*Acta Polytechnica CTU Proceedings* **53**:102–107, 2025
`https://doi.org/10.14311/APP.2025.53.0102`

Published by the `Czech Technical University in Prague`

# MONITORING THE REACTIVITY OF POZZOLANS BY THERMOGRAVIMETRIC METHOD

Martin Vyšvařil

*Brno University of Technology, Faculty of Civil Engineering, Veveří 331/95, 602 00 Brno, Czech Republic*
correspondence: `martin.vysvaril@vut.cz`

Abstract. This work focuses on comparing the effect of ten different types of pozzolans on the strength of lime pastes in relation to their pozzolanic activities as determined by the Chapelle test and monitoring the reactivity of these pozzolans using the thermogravimetric method. It was found that the Chapelle test can in some cases overestimate the reactivity of the pozzolan due to differences between the conditions during the test and in reality. The strengths of lime-pozzolan pastes did not correlate well with the pozzolanic activity values of the pozzolans used. On the contrary, the amount of reacted lime in the pastes, determined by the thermogravimetric method, correlated very well with the compressive strengths of the pastes.

Keywords: Pozzolan, pozzolanic activity, Chapelle test, thermogravimetry, compressive strength.

## 1. Introduction

Air lime-pozzolan mortars have a long tradition of application in the construction industry in many places in the world, especially in volcanic areas. Pozzolanic materials are nowadays often ground and sieved into fine particles with a high specific surface area and impart hydraulic properties to air lime mortars. At the same time, air lime-pozzolan mortars retain most of the good characteristics of pure air lime mortars, such as low modulus of elasticity and fast drying. The addition of pozzolans therefore extends the potential range of applications for air lime mortars.

The term pozzolanic activity is often used to describe the reactivity of the pozzolan, which includes all the reactions that occur between the active components of the pozzolan, calcium hydroxide and water. Pozzolanic activity essentially defines two values, the maximum amount of lime that the pozzolan can react with (bind) and the rate at which it does so. Both aspects depend on the type of pozzolan used and, above all, on the quality and quantity of the active ingredients it contains. Other influencing parameters are lime/pozzolan ratio in the mix, treatment time, specific surface area, water content in the mix, chemical composition, and temperature [1]. Pozzolanic activity can be determined by several direct or indirect methods, where direct methods monitor the presence of $Ca(OH)_2$ and subsequent reduction of its amount during the pozzolanic reaction using analytical methods, e.g. Frattini test according to EN 196-5 or Chapelle test [2]. On the other hand, indirect methods are based on measuring mainly the physical properties of the tested samples or the composition of the pozzolan, which is an indicator of the degree of pozzolanic activity. These methods include chemical and mineralogical analysis of pozzolan, determination of reactive $SiO_2$ in pozzolan according to EN 196-2, electrical conductivity test [3], calorimetric measurements [4], strength characteristics (ASTM C 593-19), or determination of Strength Activity Index (SAI) described in ASTM C311. The mentioned methods for determining pozzolanic activity differ from each other in terms of complexity, method of evaluation, time-consuming and price of their execution. Some methods determine whether and to what extent a given raw material is pozzolanic active, others only characterize a certain property that affects the level of pozzolanic activity. The results of pozzolanic activity obtained by several methods are not always similar or comparable.

Donatello et al. [5] compared different test methods for determining pozzolanic activity, namely the SAI, the Frattini test and a similar Frattini test, where the cement in the reaction mixture was replaced by lime water. A certain functional dependence was found only when comparing the Frattini test and the SAI. The results from the test with a saturated solution of $Ca(OH)_2$ did not correspond at all. Liu et al. compared the differences of six pozzolanic evaluation methods on five pozzolanic materials [6] and concluded that SAI is more objective in evaluating the activity based on strength, but there is also the aggregate effect on strength. The electrical conductivity test method is more suitable for evaluating the early pozzolanic reactivity. The evaluation results of the pozzolanicity test are limited by the slow dissolution rate of the active phase, and the dissolution characteristics of $Ca(OH)_2$. The high temperature in the modified Chapelle test makes the method more suitable for evaluating low-reactivity materials. The evaluation system of the thermogravimetric method (TG) and differential thermal analyses (DTA) is reasonable and most similar to the evaluation results of SAI. A modified R3 method is proposed to realize a more accurate simulation of the interstitial solution and a more accurate evaluation of pozzolanic reactivity [6].

