Influence of Calcining Temperature on the Mineralogical and Mechanical Performance of Calcined Impure Kaolinitic Clays in Portland Cement Mortars

Boakye, K, Khorami, M, Saidani, M, Ganjian, E, Dunster, A, Tyrer, M & Ehsani, A

DOI 10.1061/JMCEE7.MTENG-16128
ISSN 0899-1561

Publisher: ACSE

Influence of calcining temperature on the mineralogical and mechanical performance of calcined impure kaolinitic clays in Portland cement mortars

Kwabena Boakye[1]; Morteza Khorami[2]; Messaoud Saidani[3]; Eshmaiel Ganjian[4]; Andrew Dunster[5]; Mark Tyrer[6] and Ahmad Ehsani[7]

[1] Postgraduate Researcher, School of Energy, Construction & Environment, Faculty of Engineering & Computing, Coventry University, Coventry, U.K. ORCID: https://orcid.org/0000-0001-5290-0332. Email: boakyek4@uni.coventry.ac.uk
[2] Associate Professor, Civil Engineering and Structural Design, School of Energy, Construction & Environment, Faculty of Engineering & Computing, Coventry University, Coventry, U.K (Corresponding Author). ORCID: https://orcid.org/0000-0002-1656-8704. Email: aa8186@coventry.ac.uk
[3] Associate Professor, School of Energy, Construction & Environment, Faculty of Engineering & Computing, Coventry University, Coventry, U.K. Email: cbx086@coventry.ac.uk
[4] Professor, Civil Engineering Materials, Concrete Corrosion Tech Ltd., Birmingham, United Kingdom. Email: eganjian@yahoo.co.uk
[5] Principal Consultant, Building Research Establishment (BRE), UK. Email: andrew.dunster@bregroup.com
[6] Professor, Geomaterials and Geochemisty, Institute of Advanced Study ((Collegium Basilea), 4053 Basel, Switzerland. Email: m.tyrer@mtyrer.net
[7] Research Scientist, Indo-UK Centre for Environmental Research and Innovation, University of Greenwich, UK. Email: a.ehsani@greenwich.ac.uk

Abstract

In this work, the effects of calcination temperatures ranging from 600 to 1000 °C on the changes in mineralogical phases and mechanical characteristics of calcined impure kaolinite clay blended cement mortars were investigated. The impact of calcining temperature on pozzolanic activity of impure kaolinite clay was evaluated using direct and indirect methods. The findings demonstrated that at 700 °C, kaolinite changed from a crystalline to an amorphous metakaolin phase. Specific surface, water demand and setting time of the blended cements decreased as calcining temperature increased. The compressive strengths of blended cement mortar containing low-grade clay calcined at 700 °C, 800 °C and 900 °C were found to be greater than that of 600 °C and 1000 °C. Based on the results of pozzolanic reactivity evaluations and compressive strength development, the most effective calcining temperature was shown to be between 800 °C and 900 °C.

Author Keywords: calcined clay; low-grade kaolinitic clays; mineralogical properties; calcining temperature; pozzolanic reactivity

Introduction

One of the most realistic and practical ways to significantly deal with the SCM availability challenges, whiles reducing the environmental consequences of cement manufacture, has been found to be the adoption of clays with high amounts of kaolinite for the preparation of SCMs for construction purposes (Antoni et al., 2012). This is in partly due to their widespread availability in many countries. Again, the utilisation of these clays and other geologic materials in cementitious systems could significantly reduce the reliance of GGBS and fly ashes for composite cement production (Msinjili et al., 2019, Scrivener et al., 2018). However, the adoption and general use of calcined impure clays in cement replacement is restricted, in part because of a lack of understanding of the factors that define their pozzolanic reactivity and consequently, concrete properties.

The three main clay minerals that are mostly present in most of clays studied by researchers are kaolinite, illite, and smectites. In several reports, the highest and most efficient pozzolanic activities are found in clays with appreciable levels of kaolinite minerals, which also require the minimum calcining temperatures (based on their crystallinity) for the highest performance (Snellings et al., 2016). This is largely related to the number and placement of hydroxyl groups in kaolinite, which supports amorphization during heat treatment, and the existence of considerable amounts of energetically reactive five-coordinated Al in metakaolin (Msinjili et al., 2019, Scrivener et al., 2018). However, it has been demonstrated that illite and smectites can also exhibit pozzolanic properties after being heat-treated at the appropriate temperatures (800 – 950 $^{\circ}$C). Compared to kaolinite, these minerals often exhibit lower abundance of five-coordinated Al (Lothenbach et al., 2011). Furthermore, kaolinite has a higher rate of dissolution in alkaline solutions than smectites, which have an octahedral sheet firmly placed between two tetrahedral sheets (Danner et al., 2018). Likewise, comparable structural features of clay minerals may be responsible for the disparity in the degree of reactivity between illites and smectites and metakaolin, after heat treatment (Arslan et al., 2020, Karatas et al., 2020).

The particle size and mineralogical makeup of clays obtained from various places can occasionally have an impact on the level of pozzolanic activity (Zheng et al., 2022). Recent years have seen some investigations by researchers on the use of clays with low kaolinite levels in Portland cement mortar and concrete (Dixit et al., 2020, Dixit et al., 2021, Du and Pang, 2018, Zheng et al., 2022, Zhou et al., 2017). Although majority of studies base their clay classification on their kaolinite content, there is no consensus on what constitutes high- or low-grade clays. Some researchers have suggested that kaolinite levels above 40% can typically be referred to as high grade, using a firing temperature of $700 - 900$ °C. In recent times, the focus of calcined clay research has shifted to clays with lower content of kaolin due to the high cost and unavailability of high-grade kaolinitic clays in every region. Investigating the ideal temperature at which the maximum reactivity can be achieved in low kaolinitic clays, and the optimum Portland cement substitution is therefore worthwhile.

The reactivity of calcined clay in cementitious matrices is largely due to dehydroxylation of kaolinite, which is also related to the mineralogical composition of the clay and calcining conditions, thus, temperature and time (Kaminskas et al., 2023, Tironi et al., 2017). Although low-grade kaolinitic clays contain a variety of minerals, both reactive or inert minerals, they have been found to possess some level of pozzolanic reactivity after calcining at an appropriate temperature (Taylor-Lange et al., 2015). The selected calcining temperature is based on the desired properties of the resultant calcined clay. 600 °C is typically considered to be a good temperature when the aim is to increase the reactivity of the clay (He et al., 1994). However, if the goal compressive strength of regular concrete or mortar is desired, calcining at 800 °C may be appropriate, amidst other factors (Kang et al., 2022). Again, calcining temperature may also affect some physical properties of the clay including shape, size and surface area, which ultimately influences the compressive strength and durability of concrete (Ferreiro et al., 2017).

There have been investigations on the application of impure kaolinitic clays as SCM in the last few years. Alujas et al. (2015) studied the pozzolanicity of impure clays and reported that, clays possessing a kaolinite content of about 40% or more perform much better in terms of their reactivity as compared to clays containing kaolinite composition of less than 40%. The suitability of excavated waste London clay, obtained from construction site, as an SCM was evaluated by Zhou et al. (2017). The waste clay was thermally activated at temperatures between 600 °C and 1000 °C. The calcined clay showed that a relatively higher pozzolanic reactivity at temperatures beyond 700 °C. This significantly reflected in the mechanical properties of the resultant concrete, outperforming clays calcined at lower temperatures. Lower carbon footprint was recorded for concrete containing calcined clay than plain concrete. The pozzolanicity of heat-treated dredged soils, as reported by Snelling et al. (2016), indicated a higher pozzolanic reactivity as compared to fly ash and slightly lower than results obtained for metakaolin. Danner et al. (2018) concluded that, the incorporation of calcined clays in sustainable concrete production has the potential to significantly reduce the release of deleterious gases to the environment and overall production cost. The influence of calcining temperature on the hydration and mechanical properties of Tunisian clays was experimented by Nawel et al. (2020). Pozzolanic reactivity was found to be at its highest when the clay was calcined at 600 °C. Du and Pang (2018) also studied the properties of marine clay (containing a kaolinite content of 20%) after heat treatment. A high strength activity index of 0.9 was achieved for clays calcined at 600 °C.

