Influence of Eco-Friendly Mineral Additives on Early Age Compressive Strength and Temperature Development of High-Performance Concrete

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Abstract. High-performance concrete (HPC) which contains increased amount of both higher grade cement and pozzolanic additives generates more hydration heat than the ordinary concrete. Prolonged periods of elevated temperature influence the rate of hydration process in result affecting the development of early-age strength and subsequent mechanical properties. The purpose of the presented research is to determine the relationship between the kinetics of the heat generation process and the compressive strength of early-age high performance concrete. All mixes were based on the Portland Cement CEM I 52.5 with between 7.5% to 15% of the cement mass replaced by the silica fume or metakaolin. Two characteristic for HPC water/binder ratios of w/b = 0.2 and w/b = 0.3 were chosen. A superplasticizer was used to maintain a 20-50 mm slump. Compressive strength was determined at 8h, 24h, 3, 7 and 28 days on 10x10x10 cm specimens that were cured in a calorimeter in a constant temperature of T = 20°C. The temperature inside the concrete was monitored continuously for 7 days. The study determined that the early-age strength (t<24h) of concrete with reactive mineral additives is lower than concrete without them. This is clearly visible for concretes with metakaolin which had the lowest compressive strength in early stages of hardening. The amount of the superplasticizer significantly influenced the early-age compressive strength of concrete. Concretes with additives reached the maximum temperature later than the concretes without them.

1. Introduction
Modern pozzolans are often used as supplementary cementitious materials in cement pastes and can partially replace the clinker to improve the mechanical properties of hydrated cement. Portland cement production results in emission of significant amounts of CO₂ from calcination of the limestone, [1]. Considering global aim to reduce the CO₂ emissions downsizing the production of Portland cement and using replacement pozzolan materials is beneficial to the environment, [2]. Pozzolans are materials containing silica and alumina which with addition of portlandite under the effect of water have binding properties [3–6]. During the hydration process the amount of portlandite (Ca(OH)₂) will be reduced proportionally to the amount of pozzolans used to replace cement in the mixture. Amount of portlandite varies depending on the type of cement and C₃S and C₂S content in it. During cement hydration C₃S and C₂S react with water to form C-S-H (calcium-silicate-hydrate) and portlandite – Ca(OH)₂. Portlandite is particularly susceptible to carbonation, regardless of the conditions [7]. Small amount of portlandite reacts with aluminate and sulphate to create ettringite. As a result, not all of the portlandite in the process is available to react with pozzolans. Portlandite is a component of hydrated...
Portland cement, which comprises to 20-25% of its mass. [7]. Pozzolans are used in order to increase the durability (especially long term) [8], lower the hydration heat and increase the resistance to sulphate attack. An addition of the metakaolin reduces shrinkage and cracking of concrete samples [9].

The first stage of curing of concretes containing pozzolan additives is important for whole development of hydration. As soon as in 1997, Lilkov et al. [10] conducted study on early hydration of concrete. Research showed that concrete mixes with silica fume and fly ash actively effected the early hydration of cement by increasing the overall amount of reaction products and decreasing the amount of calcium hydroxide (\( \text{Ca(OH)}_2 \)). Many studies [11] have shown that the addition of metakaolin significantly impacts on the early (24 h) strength of concrete with additives. Research were conducted for both mixes with big and small amounts of binder.

Early strength of concrete is important considering safety (shorter striking time) and economical aspects. Additionally the issue of hydration heat of the mix, especially in mass constructions [12], is of a great importance as the temperature differences inside the object can cause structural damages.

The study determines the relationship between the kinetics of the heat generation process and the compressive strength of early-age high performance concrete with reactive mineral additives (metakaolin and silica fume).

2. Materials and method

2.1. Materials and concrete mix composition

All mixes were based on the Portland Cement CEM I 52.5R (according to European Standard EN 197-1:2000) with between 7.5% to 15% of the cement mass replaced by the silica fume and metakaolin. Two typical for HPC water/binder ratios of w/b = 0.2 and w/b = 0.3 were chosen. A superplasticizer was used to maintain a 20-50 mm slump (exact amounts are shown in figures 2-8). The amount of binder in every mix was set to 600 kg. Table 1 shows the chemical content of used materials.