| | **$SiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | **Σ** |
|---|---|---|---|---|
| Zeolite | 14.3 | 2.6 | 0.1 | 17.0 |
| Pumice | 52.6 | 19.9 | 2.1 | 74.6 |
| Lava | 0.0 | 3.9 | 4.7 | 8.6 |
| Spongilite | 0.0 | 0.0 | 0.0 | 0.0 |
| Chalcedonite | 0.0 | 0.0 | 0.0 | 0.0 |
| Pozzolanic earth | 7.8 | 0.0 | 8.1 | 15.1 |
| Trass | 4.1 | 1.0 | 5.5 | 10.1 |
| Diatomaceous earth | 53.4 | 0.0 | 0.0 | 53.4 |
| Metakaolin K05 | 42.8 | 37.5 | 0.6 | 80.9 |
| Metakaolin L05 | 37.0 | 32.2 | 0.7 | 70.0 |

Table 1. Content of amorphous hydraulic oxides in pozzolans (wt. %).

Due to ambiguous results when comparing pozzolanic activity by different methods, the content of this paper focuses on the correlation between the strength of ten different lime-pozzolanic paste systems and the pozzolanic activity of the pozzolan used in these pastes determined by the Chapelle test and the thermogravimetric method.

## 2. Materials and experimental procedures

Commercial hydrated lime CL 90-S (Carmeuse Czech Republic, s.r.o.) was used as a main binder in prepared pastes. Ten different pozzolanic materials was used as a partially lime substitute, namely, the natural zeolite (0–125 µm, Zeocem, a.s.) **Z**, the pumice (0–125 µm, Vulkalit WR, Vulcatec Riebensahm GmbH) **P**, the ground lava sand (0–125 µm, Der Naturstein Garten) **L**, the spongilite powder (0–125 µm, Kalcit s.r.o.) **S**, the fine chalcedonite powder (0–20 µm, CRUSIL Spółka z o.o.) **CH**, the pozzolanic earth (0–125 µm, Kremer Pigmente GmbH & Co) **PE**, the trass (0–125 µm, Tubag) **T**, the diatomaceous earth (0–40 µm, LB MINERALS, s.r.o.) **DE**, and two types of metakaolin (0–10 µm, Mefisto **K05** and Mefisto **L05**, České lupkové závody, a.s).

The particle size distribution of the pozzolans determined by laser particle analyzer, the chemical and mineralogical composition obtained by X-ray fluorescence (XRF) and X-ray diffraction analyses (XRD), as well as some fundamental physical parameters of pozzolans used have been published previously [7–11]. The chemical composition of pozzolans showed a high content of hydraulic oxides ($SiO_2$, $Al_2O_3$, $Fe_2O_3$) which provided very good conditions for its high pozzolanicity as according to the ASTM C618, the total pozzolanic content (i.e., the sum of $SiO_2$, Al2O3, and $Fe_2O_3$) must be a minimum of 70 % for class N pozzolans. All pozzolans except spongilite and lava fulfilled this condition. The reactivity of pozzolans is significantly influenced by its mineralogical composition. With the exception of chalcedonite and spongilite, the pozzolans contained an amorphous phase, mostly pumice, which was almost completely amorphous. However, the spongilite contained pozzolanically reactive opal and chalcedonite consisted of porous quartz grains with cryptocrystalline $SiO_2$ with very small crystal grains of µm size filling the void space of the quartz grains. The content of these small grains was reflected in the distinct specific surface area of the chalcedonite particles. The content of amorphous hydraulic oxides in pozzolans (Table 1) was calculated from the total content of the respective hydraulic oxides, the known representation of individual minerals containing hydraulic oxides and the total content of the amorphous phase in particular pozzolans. It should be noted that in the case of chalcedonite, it was not possible to calculate the content of amorphous hydraulic oxides due to the indistinguishability of cryptocrystalline $SiO_2$ (chalcedony) and quartz by XRD. And also, there was 14.6 wt. % of opal in spongilite; opal is pozzolanically active but is not a typical amorphous phase (it is detectable by XRD). As can be seen from Table 1, pumice and metakaolin had the highest content of amorphous hydraulic oxides.

