Advances in development of calcined clays as supplementary cementitious materials

Nailia Rakhimova and Ravil Rakhimov

1Kazan State University of Architecture and Engineering, Kazan, 420043, Russia
E-mail: nailia683@gmail.com

Abstract. Continuous development and expansion of the raw material base, in response to the increasing environmental and technical requirements for the most consumed commodities, are crucial for the sustainable development of resource- and energy-intensive materials and technologies, including cement production. In recent decades, calcined clays have become significant as supplementary cementitious materials for blended Portland cements. Extensive research and practical experience form the theoretical and practical bases for the application of calcined clays, which are diverse in composition and structure, for effective cement production. However, the scarcity of the most valuable pure kaolin clays has led to extensive feasibility studies on more abundant medium- and low-grade kaolin, multi-mineral kaolin, and non-kaolin clays. This paper reviews the last advances in the field of Portland cement-based systems using calcined clays containing different amounts of 1:1 and/or 2:1 type clay minerals, including their processing features, chemical reactivities, potential controlling factors, and requirements.

Keywords: clay, cement, pozzolan, calcination, pozzolanic activity.

1 Introduction

Portland cement and concrete are the most resource-, energy-, and pollution-intensive products in the construction industry. Because the demand for these materials is expected to increase in the near future, the ecological aspects of their application are of significant concern. Sustainability in the cement industry is currently based on many trends: (i) CO₂ emission control, capture, and utilisation[1-4]; (ii) increased utilisation of waste and by-products as raw materials or fuel in Portland cement production [5]; (iii) increased production of blended Portland cements [6-9]; and (iv) production of alternative low-carbon, low-temperature, and non-fired clinkers and cements [10-12]. The implementation of sustainable cement production requires developing new approaches and expanding and optimizing the raw materials base for modern cementitious materials to meet ecological and technical requirements. Alumino-silicate sources, such as blast furnace slag, fly ash, and natural pozzolans, have been the main sources of supplementary cementitious materials (SCM) for blended Portland cements for a long time. Relatively recently, efforts to find more widespread sources of pozzolans providing high reactivity and physical-chemical stability have led to extensive studies on calcined clays and their application at an industrial scale. Many studies and practical experience in the cement and concrete technology have demonstrated a high potential of thermally treated clays in terms of their reserves, workability, raw value, and technical efficiency. At present, calcined clays are playing an increasing role in the development of sustainable inorganic binders and materials.

2 Calcined clays as pozzolans

2.1 layer-lattice clay minerals

Calcined kaolin clay metakaolin (MK) is the most used and widely studied in terms of its production process, pozzolanic activity potential, effect on hydration, reaction products, structure, and properties. There are industrial-scale production and applications of Portland cement pastes, mortars, and concretes incorporated with MK in many counties. Since the mid-1990s, MK has been employed in various types of materials (high performance, high strength, lightweight concrete, fibre cement and concrete, mortar, and so on) in the construction of dams, bridges, towers, and other structures.
worldwide. The high popularity of MK is because of its high reactivity and compatibility with other widely used pozzolan materials such as blast furnace slag, fly ash, and silica fume. Many studies stated that MK has higher or less the same cementing efficiency compared to other pozzolans [7,13-15].

The pozzolanic behaviour of metakaolin is affected by its properties - the chemical-mineralogical composition - notably (SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$) content, calcination temperature and duration determining degree of amorphousness/dehydroxylation, shape and size of particles [16-21]. The high efficiency of MK as SCM is based on physical and chemical aspects. Physical effects include the influence of MK on the structure by reducing the total porosity and compacting the microstructure of the Portland cement paste and the interfacial transition zone with aggregates [15,22,23]. Chemical aspects include its effect on the amount and composition of cementitious reaction products [24,25]. The chemical interaction of reactive silicon and aluminium oxides of MK and portlandite (calcium hydroxide or CH) in the Portland cement paste results in a pozzolanic reaction that leads to the formation of an additional C–S–H gel, calcium aluminate hydrates, and aluminosilicate hydrates: MK[Al$_2$Si$_2$O$_7$] + CH + H $\rightarrow$ C–S–H, C$_4$AH$_13$, C$_3$AH$_6$, C$_2$ASH$_8$.