This work has examined how low-grade clay, which contains 17% kaolinite, changed in terms of its physical and mineralogical properties as a result of calcination temperature. Utilizing portlandite consumption, Frattini and compressive strength test results, the pozzolanic reactivity of the calcined clay was examined. X-ray diffraction (XRD) and differential scanning calorimetric (DSC) studies were conducted on the raw clay and blended cements. Additionally, the optimum calcination temperature was established. The impacts of calcined clay as an SCM on the characteristics of mortar were also investigated. The findings of this study will offer a theoretical underpinning for its widespread application as well as a roadmap for expanded usage of impure clays as supplementary cementitious materials in regions where there are no pure kaolinite reserves.

Materials and Methodology

Materials

Clay used for study was sampled from a deposit located in Buckinghamshire, England. Portland cement CEM I 52.5 N conforming to BS EN 197-1 was the main binder used for the preparation of blended cement pastes and mortars. The Portland cement had a specific surface area of 410 m^2/kg. Fine aggregate, conforming to BS 4550: Part 6 was supplied by local dealers.

Methodology

Calcined clay

The clay sample was dried in a laboratory oven at 105 °C for 24 h. It was then milled in a portable quartz crusher for 2 minutes into powder (150 μm) and calcined for 2 hours in a muffle furnace at varying temperatures of 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C using a heating rate of 10 °C /min. The clay removed after calcination and left on a laboratory bench to cool to an ambient temperature in air for approximately 2 hours. The calcined clay was further ground and sieved through a 75 μm sieve. The percentage passing (about 95%) was used and the rest discarded.

X-ray diffraction (XRD) technique was used for phase identification of raw and hydrated cement samples.. Thermal analysis (TG/DSC) was also conducted between 30 $^{\circ}$C and 1000 $^{\circ}$C, utilising a heating rate of 20 $^{\circ}$C/min. Nitrogen gas with a flow rate of 20 ml/min was flashed in the heating chamber to reduce the possibility of carbonation. The laser diffraction method was used in studying the particle size distribution (PSD) of the calcined clay and blended cements. Ultrasound was employed to aid the disintegration of the sample in the water inside the sample vessel. Setting times and water demand was conducted according to methods specified by ASTM C191-21.

Pozzolanic reactivity

The Frattini test, portlandite consumption test, strength activity index and the relative strength index were the methods employed to measure pozzolanic reactivity. Blended cement was prepared by partially replacing 20% by weight of CEM-I cement with calcined clay having different calcination temperatures (600 $^{\circ}$C, 700 $^{\circ}$C, 800 $^{\circ}$C, 900 $^{\circ}$C and 1000 $^{\circ}$C). According to the procedures outlined in BS EN 196-1:2016, mortar cubes of 50 *x* 50 *x* 50 mm were prepared in triplicate, using a water-to-binder ratio of 0.5 and binder/sand ratio of 1:3. After curing the mortar cubes in water for a period of 3, 7, 28 and 91 days, their individual compressive strengths were determined by crushing in a compressive strength testing machine and the results calculated. The RSI technique is predicated on the idea that the projected drop in strength will be directly related to the SCM percentage in the absence of pozzolanic activity. The RSI is calculated using the formula shown in equation 1.

$$RSI = RP - (100 - S) \tag{1}$$

Where *RP* (real potential) is the ratio between the compressive strength of the composite cement and the reference cement (same calculation as strength activity index). *S* is the quantity (in mass-percentage) of pozzolan in the mixture.

Results and Discussions

Characterisation of calcined clay

Figure 1 is a presentation the PSD of the calcined clays used in this research. As seen, the calcined clay samples showed similar and close trend of particle size distributions with an average *d*10 of 1.02 μm, a *d*50 of 9.08 μm and a *d*90 of 51 μm. Clay calcined at 900 °C was found to have the highest particle fineness whereas 800 °C and 1000 °C obtained the least in the group.

BET surface area of the calcined clay samples decreased (20 m^2/g, 18.6 m^2/g, 12.6 m^2/g, 7.4 m^2/g and 5.6 m^2/g) as the calcining temperature increased from 600 – 1000 °C respectively. The obvious decrease in surface area was seen between 700 and 800 °C (18.6 to 12.6 m^2 /g). From Section 3.2, the transformation of illite and smectite was completed at 800 °C and may undergo further structural changes beyond 850 °C as confirmed by other studies. The reduction in surface area could be due to the changes in illite and smectite at 800 °C.
Density measurements of the calcined clay also varied between 2.6 g/cm^3 and 2.9 g/cm^3 in a slightly decreasing order, as calcination temperature increased. This is due to the evaporation of combined water, reduction in weight, as shown by the TG measurement in Figure 5 and consequently a decrease in density as temperature increased.

A plot of the setting time and water demand is shown in Figure 2. The incorporation of calcined clay caused a significant increase in setting time. Initial and final setting times increased by

19%and 22.2% respectively in blended cement containing 600 °C calcined clay. However, varying calcining temperatures impacted setting times differently. As temperature of calcination increased between 600 °C and 1000 °C, setting time decreased. Similarly, water demand was observed to decrease with increasing calcining temperature.

Effect of calcination of microstructural changes

Figure 3 is the XRD analysis of the clay calcined at different temperatures. The major minerals identified in the clay by x-ray diffraction analysis were quartz, kaolinite, illite and smectite, as shown in Figure 3. The crystallinity of the clay is slowly reduced, giving way to the emergence of amorphous phases, after calcining at varying temperatures. Dehydroxylation appears to begin at 600 °C, causing the corresponding peak to fade. With the increase in temperature, the peaks corresponding to illite and montmorillonite were found to decrease, confirming observations reported other researchers. There was a low amount of spinel phase observed when the temperature was increased to 1000 °C. This could indicate the beginning of re-crystallization of the amorphous phases.

The thermogravimetric study of the clay and calcined clays are seen in Figures 4 and 5. There is an appreciable mass loss of about 1.71% between 50 – 100 °C which is usually the dissipation of water causing dehydration. Dehydroxylation of the clay minerals occur between 400 and 700 °C. As temperature is increased, there is a mass loss of 2.31% and a wider exothermic peak shows up between 458 °C and 531 °C which typically corresponds to the dehydroxylation (the removal of structural water molecules) of kaolinite and the formation of metakaolinite. The amount of kaolinite in this clay can be estimated to be 17% based on this mass loss and the molecular weights of kaolinite and water. There also appears to be two small peaks overlapping between 580 °C and 699 °C with a total mass loss of 0.24%. This could be the dehydroxylation of illite and montmorillonite which are typically dehydroxylated between 550 °C and 880 °C. There is, however, no change in structure for illite and montmorillonite after dehydroxylation.

FTIR absorption spectra of the calcined clay samples are shown in Figure 6. The absorption band at 3694 cm^{-1} signifies that kaolinite is present and can be traced to the vibration of inner-surface OH groups. The absorption band at 3619 cm^{-1} that is also assigned to the stretching of inner-surface hydroxyl groups relates to smectite or illite. As temperature drops, the band at 1470 cm^{-1} loses strength and gradually falls until it eventually vanishes at 1000 °C which is attributed to the transformation of smectite and illite. The stretching and distortion of water molecules caused by OH is what causes the bands at 911, 778, and 688 cm^{-1}, which get smaller as the temperature rises.