The pozzolanic activity of pozzolans was determined by the modified Chapelle test method according to [12] after 1 day and also after 2, 3, 4, and 5 days of reaction with $Ca(OH)_2$ in an autoclave at 90 °C (Table 2). Very high values of pozzolanic activity were achieved by metakaolin, zeolite, chalcedonite, and diatomaceous earth partly due to their porous nature and thus large specific surface area, and also due to the content of reactive $SiO_2$ and $Al_2O_3$. Pumice, which had a significantly higher content of amorphous hydraulic oxides than zeolite, had lower pozzolanic activity values after two or more days. It is possible that after the rapid initial pozzolanic reaction, it was further slowed down by the rapid increase of reaction products on the pumice grains and the slowing down of the diffusion of the $Ca(OH)_2$ solution to the surface of the pumice grains. The moderate pozzolanic activity of the spongilite confirmed the reactivity of the opal. Pozzolanic earth did not reach very high values of pozzolanic activity despite the considerable content of the amorphous phase, due to the fact that more than half of the content of amorphous oxides was $Fe_2O_3$, which is the least and slowest reactive of them. The higher content

| | **Pozzolanic activity [mg $Ca(OH)_2\,g^{-1}$]** | | | | |
|---|---|---|---|---|---|
| | **1 day** | **2 days** | **3 days** | **4 days** | **5 days** |
| Zeolite | 729 | 1 220 | 1 263 | 1 390 | 1 395 |
| Pumice | 887 | 910 | 958 | 1 002 | 1 022 |
| Lava | 359 | 370 | 382 | 447 | 515 |
| Spongilite | 694 | 803 | 849 | 887 | 910 |
| Chalcedonite | 755 | 1 259 | 1 341 | 1 349 | 1 369 |
| Pozzolanic earth | 513 | 685 | 795 | 870 | 871 |
| Trass | 516 | 618 | 641 | 735 | 762 |
| Diatomaceous earth | 998 | 1 147 | 1 185 | 1 257 | 1 292 |
| Metakaolin K05 | 1 065 | 1 159 | 1 196 | 1 283 | 1 286 |
| Metakaolin L05 | 1 135 | 1 180 | 1 224 | 1 247 | 1 266 |

TABLE 2. Pozzolanic activity of pozzolans determined by modified Chapelle test.

of amorphous $Fe_2O_3$ at the expense of $SiO_2$ or $Al_2O_3$, together with the overall low content of amorphous hydraulic oxides, resulted in relatively low values of the pozzolanic activities of the trass and especially of the lava. If the pozzolans were evaluated according to Raverdy's criterion [13], where the material is considered as pozzolanically active if its Chapelle reactivity is 650 mg $Ca(OH)_2$ per 1 g of test material and more, it is clear that metakaolin, diatomaceous earth, pumice, zeolite, chalcedonite, and spongilite were pozzolanically active already after 1 day of treatment with $Ca(OH)_2$. Pozzolanic earth met this condition after 2 days, trass after 4 days, and lava is not pozzolanically active according to this criterion.