The C-A-S-H that occurs by the replacement of Si and Al on the C-S-H chains is characterized by decreased Ca/Si ratio, higher degree of polymerization, and longer chains [26]. Furthermore, the reaction of metakaolin forms additional amounts of AFm phases due to its high aluminum content, and the forming of specific AFm phases depends on available anions in the pore solution. Frías and Cabrera [27] determined the degree of hydration of MK and cement pastes. They concluded that calcium hydroxide contents of MK/OPC samples increased with age until 3±7 days. Subsequently, the values start decreasing, more or less depending on MK content, and in the cases of mixtures with 10 and 15 % of MK, an inflexion point at 56 and 90 days, respectively was observed. Beyond this point, the calcium hydroxide content achieved a progressive increase. This behavior of calcium hydroxide content was due to different hydration mechanisms: the increase in the Ca(OH)$_2$ amounts are due to the Portland cement hydration, while the decrease in the values is related with the pozzolanic reaction of MK. The inflexion points (for 10 % and 15 % of MK) represent the end of the pozzolanic reaction, due to the total consumption of MK.

Unlike typical pozzolans reacting slowly and achieving substantial reaction degrees only after several weeks [28] MK shows a rapid reaction due to a combination of the filler effect and accelerated cement hydration [29]. Lagieret al. [30] proposed that MK might enhance the dissolution of cementitious phase and provide additional nucleation sites for hydration products. Besides, they also noted that the increasing concentration of soluble aluminate ions was due to MK dissolution at early age. Poon et al. [31] pointed out that the rate of pozzolanic reaction and calcium hydroxide consumption at early age in metakaolin blended cement pastes were larger than that in silica fume or fly ash blended cement pastes.

The application of MK as an SCM results in considerable improvement in the physical-mechanical parameters of mortars and concretes. Qian& Li [32] reported a 51 % improvement in the 3-day compressive strength of concrete at a MK content of 15 % as well as an increase in the tensile strength and modulus of elasticity. Wild et al. [33] reported that an introduction of 25 % MK increased the 28-day compressive strength of concrete by up to 35 %. According to Tironi et al. [21] contribution of influencing factors on compressive strength is time-dependent. Specific surface of calcined clay has a large influence, then the effect of structural disorder is more important and, finally the kaolinite content has greater weight in the model at later ages. Justice et al. (2007) found that 8 % of MK enhanced the flexural strength by up to 40 %. As with other SCMs, the mechanical efficiency of MK is strongly dependent on the type of cement used. According to Cyr et al. [18] the hydration of MK pastes showed that the pozzolanic reaction involving MK was postponed with low-C$_3$A cements, as characterized by a delay of portlandite consumption and stratlingite formation. The determination of the optimal content of MK was a substantial part of many research studies, which concluded that the MK content in each individual case may vary from 5 to 40 %. According to Vejmelkova et al. [34] for normal concrete (typically with a water/cement ratio (w/c) of 0.5 and minimum compressive strength
(fc) of 40–50 MPa) the optimal MK content is 20 %; and for high-performance concrete (typically with a w/c ratio of 0.3 and fc of 80–100 MPa), it is 10 %. Many researchers noted that concretes containing MK had a lower permeability [35,36], lower shrinkage [37], and higher corrosion resistance [38,39] than reference samples. In addition, MK sufficiently mitigates the deleterious expansion from the alkali-silica reaction in concrete [40]. However, according to results reported by [41], concretes based on Portland cement containing 30 % of calcined clays displayed better sulphate attack, alkali-silica reaction, and chloride induced steel, but worse freeze-thaw changes and carbonation.

MK is found to be promising not only as a single mineral addition to Portland cement but also in ternary systems when it is incorporated into Portland cement in combination with limestone to produce limestone calcined clay cement. This type of compositional Portland cement, containing no more than 50 % of Portland clinker, balances low Portland clinker consumption and exhibits good early mechanical characteristics and durability under various service conditions [42]. Complex hydration reactions among Portland clinker minerals, the reactive part of calcined clay, and limestone lead to the formation of additional reaction products such as monocarboaluminate and hemicarboaluminate[43]. Avet & Scrivener [41] reported the calcined clays for this type of cement can be impure, but should have at least 40 % kaolinite, since clays with lower amounts of kaolinite are not pozzolantically reactive.