Effect on compressive strength

Figure 7 presents the development of compressive strengths of the composite cement mortars with reference to the control mortar after 91 days curing. At 3 and 7 days, all the calcined clay blended cements recorded strengths lower than the reference cement which significantly improved after 28 days of curing. It was also observed that, compressive strength for the reference cement did not appreciate significantly after 91 days curing. Calcined clay blended cements, on the other hand, were seen to exhibit appreciable strength gains, with 900 °C obtaining similar results as the reference cement. The performance of the calcined clay at later ages can possibly be due to improved particle packing in the cement system with calcined clay having the lowest median particle size. Also, at later ages, pozzolanic reactivity is more likely to increase due to the continuous consumption of $Ca(OH)_2$ by the constituents of the calcined clay, as curing age increases, to produce extra calcium silicate hydrates needed for strength development.

Effect of calcination temperature on pozzolanic reactivity

Frattini test results showing the pozzolanic reactivity of the calcined clay is presented in Figures 8 and 9. All the calcined clay samples were found above the lime solubility curve at 3 days. This indicates that the calcined clay samples showed no significant pozzolanic reactivity at this point. In Figure 8, the pastes which had clays treated at 700 °C, 900 °C and 1000 °C were found at the lower side of the solubility curve. This confirms the consumption of $Ca(OH)_2$ by the constituents of the cement, thereby proving pozzolanicity of these calcined clays. Even though clays calcined at 600 and 1000 °C were found above the curve, their position, with respect to the curve, after 28 days confirms some amount of reactivity, however slow.

The consumption of $Ca(OH)_2$ at various curing times, derived from the TGA data after the portlandite consumption test is shown in Figure 10. The highest consumption per mass was seen in clays calcined at 900 °C and 800 °C and 700 °C, in increasing order of reactivity. It was also observed that portlandite consumption in all test materials increased with increasing curing time. As expected, silica sand, which served as a reference material, recorded the lowest reactivity.

Figure 11 presents the SAI results, computed from the compressive strength data. At 28 days, apart from 600 °C and 1000 °C which fell short of the ASTM minimum requirement of 75%, the SAI of all other samples were found to be within acceptable limits of pozzolanic reactivity. SAI at 91days showed significant improvement, with 600 °C and 1000 °C obtaining figures above the minimum 75%. Results of the relative strength index have also been presented in Figure 12. Samples containing clay calcined at 600 °C and 1000 °C showed negative RSI at 3, 7 and 28 days. This is an indication that the contribution of the 20% calcined clay was inferior to cement. 700 °C, 800 °C and 900 °C showed positive RSI values which indicates that their contribution to pozzolanic reactivity is appreciable and is likely to overcome dilution effect. It can be inferred from the findings of SAI and RSI that the ideal calcination temperature falls between 800-900 °C.

Effect of calcined clay on hydration products

Figure 13 displays the XRD patterns of hydrated blended cement paste incorporated with 20% calcined at various temperatures. Portlandite, denoted by CH, was observed in both the reference sample and the blended mortars. As seen, the portlandite peaks in the blended cement samples were shorter than that of the reference cement paste. The intensities of these peaks, except 1000 °C, were seen to decrease with increasing calcining temperatures. This observation is similar to the findings of Du and Pang (2018). The lowered portlandite peak intensities are as a result of pozzolanic reactivity of the calcined clay samples, consuming the $Ca(OH)_2$ released from the hydration process. Again, the replacement of 20% cement with calcined clay reduced the quantity of cement and consequently reduced the production of portlandite. Furthermore, substantial part of portlandite is likely to go into reaction with SiO_2 from the calcined clay to produce further cementitious compounds such as C-S-H.

Conclusion

This investigation has studied the mineralogical, pozzolanic reactivity and mechanical performance of low-grade kaolinitic clay (calcined at varying temperatures) in Portland cement mortar and the following conclusions drawn:

1. From the DSC results, kaolinite underwent partial dehydroxylation at 600 °C to generate metakaolin and at 700 °C, complete dehydration was achieved. The crystallinity of the clay was slowly reduced, giving way to the emergence of amorphous phases, after calcining at

varying temperatures. Due to recrystallization and a decrease in specific surface area, pozzolanic activity was reduced at a temperature of 1000 °C.

2. The partial replacement of cement with calcined clay caused a reduction in early strength but increased noticeably at 91 days. Water demand, as well as setting time decreased with increasing calcination temperature.
3. Frattini test revealed minimal pozzolanic reactivity at 600 °C and 1000 °C. This trend was confirmed by the portlandite consumption test, strength activity index (SAI) and the relative strength index (RSI).
4. XRD studies revealed the consumption of Portlandite after 28 days hydration of blended calcined clay-Portland cement paste. Excess $Ca(OH)_2$ was seen in samples containing 1000 °C calcined clay, confirming low pozzolanic reactivity.
5. Considering the thermogravimetric, pozzolanic reactivity and mechanical properties, the most effective calcination temperature was found between 800 and 900 °C.

Data Availability Statement

Some or all data, models, or code that support the findings of this study are available from the corresponding author upon reasonable request.

References

Alujas, A., Fernández, R., Quintana, R., Scrivener, K.L., Martirena, F., 2015. Pozzolanic reactivity of low grade kaolinitic clays: Influence of calcination temperature and impact of calcination products on OPC hydration. Appl. Clay. Sci., 94-101

Antoni, M., Rossen, J., Martirena, F., Scrivener, K., 2012. Cement substitution by a combination of metakaolin and limestone. Cem. Concr. Res. 12, 1579-1589

Aprianti S, E., 2017. A huge number of artificial waste material can be supplementary cementitious material (SCM) for concrete production – a review part II. J. Clean. Prod., 4178-4194

Arslan, F., Benli, A., Karatas, M., 2020. Effect of high temperature on the performance of self-compacting mortars produced with calcined kaolin and metakaolin. Constr. Build. Mater., 119497

Boakye, K., Khorami, M., Saidani, M., Ganjian, E., Dunster, A., Ehsani, A., Tyrer, M., 2022. Mechanochemical characterisation of calcined impure kaolinitic clay as a composite binder in cementitious mortars. Journal of Composites Science. 134

Cardinaud, G., Rozière, E., Martinage, O., Loukili, A., Barnes-Davin, L., Paris, M., Deneele, D., 2021. Calcined clay – Limestone cements: Hydration processes with high and low-grade kaolinite clays. Constr. Build. Mater., 122271

Chakchouk, A., Trifi, L., Samet, B., Bouaziz, S., 2009. Formulation of blended cement: Effect of process variables on clay pozzolanic activity. Constr. Build. Mater. 3, 1365-1373

Dixit, A., Du, H., Pang, S.D., 2021. Performance of mortar incorporating calcined marine clays with varying kaolinite content. J. Clean. Prod., 124513

Dixit, A., Du, H., Pang, S.D., 2020. Marine clay in ultra-high performance concrete for filler substitution. Constr. Build. Mater., 120250

Du, H., Pang, S.D., 2018. Value-added utilization of marine clay as cement replacement for sustainable concrete production. J. Clean. Prod., 867-873

El-Diadamony, H., Amer, A.A., Sokkary, T.M., El-Hoseny, S., 2018. Hydration and characteristics of metakaolin pozzolanic cement pastes. HBRC Journal. 2, 150-158

Ferreiro, S., Herfort, D., Damtoft, J.S., 2017. Effect of raw clay type, fineness, water-to-cement ratio and fly ash addition on workability and strength performance of calcined clay – Limestone Portland cements. Cem. Concr. Res., 1-12

He, C., Makovicky, E., Osbæck, B., 1994. Thermal stability and pozzolanic activity of calcined kaolin. Appl. Clay. Sci. 3, 165-187

Hollanders, S., Adriaens, R., Skibsted, J., Cizer, Ö, Elsen, J., 2016. Pozzolanic reactivity of pure calcined clays. Appl. Clay. Sci., 552-560