Fine pozzolans were used as a partial replacement of lime in 40 % of the lime weight. The composition of pastes mixes is given in Table 3. The amount of water required to achieve the same flow of 45 mm, determined by mini-slump cone test was added [14]. The freshly cast samples (20 × 20 × 100 mm) were freely covered by polyethylene foil to avoid their cracking caused by rapid drying. Hardened pastes specimens were demolded after 48 h and then cured in a wet chamber at temperature T = (22 ± 3) °C and a relative humidity RH = (95 ± 5) % for 26 days. The reactivity of the pozzolans and the mineral content of the lime-pozzolan pastes were investigated by TG/DTA after 7, 14, 21 and 28 days of aging. Three 2 × 2 × 2 cm samples were cut from three different beams of each paste type, crushed and ground in a planetary ball mill for 3 minutes. TG/DTA tests were carried out in the temperature range 40–1 000 °C at a heating rate of 10 °C $min^{-1}$ in a nitrogen atmosphere. The weight of the powder sample analyzed was 300 mg. The compressive strength of pastes was determined after 28 days of curing according to EN 1015-11. For the particular lime-pozzolan paste type a set of six samples was evaluated.

| **Mixture** | **Hydrated lime [g]** | **Pozzolan [g]** | **$H_2O$ [ml]** |
|---|---|---|---|
| L-ref | 100 | 0 | 80 |
| L-Z | 60 | 40 | 80 |
| L-P | 60 | 40 | 72 |
| L-L | 60 | 40 | 52 |
| L-S | 60 | 40 | 70 |
| L-CH | 60 | 40 | 70 |
| L-PE | 60 | 40 | 57 |
| L-T | 60 | 40 | 62 |
| L-DE | 60 | 40 | 120 |
| L-K05 | 60 | 40 | 100 |
| L-L05 | 60 | 40 | 92 |

TABLE 3. Composition of pastes.

## 3. RESULTS AND DISCUSSION

Thermogravimetric and differential thermal analysis are commonly used to characterize the composition of lime-pozzolan systems and can also be used to determine the reactivity of pozzolans by monitoring the decreasing $Ca(OH)_2$ content over time. The $Ca(OH)_2$ content may be underestimated due to carbonation using traditional methods that only measure the mass changes resulting from the decomposition of $Ca(OH)_2$ in the temperature range of 400 to 600 °C. The effect of carbonation should be taken into account when calculating the remaining $Ca(OH)_2$. The $Ca(OH)_2$ content can then be obtained using Equation 1 [15].

$$CH_r = 4.11(m_{CH}) + 1.68(m_{CC}) \tag{1}$$

where $CH_r$ is the mass of residual $Ca(OH)_2$ in the sample, 4.11 is the molar ratio of $Ca(OH)_2/H_2O$ and 1.68 is the molar ratio of $Ca(OH)_2/CO_2$. $m_{CH}$ is the mass loss due to dehydroxylation of $Ca(OH)_2$ and $m_{CC}$ is the mass loss due to decarbonation of $CaCO_3$ [15].

The percentage of the consumed lime by pozzolan with respect to the reference sample can be calculated using Equation 2 [16].

$$\mathit{Consumed\ lime}\,[\%] = [\tfrac{(CH_{r,r} \times C) - CH_{r,p}}{CH_{r,r} \times C}] \times 100 \tag{2}$$

where $CH_{r,r}$ and $CH_{r,p}$ is the mass of remaining $Ca(OH)_2$ in the reference and lime-pozzolan samples,

