Analysing the Pozzolanic Reactivity of Chalcedony Dust in Cement Paste

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Abstract. The considerable energy consumption and greenhouse gas emissions in the production of Portland clinker makes it extremely important to use substitutes in the form of mineral additives. Chalcedony dust, being a natural mineral raw material, is an additive that may come into pozzolanic reaction, similarly as fly ash does. The present paper reports the results of research on the reactivity of chalcedony dust of variable graining. For the measurement of the degree of the pozzolanic reactivity of mineral additives, the physical methods according to Polish Standard PN-EN 450:1:2009, the Fratini mechanical testing method and the Italian method, were used. The employed methods revealed the properties of chalcedony pozzolanic dust of a grain size smaller than 0.063 mm. Tests for the effect of chalcedony dust on cement hydration were also carried out by the differential thermal analysis (DTA/TG) method. It was shown that the Ca(OH)₂ content was lower for cement pastes with mineral additive.

1. Introduction
Additives having pozzolanic properties play a crucial role in concrete technology. These materials modify a number of service properties of cement composites, such as the setting time, the heat of hydration, or strength. The pozzolanic activity of mineral additives manifests itself in the amount of Ca(OH)₂ bonded by pozzolana, the rate of the reaction of pozzolana with Ca(OH)₂ and its influence on the strength of mineral binders [1]. Mineral additives with pozzolanic properties also influence the improvement of strength of cement composites. They can be exemplified as lithium compound [2,3] attach alkaline corrosion to concrete [4].

Several methods are used for testing the pozzolanic reactivity, which yield varying results for the same group of pozzolanas. Therefore, no single universal method can be used or selected, which would describe the pozzolanic reactivity. The best practice is to use several methods that complement one another [1]. The methods of testing pozzolanic reactivity can be categorized into chemical and physical methods. Physical methods involve primarily the determination of the effect of pozzolana on the strength of cement pastes. The paper discusses the results of tests for the pozzolanic reactivity of chalcedony dust, as specified by Polish Standard PN-EN 450:1:2009 [5, 6], by the Fratini mechanical testing method and the Italian method. The effect of the graining on the pozzolanic properties of this additive. Tests on the influence of chalcedony dust on the hydration of cement after 2, 7, 28 and 90 days were also carried out by the differential thermal analysis method.
2. Materials and testing methodology

2.1. Materials

CEM I 42,5R Portland cement was used for tests. Chemical composition of cement is shown in Table 1.

| CEM I | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | K₂O | Na₂Oc | eq Na₂O | Cl⁻ |
|-------|------|-------|-------|-----|-----|-----|-----|-------|---------|-----|
| Contents [%] | 17.52 | 5.23 | 2.81 | 60.00 | 1.44 | 3.20 | 0.84 | 0.19 | 0.734 | 0.069 |

The examination of the phase composition of the chalcedony dust used, performed by the X-ray method, is illustrated in Figure 1. The examination was carried out on PANalytical - X-ray diffractometer.

![Figure 1. Diffraction pattern of the chalcedony dust used for the tests](image)

The phase composition of the material includes chiefly quartz. The rise of the background within small angle interval indicates the presence of an amorphous phase. The examination of the chalcedony microstructure was performed on a scanning microscope. The results of the chalcedony dust microstructure examination showed the occurrence of regular grains of a compact structure. The EDS X-ray microanalysis made on the chalcedony dust surface reveals the presence of mainly silicon and oxygen [4].

2.2. Testing methods

For testing the pozzolanic reactivity of chalcedony dust, the physical methods specified by Polish Standard PN-EN 450:1:2009, the Fratini mechanical testing method and the Italian method were used.

The Standard PN-EN 450:1:2009 describes the testing of the pozzolanic reactivity index defined as the percentage ratio the compressive strength of the standard mortar with a binder containing 75 wt % of cement and 25 wt % of the pozzolanic additive to the compressive strength of the standard mortar with cement. CEM I 42,5R Portland cement was used. The pozzolanic reactivity index for the mineral additive after 28 days should amount to 75 %, while after 90 days, 85 % [5, 7]. Three fractions of chalcedony dust with a grain size of, respectively, below 0.063 mm, 0.063-0.125 mm and 0.125-0.25 mm, were used for the pozzolanic reactivity tests. The grading of the mineral additive was determined by the laser diffraction method. Four series of 40x40x160 mm specimens were prepared, which were
held for 28 and 90 days at a temperature of 20 °C. After that time, mechanical tests were performed on the cement mortars.

