Estimation of pozzolanic activity of artificial mineral additive using thermal analysis

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Abstract. Application of various supplementary cementitious materials was adopted currently by number of research institutions worldwide. The main motivation is to find out predominantly environmental friendly technologies applicable in cement industry; however this technology is not new. Historically were various active mineral additives used in Ancient times and this technology was rediscovered at the end of 19th century with gradual development of cement and lime industry. This paper is focused on the long-term experimental study of pozzolanic reaction monitored in terms of thermogravimetry by the determination of the consumption of lime. Various types of ceramic powder were studied during two years and their activity was estimated using predictive method. Obtained results confirmed significant impact of the finesses on the reaction kinetics and also on the total hydration potential.

1. Introduction
Utilization of hydraulic lime or lime with addition of active mineral additive has long tradition in building industry. Development of this technology allowed dynamic of various human civilizations. Probably the most famous example offers Ancient Rome, where hydraulic lime was used for the most exposed structures of advanced Roman infrastructure. It was applied for the substructure of roads, bridges, and other iconic structures such as aqueducts or Pantheon, which is the most famous building made of predecessor of modern concrete. Romans used lime with addition of volcanic ash, which was used on the construction of the port in Caesarea [1-3]. However, as time went on, the natural pozzolan was replaced by artificial material in form of waste ceramic. Proofs of its utilization are confirmed by number of studies [4-5]. Due to limited finesses served applied ceramics predominantly as active filler. This technology was over time forgotten and replaced by other building procedures based on the utilization of clay, wood and stone. Further development of utilization of hydraulic lime started during 19th century in relation with the production of Portland cement [6].

Lime mortars with addition of pozzolanic additives were intensively used in Bohemia at the turn of the 19th century for the production of modern mosaic. This decorative element is typical architectural component of building structures from this period. They were used in interiors, however number of works was situated in exterior. In the exterior applications, it was obviously necessary to use mortar with suitable resistance to the environment. These mortars could be based on the cement or hydraulic lime; some of them were created from lime with addition of milled bricks, which ensured formation of hydraulic bond. These mortars primarily served for the fixation of tesseraes, which was most frequently represented by pieces of colored glass.

Actual state of binder system of these mortars is crucial information for the assessment of mosaics’ properties and possibly for the procedure of their protection. The main aim of present paper is to estimate hydration process of lime mortar with various types of ceramic powder. This research
partially follows previous research [7], where pozzolanic activity of ceramic powder using thermogravimetry was monitored. In this paper, predictive model for hydration monitoring was applied for the description of chemical processes with determined hydration capacity. The used mathematical model is based on Michaelis-Menten equation, which is commonly applied in chemical engineering [8-10].

2. Experimental program
Ceramic powder produced by Heluz Ltd. (Hevlín clay quarry) was used in performed experimental program. Subject material originates during hollow brick blocks production by grinding of load areas, what allows precious brick-laying; thickness of loading gap is approximately just about 1 mm. Chemical composition of produced ceramic in the studied factory is very stable in time (table 1). This composition perform annual average, however particular components are varying in order of tenth of percent.

Table 1. Chemical composition of studied ceramic powder [%].

|       | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | Na₂O | TiO₂ | SO₃ |
|-------|------|-------|-------|-----|-----|-----|------|------|-----|
| Value | 51.3 | 20.0  | 6.0   | 11.5| 4.5 | 3.2 | 1.3  | 0.8  | 1.0 |

Illitic clay is used as raw material for the production in given factory. Mineralogical composition of studied material determining its pozzolanic activity is shown in table 2. Amorphous part of the ceramic powder indicates its pozzolanic activity. This pozzolanic material was studied by Keppert et al. [11], where ceramic powder with \( D_{\text{max}} \) 125 μm exhibited pozzolanic activity in terms of Chapelle test consumption of Ca(OH)₂ after 7 days 1066 mg/g. The finesses of ceramic powder has crucial impact on the reactivity, what was also published by Navrátilová et al. [12]. Different types of ceramic powders were also used in this program; particular materials were prepared by sieving with sieves 0.125, 0.063, 0.050, 0.030 and 0.015 μm, respectively. They were designated with increased finesses CP-1 to CP-5. Particle size distribution is shown on Figure 1.

Table 2. Mineralogical composition of studied ceramic powder [%] [7,11].

| Component      |   |
|----------------|---|
| Amorphous components | 45.3 |
| Quartz          | 26.8 |
| Albite          | 7.2  |
| Microcline      | 6.3  |
| Muscovite       | 3.1  |
| Åkermanite      | 3.2  |
| Hedenbergite    | 4.1  |
| Gypsum          | 0.6  |
| Hematite        | 1.9  |

Such prepared ceramic powders were mixed with slaked lime CL90 – S, which contains over 99% of CaO. Mixing ratio was 50:50 by mass, water to binder ratio was set to constant 0.75. Prepared fresh mixtures were placed into plastic containers with sealed lid to eliminate carbonation during hydration. The progress of pozzolanic reaction was monitored by using thermogravimetry and determination of the content of Ca(OH)₂ in time. Measurement was carried out using Schimadzu DTG60-H with heating rate 10K/min. Exact boundaries of the occurring portlandite decomposition were derived from derivative curves of TG curve. Single measurements were conducted after 7, 14, 21, 28, 60, 180, 360 and 720 days, respectively. Mass of samples subjected to thermal analysis was about 40 mg.
Figure 1. Particle size distribution of used ceramic powders.