Huang, W., Kazemi-Kamyab, H., Sun, W., Scrivener, K., 2017. Effect of replacement of silica fume with calcined clay on the hydration and microstructural development of eco-UHPFRC. Mater Des, 36-46

Jafari, K., Rajabipour, F., 2020. Performance of Impure Calcined Clay as a Pozzolan in Concrete. Transport Research Record. 2, 643-645

Jafari, K., Rajabipour, Farshad, 2020. Performance of Impure Calcined Clay as a Pozzolan in Concrete. Transportation Research Record: Journal of Transportation Research Board. 2, 98-107

Juenger, M.C.G., Siddique, R., 2015. Recent advances in understanding the role of supplementary cementitious materials in concrete. Cem. Concr. Res., 71-80

Juenger, M.C.G., Snellings, R., Bernal, S.A., 2019. Supplementary cementitious materials: New sources, characterization, and performance insights. Cem. Concr. Res., 257-273

Kaminskas, R., Barauskas, I., Laskevicius, K., 2023. Improvement of the Pozzolanic Properties of Calcined Mica Clay. J. Mater. Civ. Eng. 1, 04022373

Kang, S., Kwon, Y., Moon, J., 2022. Influence of calcination temperature of impure kaolinitic clay on hydration and strength development of ultra-high-performance cementitious composite. Constr. Build. Mater., 126920

Karatas, M., Benli, A., Arslan, F., 2020. The effects of kaolin and calcined kaolin on the durability and mechanical properties of self-compacting mortars subjected to high temperatures. Constr. Build. Mater., 120300

Kovářík, T., Bělský, P., Novotný, P., Říha, J., Savková, J., Medlín, R., Rieger, D., Holba, P., 2015. Structural and physical changes of re-calcined metakaolin regarding its reactivity. Constr. Build. Mater., 98-104

McCarthy, M.J., Robl, T., Csetenyi, L.J., 2017. 14 - Recovery, processing, and usage of wet-stored fly ash, in: Robl, T., Oberlink, A., Jones, R. (Eds.), Coal Combustion Products (CCP's). Woodhead Publishing, pp. 343-367

Msinjili, N.S., Gluth, G.J.G., Sturm, P., Vogler, N., Kune, H., 2019. Comparison of calcined illitic clays (brick clays) and lowgrade kaolinitic clays as supplementary cementitious materials. Materials and Structures. 94

Scrivener, K., Martirena, F., Bishnoi, S., Maity, S., 2018. Calcined clay limestone cements (LC3). Cem. Concr. Res., 49-56

Seiffarth, T., Hohmann, M., Posern, K., Kaps, C., 2013. Effect of thermal pre-treatment conditions of common clays on the performance of clay-based geopolymeric binders. Appl. Clay. Sci., 35-41

Siddika, A., Mamun, M.A.A., Alyousef, R., Mohammadhosseini, H., 2020. State-of-the-art-review on rice husk ash: A supplementary cementitious material in concrete. Journal of King Saud University - Engineering Sciences

Taylor-Lange, S.C., Lamon, E.L., Riding, K.A., Juenger, M.C.G., 2015. Calcined kaolinite–bentonite clay blends as supplementary cementitious materials. Appl. Clay. Sci., 84-93

Thapa, V.B., Waldmann, D., Simon, C., 2019. Gravel wash mud, a quarry waste material as supplementary cementitious material (SCM). Cem. Concr. Res., 105833

Tironi, A., Scian, A.N., Irassar, E.F., 2017. Blended cements with limestone filler and kaolinitic calcined clay: Filler and pozzolanic effects. J. Mater. Civ. Eng. 9, 04017116

Tironi, A., Trezza, M.A., Scian, A.N., Irassar, E.F., 2013. Assessment of pozzolanic activity of different calcined clays. Cement and Concrete Composites, 319-327

Zhao, D., Khoshnazar, R., 2020. Microstructure of cement paste incorporating high volume of low-grade metakaolin. Cement and Concrete Composites, 103453

Zheng, D., Liang, X., Cui, H., Tang, W., Liu, W., Zhou, D., 2022. Study of performances and microstructures of mortar with calcined low-grade clay. Constr. Build. Mater., 126963

Zhou, D., Wang, R., Tyrer, M., Wong, H., Cheeseman, C., 2017. Sustainable infrastructure development through use of calcined excavated waste clay as a supplementary cementitious material. J. Clean. Prod., 1180-1192

Zhou, Y., Zhang, Z., 2020. Effect of fineness on the pozzolanic reaction kinetics of slag in composite binders: Experiment and modelling. Constr. Build. Mater., 121695

Antoni, M., Rossen, J., Martirena, F., Scrivener, K., 2012. Cement substitution by a combination of metakaolin and limestone. Cem. Concr. Res. 12, 1579-1589

Arslan, F., Benli, A., Karatas, M., 2020. Effect of high temperature on the performance of self-compacting mortars produced with calcined kaolin and metakaolin. Constr. Build. Mater., 119497

Danner, T., Norden, G., Justnes, H., 2018. Characterisation of calcined raw clays suitable as supplementary cementitious materials. Appl. Clay. Sci., 391-402

Dixit, A., Du, H., Pang, S.D., 2021. Performance of mortar incorporating calcined marine clays with varying kaolinite content. J. Clean. Prod., 124513

Dixit, A., Du, H., Pang, S.D., 2020. Marine clay in ultra-high performance concrete for filler substitution. Constr. Build. Mater., 120250

Du, H., Pang, S.D., 2018. Value-added utilization of marine clay as cement replacement for sustainable concrete production. J. Clean. Prod., 867-873

Ferreiro, S., Herfort, D., Damtoft, J.S., 2017. Effect of raw clay type, fineness, water-to-cement ratio and fly ash addition on workability and strength performance of calcined clay – Limestone Portland cements. Cem. Concr. Res., 1-12

He, C., Makovicky, E., Osbæck, B., 1994. Thermal stability and pozzolanic activity of calcined kaolin. Appl. Clay. Sci. 3, 165-187

Kaminskas, R., Barauskas, I., Laskevicius, K., 2023. Improvement of the Pozzolanic Properties of Calcined Mica Clay. J. Mater. Civ. Eng. 1, 04022373

Kang, S., Kwon, Y., Moon, J., 2022. Influence of calcination temperature of impure kaolinitic clay on hydration and strength development of ultra-high-performance cementitious composite. Constr. Build. Mater., 126920

Karatas, M., Benli, A., Arslan, F., 2020. The effects of kaolin and calcined kaolin on the durability and mechanical properties of self-compacting mortars subjected to high temperatures. Constr. Build. Mater., 120300

Lothenbach, B., Scrivener, K., Hooton, R.D., 2011. Supplementary cementitious materials. Cem. Concr. Res. 12, 1244-1256

Msinjili, N.S., Gluth, G.J.G., Sturm, P., Vogler, N., Kune, H., 2019. Comparison of calcined illitic clays (brick clays) and lowgrade kaolinitic clays as supplementary cementitious materials. Materials and Structures. 94

Scrivener, K., Martirena, F., Bishnoi, S., Maity, S., 2018. Calcined clay limestone cements (LC3). Cem. Concr. Res., 49-56

Snellings, R., Cizer, Ö, Horckmans, L., Durdziński, P.T., Dierckx, P., Nielsen, P., Van Balen, K., Vandewalle, L., 2016. Properties and pozzolanic reactivity of flash calcined dredging sediments. Appl. Clay. Sci., 35-39

Taylor-Lange, S.C., Lamon, E.L., Riding, K.A., Juenger, M.C.G., 2015. Calcined kaolinite–bentonite clay blends as supplementary cementitious materials. Appl. Clay. Sci., 84-93

Tironi, A., Scian, A.N., Irassar, E.F., 2017. Blended cements with limestone filler and kaolinitic calcined clay: Filler and pozzolanic effects. J. Mater. Civ. Eng. 9, 04017116

Zheng, D., Liang, X., Cui, H., Tang, W., Liu, W., Zhou, D., 2022. Study of performances and microstructures of mortar with calcined low-grade clay. Constr. Build. Mater., 126963

Zhou, D., Wang, R., Tyrer, M., Wong, H., Cheeseman, C., 2017. Sustainable infrastructure development through use of calcined excavated waste clay as a supplementary cementitious material. J. Clean. Prod., 1180-1192

.