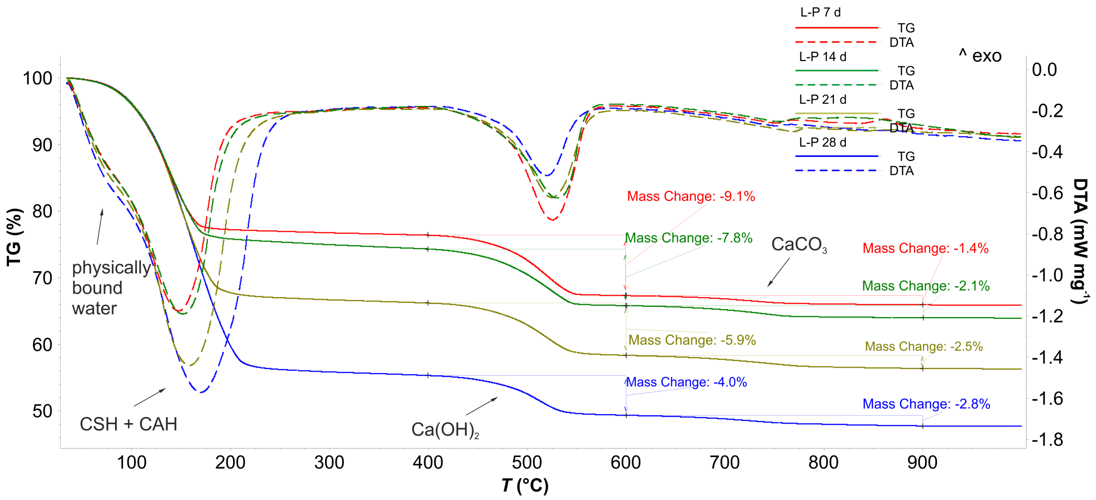


Figure 1. TG/DTA curves of lime-pumice paste after 7 days (red), 14 days (green), 21 days (olive), and 28 days (blue).

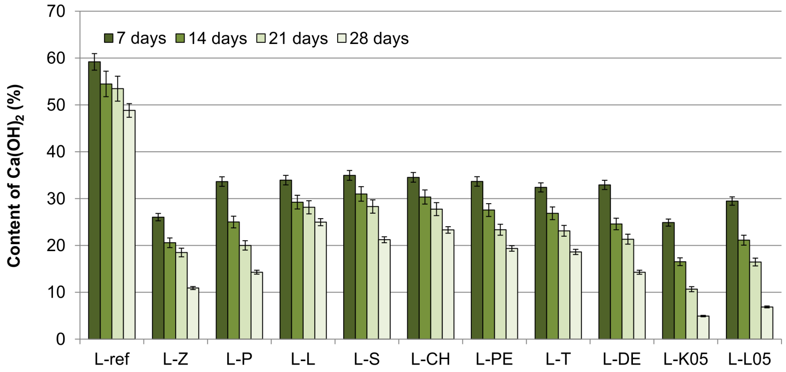


Figure 2. Content of $Ca(OH)_2$ in lime pastes determined by TG/DTA.

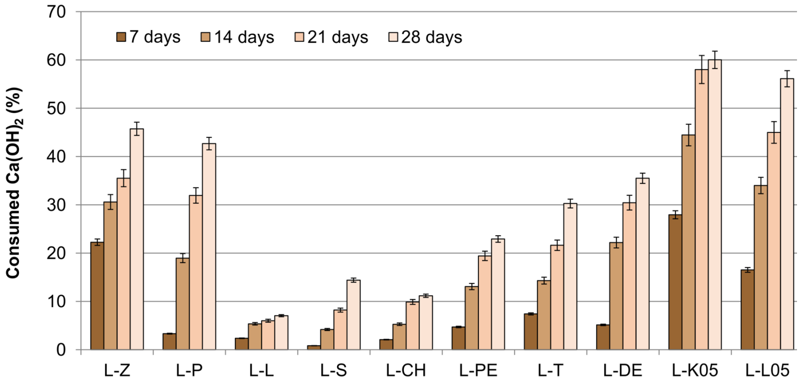


Figure 3. Amount of $Ca(OH)_2$ reacted with pozzolan in lime-pozzolan paste.

respectively. $C$ is the proportion of lime in the lime-pozzolan samples (e.g., for a lime-pozzolan sample with 60 % of lime and 40 % of pozzolan, C is 0.6).