Chemical and physical requirements for pozzolanic materials are specified in many standards:

- content of reactive SiO$_2$ at least 25 % (EN 197-1:2011),
- SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ more than 70 % (ASTM C 595),
- content of reactive SiO$_2$ more than 90 % (NFP 18513 (2010), and
- compressive strength at least 75 % of that of reference cements after 7 days and 28 days (ASTM C 595).

According to EN 197-1, the reactive SiO$_2$ is the fraction of SiO$_2$ which is dissolved after treatment with hydrochloric acid and with boiling potassium hydroxide solution. The test methods are used to define the pozzolanic activity of calcined clays mainly based on a determination of the Ca(OH)$_2$ consumption by the reactive part of the pozzolanic addition [21,43].

Alujas et al. [51] reported that the pozzolanic reactivity of clays related to complete dehydroxylation can be qualitatively found by their relative position along the diagonal trend in an Al$_2$O$_3$–SiO$_2$–OH ternary plot, where pozzolanic reactivity is calculated as the percentage of structural hydroxyl groups and Al$_2$O$_3$ in the raw clay.

As for fineness, the average particle size and specific surface area of MKs are in 1.20–38 μm and 2.16–22 m$^2$/g ranges. With an increase in the fineness of MK, the pozzolanic reactivity increases [21,37].

The required concentration of kaolinite in kaolin clay is a relevant point concerning the production of MK. On the one hand, the pozzolanic reactivity of the calcined clay is proportional to the kaolinite content in the clay, and the use of high-grade kaolin clay usually guarantees a high reactivity of the resulting product. On the other hand, good-quality MK can be produced from medium- and low-grade kaolin clays, but only if kaolinite has a low-ordered structure [28,38,44]. Badogiannis&Tsivilis[24]investigated the pozzolanic activity of commercial MKs containing 95 % metakaolinite and MK obtained from Greek kaolin containing only 49 % metakaolinite and, based on the Chapelle test, concluded that these samples had almost the same pozzolanic reactivity rates. Badogiannis concluded that Greek kaolin having less-ordered kaolinite after calcination favoured the formation of metakaolinite with a high reactivity. Beyond that, 40 % of quartz improved the porous structure and reduced the permeability of concrete based on blended Portland cement. According to Duan et al. [15], the high reactivity of the less-ordered structure is related to the presence of active sites in the crystals both in the field of break chemical bonds and on the surfaces of borders and cleavage planes. Another important finding is that the structural disorder of kaolinites affects their optimum calcination temperature and the consumption of portlandite [15,34,44]. Medium- and low-
ordered kaolinites can be calcined at temperatures of 550–600 °C, whereas high-ordered kaolinites need higher temperatures to reach complete dehydroxylation.

Reactivity can also be affected by the composition and percentage of impurities. In the case of Fe$_2$O$_3$, Ghorbel&Samet [45] found that an impurity percentage of 2.7 % improves the pozzolanic activity of kaolin by increasing the consumption of portlandite and by compacting the structure.

Not only kaolinite but also halloysite/kaolinite blends (100/0, 75/25, or 60/40) were found to be highly reactive pozzolanas based on the results of the electrical conductivity test, Frattini test, and compressive strength index [46]. The clays were calcined at 700 °C and ground to 80 % of particles with a size less than 45 μm. The compressive strength of hardened Portland cement pastes was dependent on the halloysite/kaolinite ratio and the morphology of the halloysite. Halloysite/kaolinite 60/40 clay was more effective than 75/25 and 100/0 clays at 2 days because of the availability of reactive alumina, whereas 100/0 clay was better at 28 days owing to the delayed reaction of alumina.

2.2 layer-lattice clay minerals

Tironi et al. [47] and Bratoev et al. [22] compared kaolin clays and multi-mineral kaolin and non-kaolin clays. The pozzolanic reactivities of five clays, containing 19–95 % of kaolinite and 54–59 % of montmorillonite, reduced with the decreasing content of kaolinite; however, it was found to be possible to replace 30 % of Portland cement by calcined clays containing more than 40 % of quartz, which resulted in an increase in the 28-day strength of the blended Portland cement paste compared to the reference sample [47]. Tironi found that calcined bentonites favour the formation of silicate phases, whereas calcined kaolins favour the formation of early AFm phases (C$_3$A.CH.H$_{12}$) and strätlingite (C$_2$ASH$_8$). Bratoev et al. [22], based on the statistical analyses of experimental data and calculated pozzolanic activity data of six kaolinite-montmorillonite clays, reported a dependency of the reactivity of multi-component clays on the kaolinite and montmorillonite contents; the influence of illite and chlorite was negligible. As can be seen, the pozzolanic reactivity can be higher at a higher content of montmorillonite than that of kaolinite.