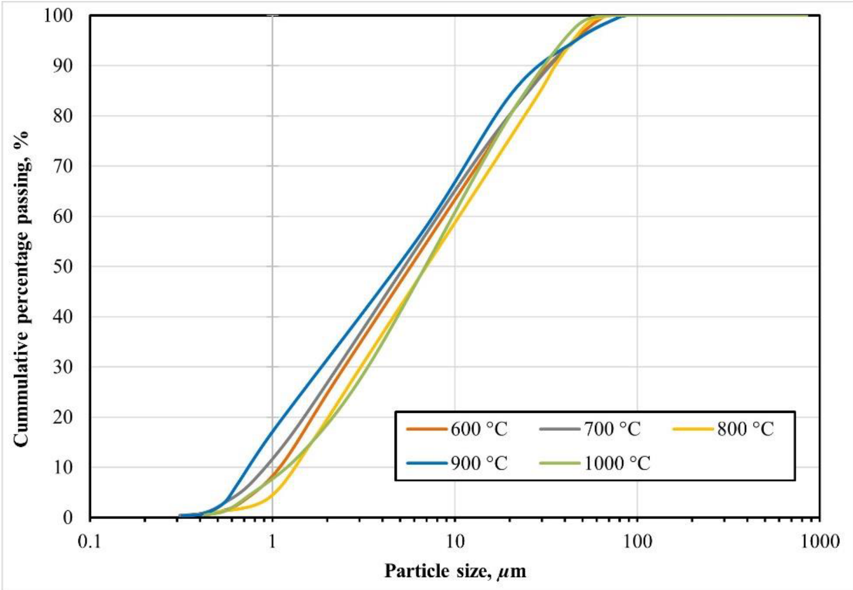
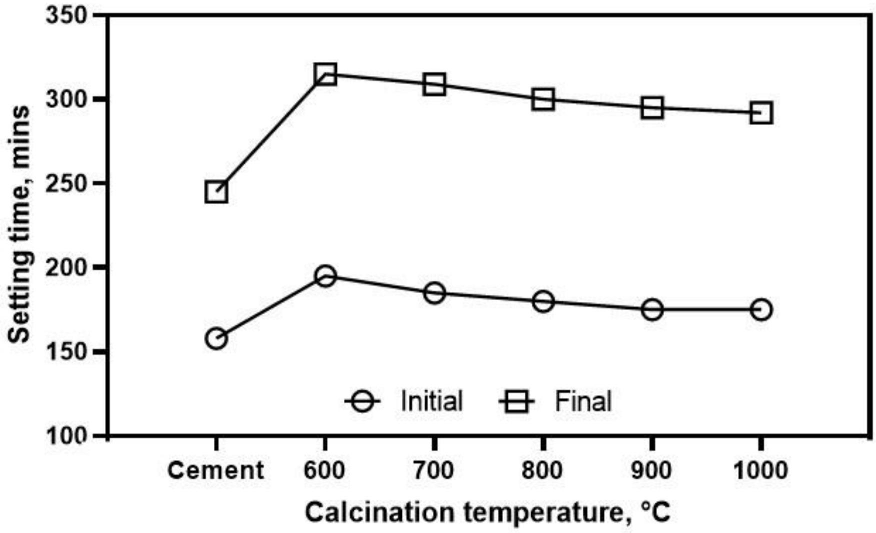


Fig. 1. Particle size distribution of clay calcined at varying temperatures.



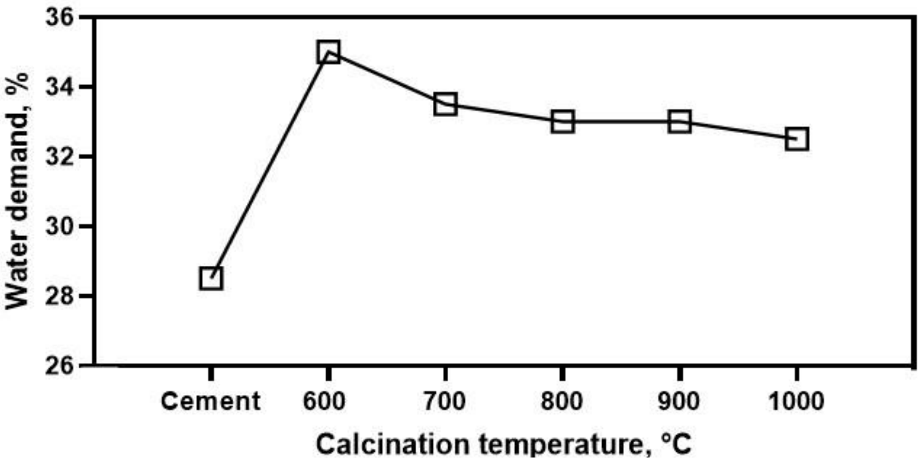


Fig. 2. Setting time (a) and water demand (b) of CEM I and paste containing calcined clay of different temperatures.

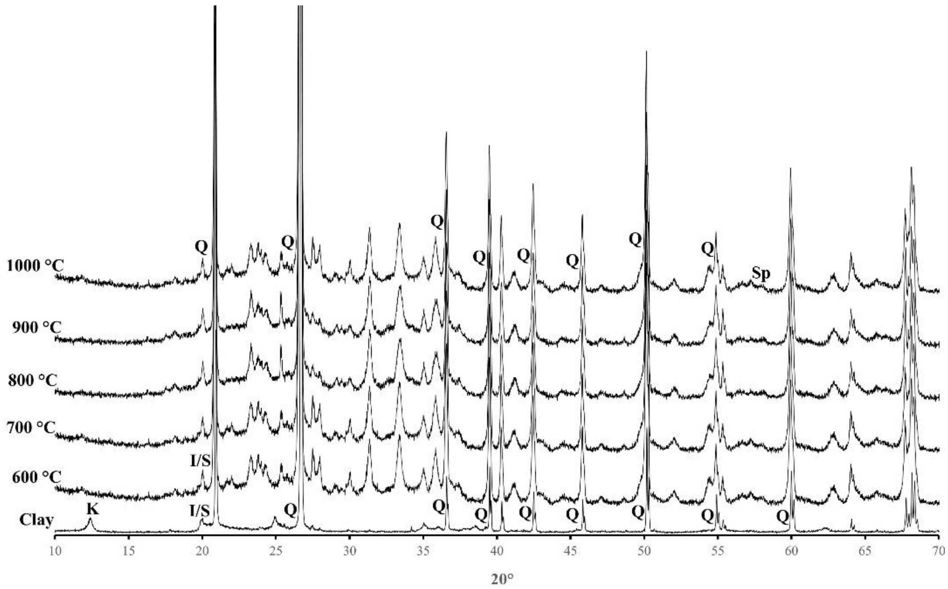


Fig. 3. XRD pattern of raw and calcined clays (K: Kaolinite; I: Illite; S: Smectite; Q: Quartz; Sp: Spinel).