The Fratini mechanical testing method relies on determining the difference in compressive strength between specimens stored in standard conditions and specimens stored at elevated temperature. Two series of specimens were prepared, each of them being made of the standard mortar with a binder containing the addition of 30 % of chalcedony dust relative to the cement mass. One of the specimen series was stored for 7 days under standard conditions (in water at a temperature of 20° C), while the other specimen series, after three days of curing under standard conditions, was transferred to water at a temperature of 50° C and stored in these conditions for another 4 days. The increase in the strength of specimens held at elevated temperature relative to that of specimens held under standard conditions indicates the pozzolanic reactivity of the mineral additive used [8].

The next pozzolanic reactivity testing method presented in the paper is the Italian method. It involves the determination of the strength of specimens prepared from calcium hydroxide and a mineral additive in a mass ratio of 1:3. One series of 40x40x160 mm specimens was made. The specimens were held for 7 days in a moisture atmosphere, and then transferred to water for subsequent 21 days. Cement paste containing highly reactive pozzolana should attain bending strength greater than or equal to 0.5 MPa and compressive strength greater than or equal to 2.5 MPa [8, 9].

The differential thermal analysis of cement pastes and pastes with a binder containing the addition of chalcedony dust of a grain size smaller than 0.063 mm was made. Tests were performed after 2, 7, 28 and 90 days on cement paste specimens with a constant ratio of w/c= 0.5. A measure of pozzolanicity is the quantity of calcium hydroxide bonded in the pozzolanic reaction. The quantity of unbounded Ca(OH)₂ in the paste was determined from DTA/TG thermal examinations by comparing the magnitude of the specimen mass loss (the TG curve) in the range of temperatures corresponding to the endothermic effect recorded at a temperature of approx. 490- 510 °C (the DTA curve). This is the effect associated with the thermal decomposition of Ca(OH)₂ [9, 10].

3. Investigation results and discuss
For testing the pozzolanic reactivity index according to PN-EN 450-1:2009, three fractions of chalcedony dust were used, namely: < 0.063 mm, 0.063 - 0.125 mm and 0.125- 0.25 mm. Chalcedony dust graining is shown in Figure 2.

![Figure 2. Graining of the mineral additive](image)

The reactivity index of chalcedony dust of a different grain size fraction was determined following the procedure specified in Standard PN-EN 450-1:2009.

The following specimen designations were taken for the tests:

- P0 - specimen with no chalcedony dust addition
- P1 - specimen with the addition of chalcedony dust in grain size fraction < 0.063 mm
- P2 - specimen with the addition of chalcedony dust in grain size fraction 0.063- 0.125 mm
- P3 - specimen with the addition of chalcedony dust in grain size fraction 0.125- 0.25 mm.

The test results are shown in Table 2.

**Table 2. Reactivity indices of chalcedony dust of varying graining**

| Specimen symbol | Compressive strength after 28 days [MPa] | Reactivity index after 28 days [%] | Compressive strength after 90 days [MPa] | Reactivity index after 90 days [%] |
|-----------------|------------------------------------------|-----------------------------------|------------------------------------------|-----------------------------------|
| P0              | 53.35                                    | -                                 | 64.21                                    | -                                 |
| P1              | 41.84                                    | 78.4                              | 55.57                                    | 86.5                              |
| P2              | 33.87                                    | 63.4                              | 44.32                                    | 69.0                              |
| P3              | 27.05                                    | 50.7                              | 38.54                                    | 60.0                              |

The tests showed that only chalcedony dust of a grain size smaller than 0.063 mm had pozzolanic properties. The pozzolanic reactivity index of specimens with this fraction amounted to 78.4 % after 28 days and 86.5 % after 90 days, which, according to the standard requirements, indicates the pozzolanic properties of the mineral additive.