In the thermogravimetric determination of $Ca(OH)_2$ and $CaCO_3$ contents in lime pastes, the weight losses of samples from the temperature ranges 400–600 °C (dehydroxylation of $Ca(OH)_2$) and 600–900 °C (decarbonation of $CaCO_3$) were evaluated, as shown in Figure 1. When comparing the TG and DTA curves of lime-pozzolan pastes after 7-day intervals, an increase in the content of pozzolanic reaction products (hydrated calcium silicates and aluminates – CSH and CAH), a decrease in $Ca(OH)_2$ content and a very slight increase in $CaCO_3$ content due to carbonation of the pastes were evident (Figure 1). The amount of remaining $Ca(OH)_2$ in the pastes (Figure 2) decreased significantly over time in lime-pozzolan pastes due to the ongoing pozzolanic reaction. Lime pastes with metakaolin, zeolite, pumice and diatomaceous earth, i.e. with pozzolans with high pozzolanic activity, showed a low $Ca(OH)_2$ content. The high reactivity of chalcedonite according to the Chapelle test was not confirmed by the amount of remaining $Ca(OH)_2$ in the paste.

The reactivity of the pozzolans was expressed by the amount of $Ca(OH)_2$ consumed in lime-pozzolan pastes (Figure 3), which increased with time as the pozzolanic reaction progressed. Metakaolin and natural zeolite showed a significant and rapid pozzolanic reaction, in agreement with the results of the Chapelle test. Pumice showed low reactivity initially, but after 14 days it showed a significant increase in $Ca(OH)_2$ consumed, similar to diatomaceous earth. Very low, but expected, amounts of consumed lime were observed for the lime-lava and lime-spongilite pastes. The low value of reacted lime for the lime-chalcedonite paste was surprising as a much higher value was expected based on the high pozzolanic activities from the Chapelle test. From the time evolution of the amount of reacted lime, it is clear that after 21 days almost all amount of the metakaolin K05 is reacted, while for other pozzolans the pozzolanic reaction continues even at 28 days.

After 28 days of curing, the compressive strength of the paste samples was determined (Figure 4). All lime-pozzolan pastes outperformed the reference lime paste, although lime-lava and lime-chalcedonite pastes only slightly. This confirms that chalcedonite is not very reactive in lime under standard conditions and that its high pozzolanic activity values from the Chapelle test are probably due to different conditions during the test (high temperature, constant stirring). It can therefore be seen that in some cases the Chapelle test may overestimate the pozzolanic activity. High strength values were obtained with pastes containing metakaolin, zeolite and pumice, consistent with the amount of lime consumed by these pozzolans, due to the high amount of amorphous hydraulic oxides in these pozzolans. In order to estimate the reactivity of the pozzolans in real conditions, correlations were made between the compressive strengths of the pastes and the values of pozzolanic activity determined by the Chapelle test after 24 hours (Figure 5a) and after 5 days (Figure 5b). As can be seen from the graphs and $R^2$ values, neither of these correlations is very good. Therefore, it is not possible to draw any conclusions from the pozzolanic activity values as to the real influence of the pozzolans on the strength of the pastes. There is a much better correlation between the amount of lime consumed by pozzolan (after 28 days) and the compressive strength of the pastes, as can be seen in Figure 6 ($R^2 = 0.9849$). The higher the amount of $Ca(OH)_2$ consumed, the higher the strength values can be expected. From the amount of reacted lime under real conditions, it is possible to infer the influence of pozzolan on the strength of lime mixtures, and the thermogravimetric method can be used relatively easily to determine the amount of reacted lime.