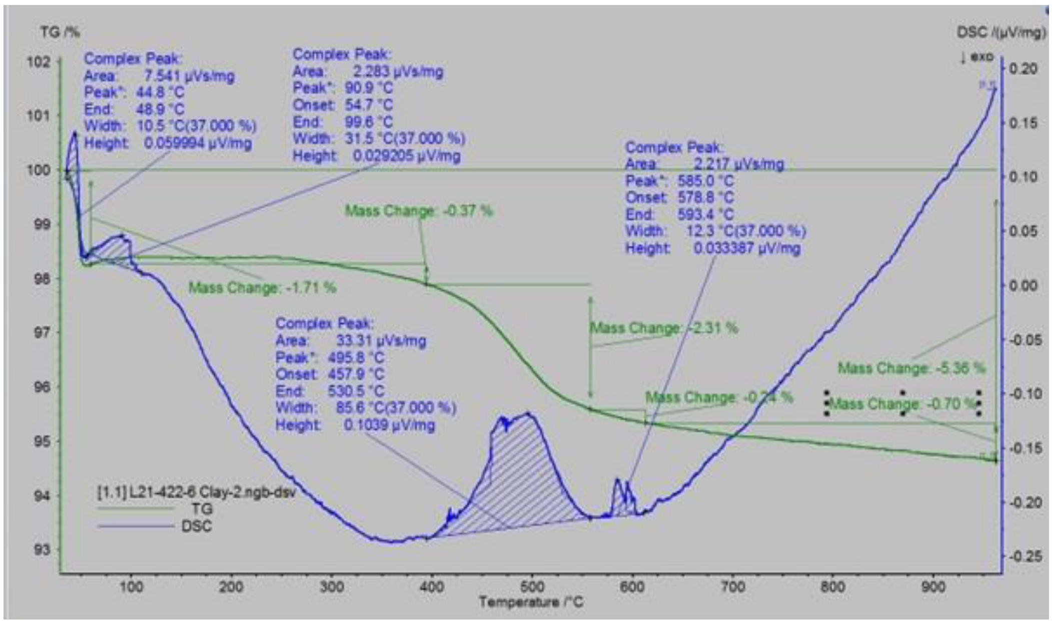


Fig. 4. TG/DSC of raw clay

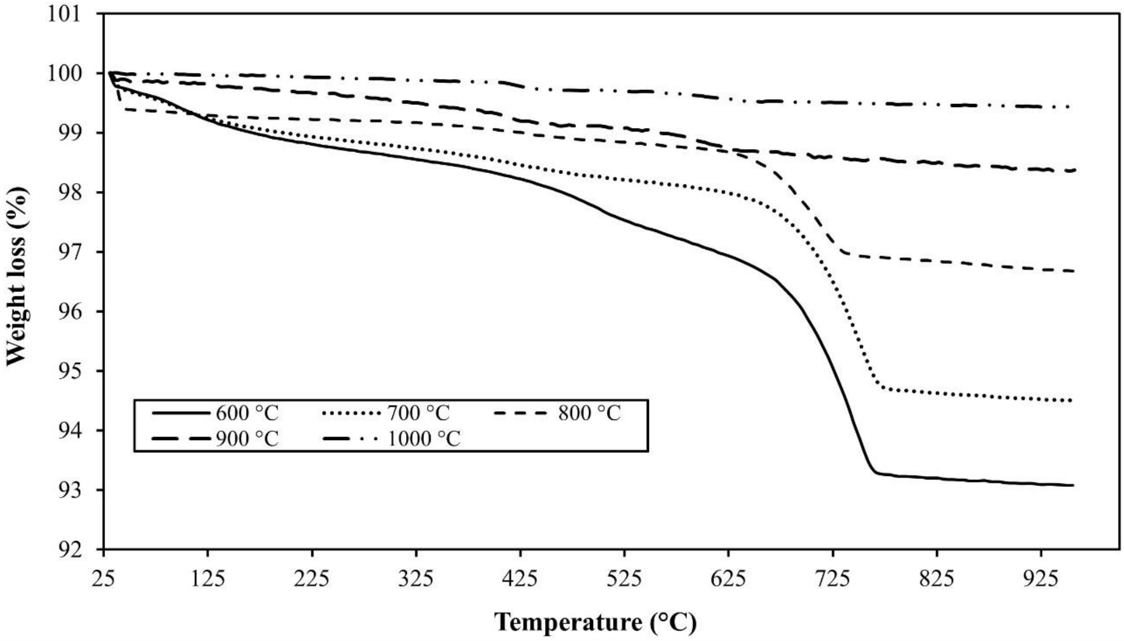


Fig. 5. Thermogravimetric analysis of calcined clays.

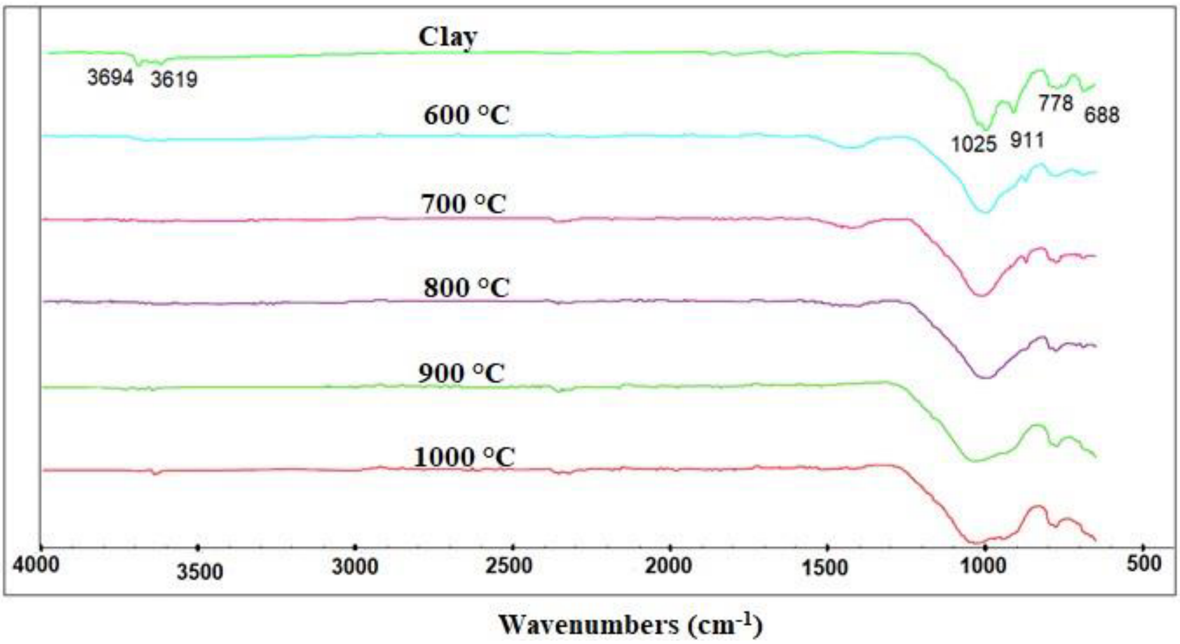


Fig. 6. FTIR patterns of calcined clays.