According to Alujas et al. [48], clays consisting of 40 % kaolinite and 40 % of 2:1 clay minerals when calcined at 800 °C can replace Portland cement without any loss of strength.

In an effort to avoid undesirable costs and energy inefficiency, Taylor-Lange et al. [49] proposed a method of optimizing clay reactivity and calcination temperature of impure clays by determining the amorphous content and dehydroxylated content through the Rietveld quantitative X-ray diffraction–thermal gravimetric analysis (RQXRD-TGA). For non-kaolinite minerals, it was found that the amount of amorphous material was a better predictor of clay reactivity than the dehydroxylation level. The authors compared the commercial kaolinite–calcium bentonite clay to the laboratory-blended kaolinite-sodium bentonite clay and found that kaolinite-sodium bentonite clay containing 35 % of kaolinite calcined at 830 °C showed better results in terms of reactivity, which is a finding similar to the case of MK discussed in Section 4.1.

Excavated waste clay consisting of kaolinite, illite, and smectite, calcined at 800–900 °C and introduced in Portland cement at a content of 30 %, improved the 28-day compressive strength, lowered the carbon emissions of the blended cement by 18–27 %, and maintained the workability and 90-day strength of the concretes based on blended Portland cement[50].

Trezza et al. [51] studied complex kaolinite-pyrophyllite-illite clays. According to data obtained by him, the pozzolanic activity, determined by the compressive strength activity index after 7 days, and compressive strength values exceeded the rate of replacement for both clays.

2.3 layer-lattice clay minerals

Comparative analyses of kaolin clays and 2:1 type clays, notably smectite and illite containing clays, have been reported by Ferreiro et al. [52], Hollanders et al. [44], and Rakhimov et al. [53]. Ferreiro et al. [52] analysed the effect of two types of clays: smectite-illite (montmorillonite 68, illite 8, quartz 9, muscovite 9, anorthite 6 wt. %) and kaolin clays (kaolinite 92, quartz 86 wt. %) on the properties of calcined clay/limestone Portland cements. The results showed that the calcined kaolin clay was more
reactive, thereby providing a higher strength and limestone content. However, the smectite-illite clay required lower water content and, therefore, was more effective to improve the 28-day strength at a low Portland clinker content and superplasticiser dosage at the same workability. Hollander et al. (2016) compared the pozzolanic activities of eight pure calcined clays and found that the activity diminished as follows: kaolinitic clays > Ca-montmorillonite > Na-montmorillonite > illite > hectorite. Moreover, Hollander reported the morphology changes occurring during calcination and consumption of portlandite of Ca- and Na-montmorillonites. Ca-montmorillonite completely amorphised with Al in tetrahedral sites at 800 °C and, as a result, its consumption of portlandite was faster than that of Na-montmorillonite, whose structure becomes semicrystalline with Al in less-ordered tetrahedral, fivefold, and octahedral positions. Rakhimov et al. [53] studied the dependence of the effectiveness of five multi-mineral clays on the temperature (400, 600, 800 °C), specific surface area (250, 500, 800 m²/kg), and concentration 5–20 % compared to MK and silica fume. Of the 180 tested formulations of hardened Portland cement pastes mixed with the five varieties of calcined clays at different concentrations, calcined at different temperatures and ground to different fineness, more than 50 % showed higher strengths than that of the reference and MK samples. In addition, 90 % of the samples of hardened Portland cement pastes with 5–10 % added calcined clays showed higher strengths (up to 30 %) than that of the reference sample, and 50 % of these same samples had higher strengths than that of the samples with 5–10 % MK.