Gradual consumption of Ca(OH)$_2$ was monitored in time and processed using Michaelis-Menten equation (1), which is often used for the prediction of entire reaction capacity. In knowledge of a few points of subject reaction, it is possible to estimate ultimate value ($V_{\text{max}}$). $T$ means time (hours), $v$ is partial value of studied property and $K$ is rate constant. Illustrative example is drawn on Figure 2. It is obvious that present shape has good fit with progress of hydration of lime with pozzolanic addition.

$$v = V_{\text{max}} \frac{T}{K + T}$$

(1)

![Figure 2. Illustration of Michaelis-Menten function.](image)

Obtained values of Ca(OH)$_2$ consumption in time for single mixtures were processed by Matlab using Least Square Method (LSM). Present nonlinear solution allows acquisition of optimal fit and precision of the estimation. Besides acquisition of ultimate reaction capacity, it is also possible to monitor reaction kinetic for a single mixture. Amorphous content of ceramic powder is about 0.45, what is supposed to be the theoretically limit value.

3. Results and discussion

Performed experimental program was focused on the estimation and monitoring of pozzolanic reaction. The monitoring was conducted by using thermogravimetry and determination of actual
content of Ca(OH)$_2$. Obtained results were processed by LSM to obtain estimation in terms of Michaelis-Menten equation.

Obtained values of Michaelis-Menten constant and ultimate reaction capacity are shown in table 3. There is obvious, that finesses of ceramic powder has significant role in the pozzolanic reaction of studied material and entire kinetic. The highest value of $V_{\text{max}}$ was obtained, as expected, by the mixture CP-5, which contained the ceramic powder with the highest finesse. Mixtures CP-1 and CP-2 exhibited nearly similar results; following mixtures reached proved gradually increased reactivity.

**Table 3. Obtained values from estimation process.**

|       | $V_{\text{max}}$ | K     |
|-------|------------------|-------|
| CP-1  | 45.5             | 2768.7|
| CP-2  | 43.7             | 1763.7|
| CP-3  | 44.8             | 1672.1|
| CP-4  | 46.6             | 1748.5|
| CP-5  | 48.4             | 1409.9|

**Figure 3.** Estimation using Michealis-Menten equation.

However, the experiment was conducted in specific conditions excluding the process of carbonation, which plays an important role in case of lime mortars. The kinetics of particular mixtures are well visible in Figure 3. It is obvious, that mixture CP-1 (with grains up to 0.125mm) exhibited the slowest progress of pozzolanic reaction, on the other hand CP-5 exhibited rapid progress of pozzolanic reaction during initial phases of hydration. CP-5 during initial 14 days of hydration obtained more than two time higher consumption of Ca(OH)$_2$ in comparison with CP-1. Thorough experimental study was carried out by Cachova et al. [13], who oriented the research on the monitoring of pozzolanic reaction kinetic of ceramic powder, which corresponds with CP-1. In this study was pozzolanic reaction compared with kinetics of carbonation, which are competitive process during the lime based mortars hardening, what is described by equation 2 and equation 3.

\[
\text{Ca(OH)}_2 + \text{Ceramic Powder} \rightarrow \text{hydration products} \tag{2}
\]

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \tag{3}
\]
Kinetic of Ca(OH)$_2$ consumption for carbonation was obtained from compressive strength evolution of lime based plasters published in [12-13], who studied similar systems with addition of pozzolans. These data shows, that carbonation plays a dominant role in the process of hardening. Obtained results were integrated to previous results, Figure 4. For better illustration of initial kinetic of all studied processes, it was transformed to logarithmic scale, Figure 5.

**Figure 4.** Comparison of Ca(OH)$_2$ consumption due to carbonation and pozzolanic reaction using Michaelis-Menten estimation.

**Figure 5.** Comparison of Ca(OH)$_2$ consumption due to carbonation and pozzolanic reaction using Michaelis-Menten estimation.

It is obvious, that carbonation is the dominant process during hardening, so the reaction kinetic is controlled by diffusion. That means, that conversion of lime to calcite is much faster, than pozzolanic reaction. These conclusions confirms research published in [13-14], where thorough research of
cement-ceramic powder system was realized. Cement based system is a specific, due to continuous formation of new Portlandite, that is why was applied model by Kondo [15].

4. Conclusion
Experimental program with aim at the reaction kinetic of various ceramic powder was realized in this work. Applied ceramic powders had different finesses, what caused various kinetic of pozzolanic reaction, which was estimated using Michaelis-Menten equation. Organizing of conducted experimental work eliminated the influence of carbonation. Performed work confirm original prerequisite, that finesses of the pozzolan has significant impact on the reaction progress. However, obtained results confirmed very slow progress of pozzolanic reaction in studied mixtures. Carbonation was considered as faster mechanism in comparison with obtained results on lime-ceramic powder pastes. These results also well correspond with current construction praxis, which applies the duration of hardening to approximately 7days per 10 mm of the plaster. It is necessary to note, that in this is not consumed entire lime for the carbonation, however this process considerably retards consequent pozzolanic reaction. That means that part of the used pozzolan is fixed in the system as active filler. This fact could be successively exploited during renovation and restauration work by lime water curing, which is often used as in conservation practice, despite that present treatment is based in the carbonation.

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