|                | CEM I 52.5R | Silica Fume | Metakaolin |
|----------------|-------------|-------------|------------|
| SiO₂           | 19.7        | 85-96       | 52.9       |
| Al₂O₃          | 4.93        | -           | 44.19      |
| Fe₂O₃          | 2.54        | -           | 0.4        |
| CaO            | 64.23       | -           | 0.02       |
| MgO            | 1.32        | -           | 0.06       |
| SO₃            | 2.91        | 0.3-0.7     | -          |
| Na₂O           | 0.12        | -           | 0.16       |
| K₂O            | 0.76        | -           | 0.09       |
| Cl             | 0.07        | -           | -          |
| Na₂Oeq         | 0.63        | -           | -          |

2.2. Experimental procedure

Compressive strength tests were conducted on standard cubes of 100 × 100 × 100 mm at the age of 4, 8, 24, 72, 168 and 672 hours for all of the mixes. The mixing was done in a planetary concrete mixer. The samples were cast and kept in climatic chamber with constant temperature (20°C) and humidity (60%).

3. Results and discussions

3.1. Compressive strength

Table 2 shows the mean value of the compressive strength (f cm) for specific curing times and coefficient of variation (CoV) for each set of specimen.
For \( w/c = 0.3 \) the early (up till 24 h) strength of concretes without additives is higher than for concretes with them. Metakaolin and silica fume were used as partial replacement of the cement in the mixes. During the hydration lower amounts of available cement, results in slower development of strength [13–15]. The pozzolan additives start reacting with \( \text{Ca(OH)}_2 \) after 24 h [16,17] improving the development of strength in concretes with additives. Similar results were acquired by Mansour et al. [14], who replaced 10% of cement with metakaolin. Lower early strength was also acquired by Kadri et al. [13] who also replaced 10% of cement with additives.

Figure 1 shows that the addition of silica fume results in increase of the compressive strength in concrete cured for at least 72h. Similar results were acquired in other studies [15,18].

The addition of metakaolin decreases the strength of concrete in the first 24 h (Figure 1) even more than the silica fume. After 72 h metakaolin increases the strength of concrete more than silica fume. Similar results were acquired by other scholars [11]. A study performed by Curcio et al. [19] showed that use of metakaolin even of different origin and density increased the compressive strength of concretes. Test also showed that the optimal amount of metakaolin depends on the water/binder ratio and the amount and type of cement [11]. This study also showed that the development of early strength is lower for concrete with metakaolin than for ordinary concrete. Study showed the effectiveness of metakaolin is lower when used with cements with rapid strength development [5,19,20]. The same conclusions can be drawn from results from this study.

![Figure 1. Compressive strength of concretes with \( w/b = 0.3 \)](image-url)

After 28 days of curing concretes with metakaolin have higher compressive strength than concretes with silica fume. Similar conclusions can be seen in other studies. In a study [21] several mixes with \( w/b = 0.3 \) (500 kg of binder) and \( w/b = 0.5 \) (410 kg of binder) were tested. Mixes contained 5, 10, 20% of metakaolin and 5%, 10% of silica fume. The strength of concretes with metakaolin in that study was higher starting from the 3rd day of curing (early strength was not tested). In other study [22] concretes with \( w/b = 0.25 \) (550 kg of binder) and \( w/b = 0.35 \) (470 kg of binder) were evaluated. Results
showed that for higher w/b ratio concretes with metakaolin had higher compressive strength than concrete with silica fume. For w/b ratio of 0.25 metakaolin concrete had approx. 3% lower compressive strength. Study [23] showed that concrete with silica fume had higher strength after 28 days. Above mentioned study tested mixes containing 400 kg of binder with metakaolin and silica fume content of 5%, 7.5%, 15% and w/c = 0.4. Different study [24] of concrete with w/b = 0.5 with silica fume and metakaolin content of 10% showed that the addition of metakaolin is a better enhancer of compressive strength than silica fume.

Results for concretes with w/b=0.2 are presented in Figure 2. The addition of 7.5% of silica fume enhanced the compressive strength of concrete regardless of curing time. Addition of 15% of silica fume did not significantly influence the strength of concrete comparing to the ordinary concrete. Only after 28 days, the samples with silica fume exhibited higher compressive strength.

Regardless of the added amount of metakaolin the early strength was lower than in a control sample. Only after 7 and 28 days the samples have increased compressive strength.

The addition of metakaolin negatively influenced the workability of the concrete mix comparing to ordinary concrete and concrete with silica fume. To acquire the necessary workability, the mix required higher amounts of superplasticizer.
3.2. The measurements of concrete’s temperature

Figures 3-8 show the results of temperature measurements of the interior of the concrete cubes. The temperature was measured with PT-100 sensor placed inside the sample. The recording was continued during the whole curing period of the sample in the climatic chamber.