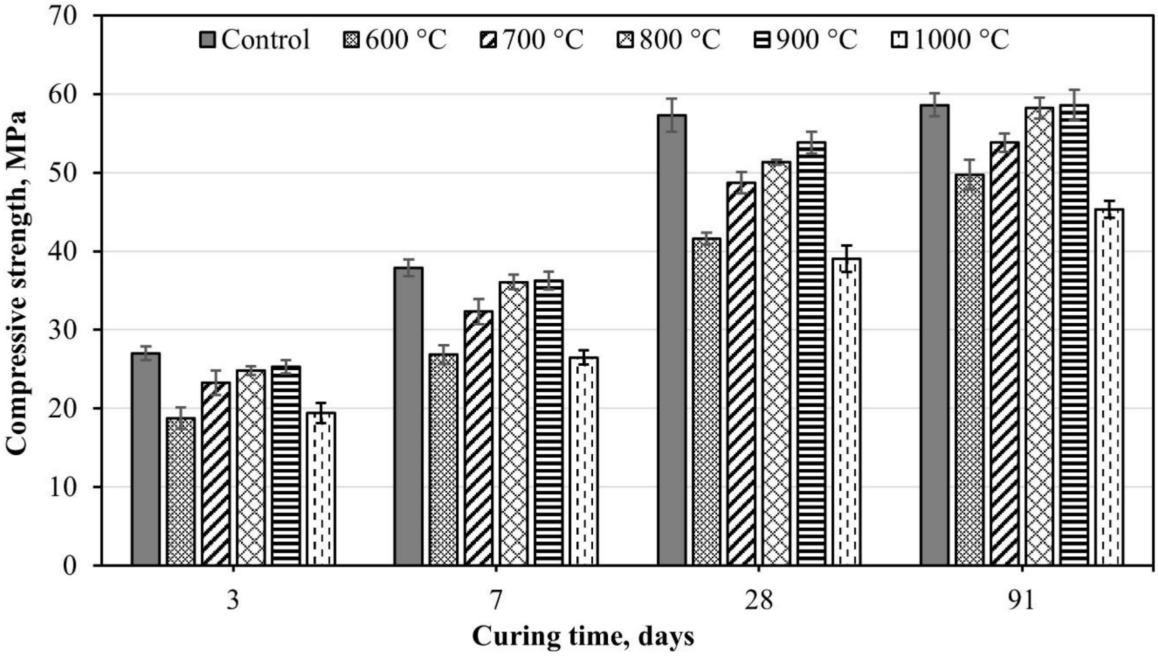


Fig. 7. Compressive strength development of blended cement containing clay calcined at varying temperatures.

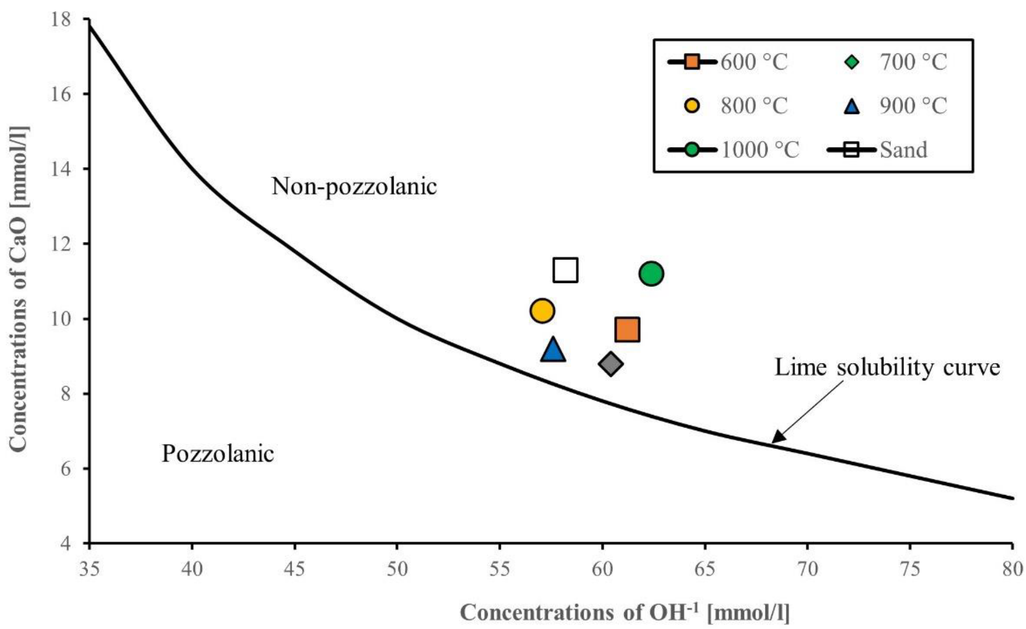


Fig. 8. Frattini test showing reactivity of calcined clay at 3 days.

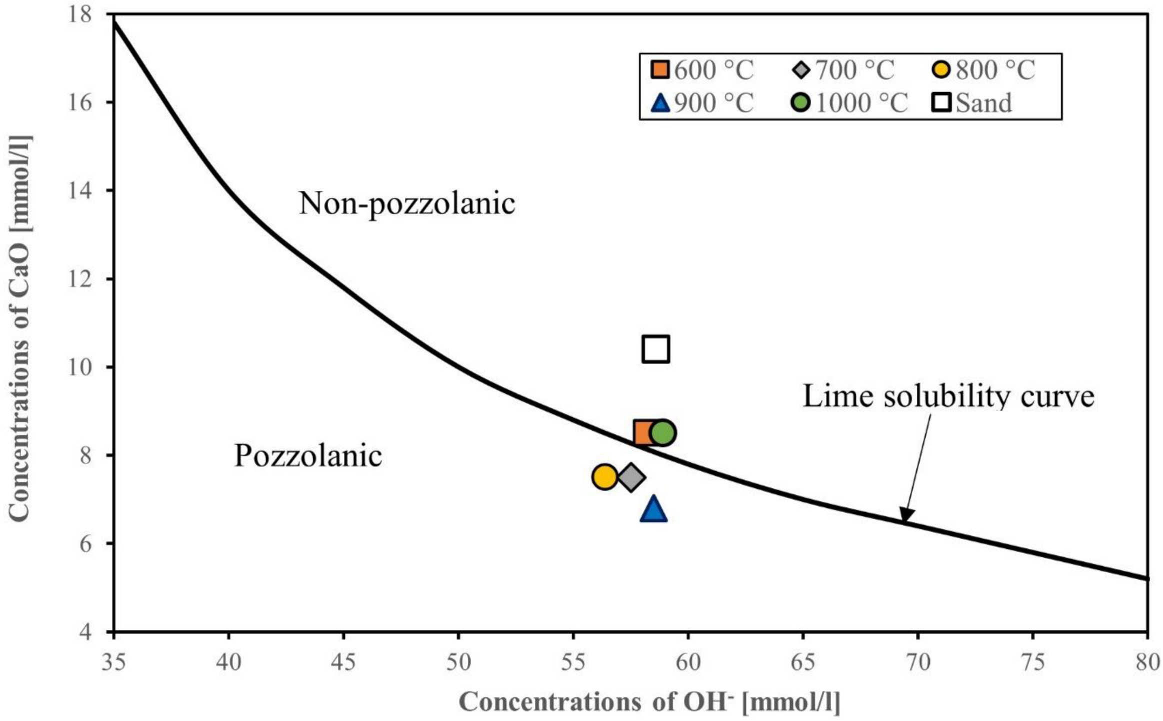


Fig. 9. Frattini test showing reactivity of calcined clay at 28 days.