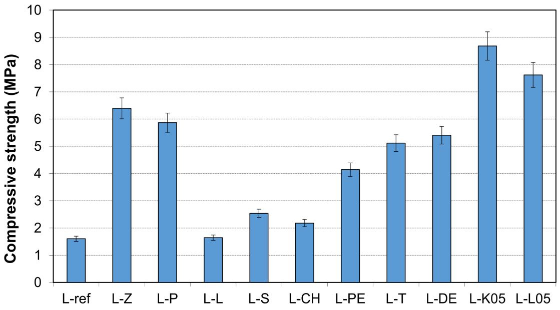
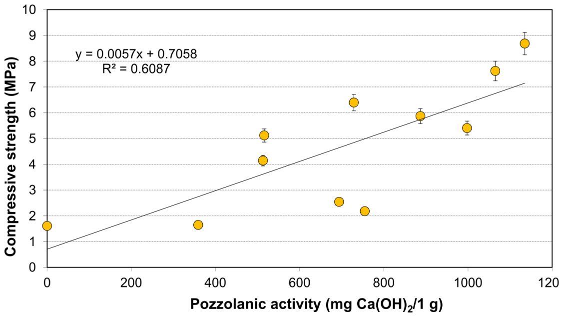
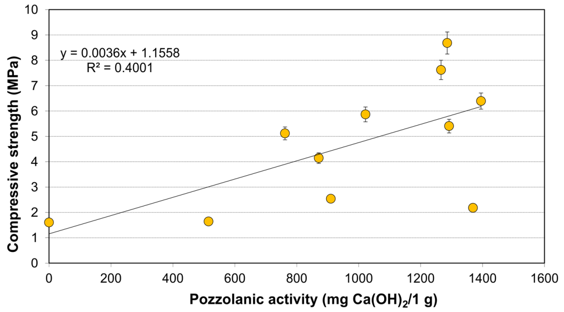


Figure 4. Compressive strength of lime pastes at 28 days.



(a).



(b).

Figure 5. Correlation between 28 days compressive strength of pastes and pozzolanic activity of pozzolans determined by modified Chapelle test after 1 day of treatment (A); after 5 days of treatment (B).

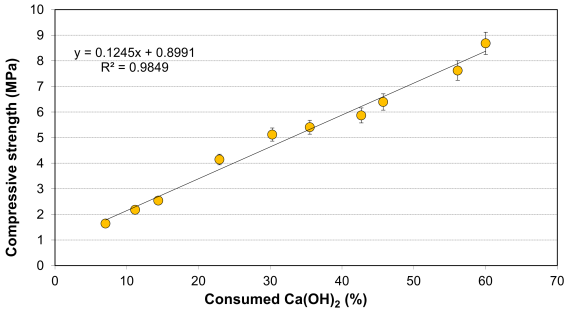


Figure 6. Correlation between 28 days compressive strength of pastes and amount of reacted $Ca(OH)_2$ with pozzolan in lime-pozzolan paste after 28 days.

## 4. Conclusions

After comparing the effect of ten different types of pozzolans on the strength of lime pastes in relation to their pozzolanic activities determined by the Chapelle test and monitoring the reactivity of these pozzolans using the thermogravimetric method, the following conclusions were made.

The true influence of pozzolans on the strength properties of lime pastes can be predicted from the content of amorphous hydraulic oxides and also from the specific surface area of the pozzolan particles. The Chapelle test is a fast and suitable method for determining pozzolanic activity for most of the pozzolans, but in some cases it may overestimate the pozzolanic activity due to the elevated temperature and constant mixing of the mixture during the test. Determining the amount of lime consumed by pozzolan using thermogravimetry is a time-consuming method for evaluating the effect of pozzolan on the strength of lime composites under real conditions, but it gives better results than the Chapelle test, because it is not affected by unrealistic conditions during the determination. In any case, the pozzolanic activity of a pozzolan should be determined by several methods and the subsequent comparison should lead to a critical assessment of the influence of the pozzolan in question on the properties of the prepared mixtures, in order to avoid simplistic conclusions.

## Acknowledgements

The results in this work have been achieved with financial support from the BUT specific research project FAST-S-24-8512.

## References

[1] P. C. Hewlett. *Lea's Chemistry of Cement and Concrete*. Elsevier, Oxford, 2004. ISBN 9780750662567.

