/g] | Time 2 [h] | 1 hour [J/g] | 48 hours [J/g] |
| Pure cement           | -                | 19.83     | 0.08      | 3.04   | 10.78   | 14.04   | 255.96       |
| Metakaolin            | 10               | 19.04     | 0.08      | 2.90   | 10.59   | 13.46   | 242.71       |
|                       | 20               | 16.11     | 0.08      | 2.91   | 15.44   | 11.87   | 241.31       |
|                       | 50               | 18.82     | 0.07      | 3.37   | 11.45   | 13.50   | 219.23       |
| Microsilica           | 10               | 17.81     | 0.08      | 3.26   | 11.34   | 13.43   | 265.53       |
|                       | 20               | 15.91     | 0.08      | 2.87   | 12.72   | 12.80   | 240.53       |
|                       | 50               | 15.43     | 0.08      | 2.28   | 17.12   | 13.04   | 205.70       |
| Fly ash               | 10               | 19.81     | 0.07      | 3.00   | 10.86   | 13.75   | 255.12       |
|                       | 20               | 19.56     | 0.08      | 2.54   | 11.18   | 13.45   | 222.06       |
|                       | 50               | 20.15     | 0.06      | 1.92   | 12.25   | 12.70   | 174.94       |
Microsilica decreased the heat flow in the induction period, probably due to low contents of aluminates and sulphates in microsilica. The reduction was notable even for 10% replacement.

Hydration heat released during the initial 1 hour was almost equal for all the additives and replacement ratios.

Heat flow in the acceleration period remained practically unchanged up to 20% cement replacement for all the additives. Substantial decrease was observed for microsilica and fly ash at 50% replacement.

Total hydration heat measured at 48 hours decreased with increasing replacement ratio for all the additives. Substantial decrease was observed at 50% replacement for all the additives. In case of fly ash, it became notable already at 20% replacement, probably due to coarser nature of the additive.

In general, it can be stated that 20% cement replacement by any of the tested additives should not affect the hydration process of the cement paste significantly. This is in agreement with the results of tests of mechanical properties of the studied cement pastes that have been carried out recently [8].

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