Considering the results of the tests according to PN-EN 450-1:2009, only one chalcedony dust fraction of a grain size smaller than 0.063 mm was used in subsequent pozzolanic reactivity tests.

For tests by the Fratini method, two specimen series were prepared, each made up of 3 specimens with the addition of chalcedony dust in the amount of 30 % of cement mass. Average mechanical test results of each series are shown in Table 3.

**Table 3. Average results of the compression test by the Fratini method**

| Compressive strength after 7 days, temp. 20º C [MPa] | Compressive strength after 3 days, temp. 20º C + 4 days temp.50º C [MPa] | Difference [MPa] R3 - R7 |
|--------------------------------------------------|------------------------------------------------------------------------|------------------------|
| R7                                               | 29.79                                                                  | 39.09                  | 9.3                    |

The test results showed that the specimens, which had been initially held under standard conditions and then at 50º C, had their compressive strength higher by 9.3 MPa, compared to specimens cured under standard conditions. The increased strength of the specimens cured at the higher temperature indicates the pozzolanic properties of chalcedony dust. The tests demonstrated that the increase in temperature caused the acceleration of the pozzolanic reaction.

Pozzolanic reactivity tests were also performed on specimens with the calcareous binder following the Italian method. The results of bend and compression testing of specimens’ calcium pozzolanic paste (mass ratio 1:3) after 28 days are given in Table 4.

**Table 4. Average results of bend and compression testing after 28 days**

| Average bending strength [MPa] | Average compression strength [MPa] |
|-------------------------------|------------------------------------|
| 0.5                           | 2.7                                |

The bending strength of mineral additives having pozzolanic properties, as determined by the Italian method, should be greater than or equal to 0.5 MPa, whereas the compressive strength should be greater than or equal to 2.5 MPa. The test results have shown that chalcedony dust has pozzolanic properties, because the guidelines for the strength values, as specified for the method, have been met.
The differential thermal analysis tests were carried out on cement pastes (Z0) and on pastes with the 25 % addition of chalcedony (Z1) dust with w/c = 0.5. The results of testing the pastes after a different hydration time are shown in Figures 3, 4 and 5.

![Figure 3](image1.png)  
**Figure 3 (a)** DTA profile and **(b)** TG profile of cement pastes (Z0) after 2, 7, and 28 days in sealed condition.

![Figure 4](image2.png)  
**Figure 4 (a)** DTA profile and **(b)** profile of cement pastes with 25 % chalcedony dust (Z1) after 2, 7, and 28 days in sealed condition.

![Figure 5](image3.png)  
**Figure 5 (a)** DTA profile and **(b)** TG profile of cement pastes (Z0) and cement pastes with 25 % chalcedony dust (Z1) after 90 days in sealed condition.

The tests showed a mass loss after 2, 7, 28 and 90 days. In specimens with the chalcedony dust addition, a smaller quantity of unbounded Ca(OH)$_2$ was observed in the temperature range of 480 – 510°C.
4. Conclusions
The obtained results allow the following conclusions to be drawn:

- The obtained results confirm the literature data, which indicate that the pozzolanicity of chalcedony dust depends not only on its phase and chemical composition, but above all, on its graining.
- The tests carried out following the PN-EN 450:1:2009 Standard have found that pozzolanic properties are exhibited by chalcedony dust of a grain size smaller than 0.063 mm. The pozzolanic reactivity index of the cement paste with the mineral additive of this graining amounts to, respectively, 74.8 % and 86.5% after 28 and 90 days.
- Increasing the temperature has the effect of accelerating the pozzolanic reaction. The results of testing by the Fratini method have revealed a difference in compressive strength between specimens cured at 20°C and 50°C. Specimens cured at a temperature of 50°C exhibited compressive strength higher by 9.3 MPa compared to specimens cured in standard conditions.
- The tests carried out based on the Italian method have also allowed chalcedony dust to be classified into materials having pozzolanic properties. The bending strength is 0.5 MPa and the compressive strength is 2.7 MPa. The strength values meet the criteria of this method.
- The results of the differential thermal analysis tests showed a loss in Ca(OH)₂ mass after 2, 7, 28 and 90 days in specimens with the addition of chalcedony dust, compared to control specimens.

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