[2] Pozzolanic addition for concrete-metakaolin: Definitions, specifications and conformity criteria, Annex A. Standard, Association Francaise de Normalisation, Paris, 2009.

[3] M. Luxán, F. Madruga, J. Saavedra. Rapid evaluation of pozzolanic activity of natural products by conductivity measurement. *Cement and Concrete Research* **19**(1):63–68, 1989. `https://doi.org/10.1016/0008-8846(89)90066-5`

[4] F. Avet, R. Snellings, A. Alujas Diaz, et al. Development of a new rapid, relevant and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays. *Cement and Concrete Research* **85**:1–11, 2016. `https://doi.org/10.1016/j.cemconres.2016.02.015`

[5] S. Donatello, M. Tyrer, C. R. Cheeseman. Comparison of test methods to assess pozzolanic activity. *Cement and Concrete Composites* **32**(2):121–127, 2010. `https://doi.org/10.1016/j.cemconcomp.2009.10.008`

[6] Y. Liu, Q. Yuan, Y. Tan, M. J. Garba. Comparative analysis and modification of evaluation methods for the pozzolanic reactivity of natural volcanic powders. *Journal of Building Engineering* **78**:107590, 2023. `https://doi.org/10.1016/j.jobe.2023.107590`

[7] M. Vyšvařil, T. Žižlavský, K. Dvořák, E. Spychał. Long-term mechanical properties of lime-pozzolan mortars: The role of amorphous $Al_2O_3$. *MATEC Web of Conferences* **403**:02009, 2024. `https://doi.org/10.1051/matecconf/202440302009`

[8] M. Vyšvařil, M. Krebs, P. Bayer. Long-term mechanical properties and durability of lime-spongilite mortars. In *Conservation and Restoration of Historic Mortars and Masonry Structures*, p. 405–415. Springer Nature Switzerland, 2023. `https://doi.org/10.1007/978-3-031-31472-8_32`

[9] M. Pavlíková, P. Rovnaníková, M. Záleská, Z. Pavlík. Diatomaceous earth – Lightweight pozzolanic admixtures for repair mortars – Complex chemical and physical assessment. *Materials* **15**(19):6881, 2022. `https://doi.org/10.3390/ma15196881`

[10] M. Vyšvařil, M. Krebs, P. Bayer. Use of chalcedonite powder as a supplementary materiál in lime mortars. p. 1314–1320. 2022.

[11] M. Vyšvařil, P. Bayer, P. Rovnaníková. Use of lava sand as an alternative to standard quartz aggregate in lime mortars. *Solid State Phenomena* **296**:73–78, 2019. `https://doi.org/10.4028/www.scientific.net/ssp.296.73`

[12] E. Navrátilová, P. Rovnaníková. Pozzolanic properties of brick powders and their effect on the properties of modified lime mortars. *Construction and Building Materials* **120**:530–539, 2016. `https://doi.org/10.1016/j.conbuildmat.2016.05.062`

[13] M. Raverdy, F. Brivot, A. M. Paillere, R. Dron. Appreciation de l'activite pouzzolanique des constituants secondaires. In *Proceedings of the 7th International Congress on the Chemistry of Cement*, vol. 3, pp. 36–41. 1980.

[14] Z. Tan, S. A. Bernal, J. L. Provis. Reproducible mini-slump test procedure for measuring the yield stress of cementitious pastes. *Materials and Structures* **50**(6):235, 2017. `https://doi.org/10.1617/s11527-017-1103-x`

[15] S. C. L. Lima, L. C. B. Costa, K. C. S. Defáveri, et al. Study on assessment of pozzolanic activity: Slate cutting waste. *ACI Materials Journal* **117**(3):3–10, 2020. `https://doi.org/10.14359/51724611`

[16] F. Elyasigorji, F. Farajiani, M. Hajipour Manjili, et al. Comprehensive review of direct and indirect pozzolanic reactivity testing methods. *Buildings* **13**(11):2789, 2023. `https://doi.org/10.3390/buildings13112789`