**Figure 3.** Temperature in concrete with silica fume (SF) admixture (w/b=0.3)

Figure 3 presents the temperature development in concrete with w/b=0.3 and added silica fume. The graph shows that the concrete without silica fume reached highest temperature. The increase of the silica fume content decreases the maximum temperature simultaneously stopping the generation process more quickly. Similar results were published by Kadri & Duval [25], where they studied concretes with w/b between 0.25 to 0.35 under semi-adiabatic conditions. The heat generation process shown in that study is concurring to the one presented here. However, concretes presented in their study reached peak temperature after 10 to 12 hours, which can be explained by different testing conditions.

**Figure 4.** Temperature in concrete with metakaolin (MK) admixture (w/b=0.3)

Different study was conducted by Langan et al. [26], where the authors tested concretes with w/b between 0.35 and 0.5 in isothermal calorimeter. The samples with 5% and 10% of silica fume additive where cured under 25°C. The results of that study show that the highest temperature point occurs
between 8 and 12 hours. The addition of silica fume slowed the hydration process but increased the maximum temperature of the concrete. The differences between the study of Langan et al. [26] and [25] and this research can be explained by different w/b ratios and lower amounts of cement in the mix.

Figure 4 shows the temperature development of w/b=0.3 concrete with addition of metakaolin. Concrete without additives reaches higher temperatures and faster. The higher the content of metakaolin the lower the maximum temperature that is reached with a delay. This proves the effectiveness of metakaolin in hindering the heat generation process. Similar results where shown in [27]. The study tests different amounts of metakaolin content (5%; 10%; 15%; 20%). Similarly to [27], in this study the highest temperature was reached after 8h. It was also noticed that the temperature decreases with the content of metakaolin of more than 10%. In a different study conducted by Janotka et al. [28] the maximum temperature and time of reaching it are concurring to results presented here.

Figure 5 shows the development of the temperature in concrete with w/b=0.2 and silica fume additive. Results showed that the maximum temperatures are similar as in concretes with w/b=0.3. The difference occurred in the point of reaching maximum temperature. Concretes with lower w/b ratio and silica fume reach the maximum temperature later than concretes with w/b=0.3 in comparison to reference sample. The probable cause lays in the amount of the superplasticizer used for achieving proper workability. The amount of superplasticizer in ordinary concrete with w/b=0.2 was 2.52%, whereas in concrete with silica fume 3.3%. Increased amount of admixture allowed to increase the workability, but also hindered the time of reaching the maximum temperature. This effect of superplasticizer was proven elsewhere [29,30].

![Figure 5. Temperature in concrete with silica fume (SF) admixture (w/b=0.2)](image)

Figure 6 shows the development of temperature in concrete with w/b=0.2 and metakaolin additives. The results of temperature peak and reaching period are similar to the ones acquired for w/b=0.3. The peak of the temperature was reached later than in concretes with higher w/b ratio. The concretes however contain much higher amounts of superplasticizer than the reference mix. The addition of metakaolin decreased the workability more than the addition of silica fume, which can be seen in almost 1% higher content of superplasticizer in the mix.
The results show that concrete reaches the peak of the temperature more rapidly if it contains no additives. The higher the content of additives the bigger the delay in reaching the maximum temperature. Delay of reaching the peak temperature was higher for mixes with metakaolin. Results are visible in Figure 7.

Concretes without additives reached higher temperatures than concretes with additives. The lowest temperature was measured for concretes with high amounts of metakaolin. Based on those results it can be said that the maximum temperature decreased proportionally to the amount of additive. Results are visible in Figure 8.
4. Conclusions
The additives can replace partially the cement amount. The process is beneficial not only considering improvement of mechanical properties but also the environment. Use of pozzolan additives is environmentally friendly because it allows to reduce the emission of CO$_2$ by decreasing the production of cement. Moreover, the additives are mostly considered as waste products, so their use fits perfectly to the notion of sustainable development.

To sum up, results presented in this study showed that the metakaolin and silica fume additives added to the concrete (7.5% and 15% of cement mass) with 600 kg of binder changed the process of heat generation. Concrete without additives reaches the maximum temperature faster. The higher the content of the additives the more delayed was the peak temperature point. Additionally, delay in reaching the peak temperature was higher for concretes with metakaolin. The compressive strength of concretes containing any amounts of additives was higher after 28 days.

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