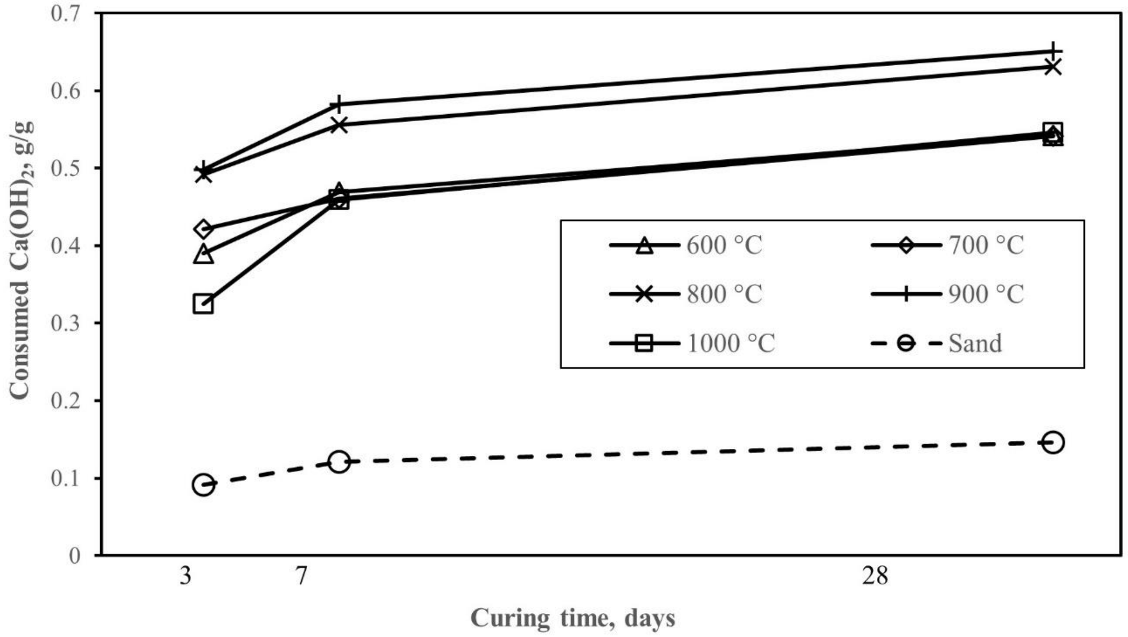


Fig. 10. Portlandite consumption of calcined clay samples

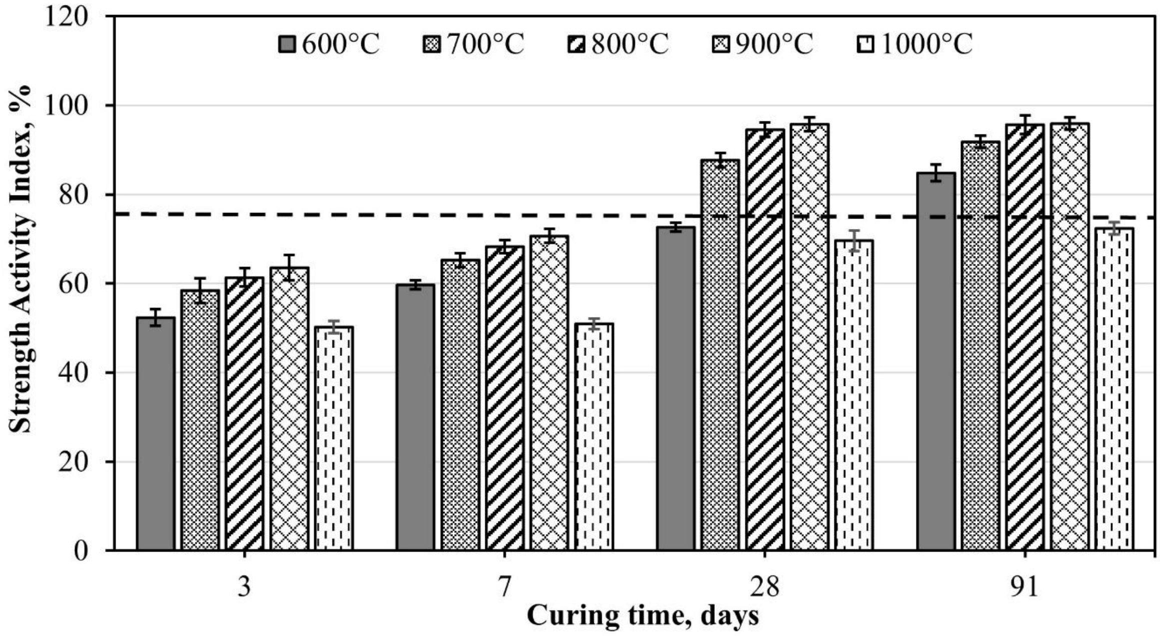


Fig. 11. Strength activity index (SAI) of mortar containing 20% calcined clay at varying temperatures.

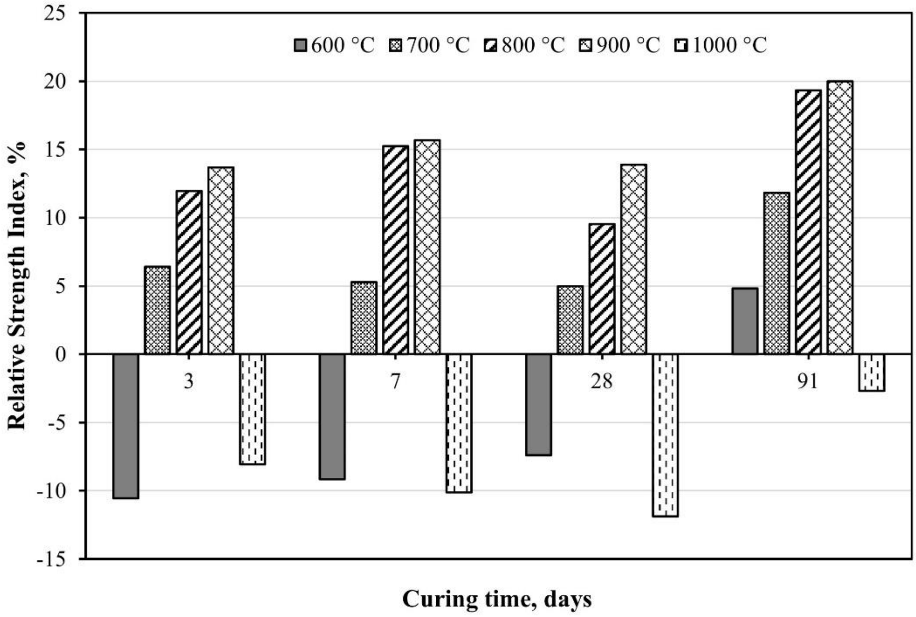


Fig. 12. Relative strength index (RSI) of mortar containing 20% calcined clay at varying temperatures.

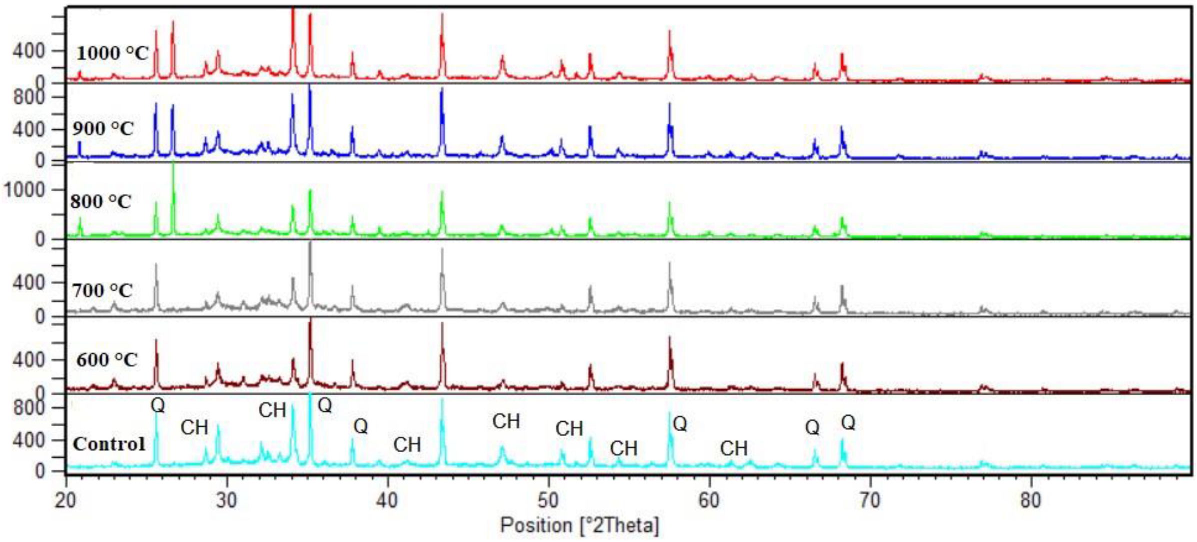


Fig. 13. XRD pattern of cement paste containing 20% calcined clays of different calcination temperatures and cured for 28 days.