Of the 2:1 type clays, multi-mineral illite, illite/smectite, illite/muscovite, and illite-chlorite clays have been investigated [54-57]. Garg & Skibsted [54] studied pozzolanic reactivity through the solid-state NMR and thermal treatment features of an interstratified illite/smectite (70/30) clay with quartz impurity and described a four-stage transformation process: dehydration (25–200 °C), dehydroxylation (600–800 °C), amorphisation (800–900 °C), and recrystallisation (950 °C and above). The optimum temperature was found to be 900 °C. Distinct from the behaviour of MK, the thermal treatment of the illite/smectite clay did not result in the formation of any metastable phase. The pozzolanic reactivity of this type of calcined clay is subject to the degree of disorder and dehydroxylation of the heated clay. Garg also reported an increase in the mean alumino-silicate chain length in the formed C–S–H phase and a higher Al/Si ratio compared to the C–S–H formed by the hydration of the reference Portland cement. Mohammed et al. [56] studied multi-mineral illite/muscovite clay (calcite 30.5, dolomite 16.5, illite/muscovite 20, chlorite 9, quartz 7, gypsum 2 wt. %) as an SCM. He found that the clay loses free water at 100°C and, between 450 and 600 °C, quartz α changes to quartz β and dehydroxylation of muscovite, illite, and chlorite occurs. Complete dehydroxylation occurs at temperatures above 600 °C, and complete decarbonisation at temperatures above 875 °C. An addition of 10 % of the calcinedillite/muscovite clay improved the mechanical characteristics of Portland cement. Lemma investigated the thermal behaviour and pozzolanic reactivity of iliteand illite-chlorite clays [55]. Illitic clays showed pozzolanic properties at 950°C (Frattini test), and the strength activity index at 28 days was in the 0.75–0.94 range, proportional to the content of clay minerals. The influence of the secondary clay minerals on the pozzolanic reactivity of calcinedillitic clays was found to be negligible. In the case of illite-chlorite clays, the following transformations occur as the temperature rises: in the 500–600°C range, the chlorite structure is modified because of partial dehydroxylation; at 800°C, the chlorite structure collapses; the structure of illite collapses at 900°C; and at 1000°C, amorphous compounds are formed as a result of the decomposition of clay minerals. Illite-chlorite clays calcined at 900°C displayed pozzolanic reactivity after 7 days (Frattini test), and after 28 days when calcined at 1100°C (strength activity index ~1.00).

According to the results of Rakhimov et al. [53], approximately 5–15 % of loamy clay (albite 13.66 %, microcline 15.9 %, chlorite 3.4 %, kaolinite 2.27 %, montmorillonite 19.3 %, calcite 2.01 %, quartz 38.0 %, mica 5.4 %), calcined at 400–600 °C and ground to 250–500 m²/kg, was found to be more effective than MK of a specific surface area of 1200 m²/kg to improve the compressive strength, water resistance, and density of the hardened Portland cement paste.

Rakhimova et al. [8] reported that, of the 36 hardened Portland cement paste samples obtained by mixing of Portland cement incorporated with 5–20 % of light loam (kaolin 3.25, montmorillonite 5.78,
chlorite 0.66, quartz 51.70, mica 3.08, microcline 8.44, dolomite 7.58 wt. %) calcined at temperatures of 400, 600, 800 °C and ground to 250, 500, 800 m$^2$/kg, 13 samples showed higher density, 16 higher compressive strength, 16 higher water resistance, and 23 higher water adsorption than that of Portland cement pastes with the same content of MK.

In the studies by Ng & Justnes [58], Østnor & Justnes [59], and Rakhimov [60], calcined marl was investigated. Østnor & Justnes [59] studied calcined marl (70% of clay minerals, 20% of calcium carbonate, impurities of quartz and feldspars). Introduction of 50% of calcined marl into CEMI improved the strengths at 1 and 28 days and the 1-year pore structure of the studied mortars. However, it is noted that calcined marl may cause carbonation. Rakhimov et al. [60] found that the addition of 15% of marl (kaolin 7.12, montmorillonite 12.4, chlorite 4.00, calcite 46.9, quartz 13.44, albite 7.83, mica 6.90, gypsum 1.40 wt. %) calcined at a temperature of 800 °C increased the 28-day compressive strength and reduced water permeability. Furthermore, the calcined marl effect was comparable with that of the commercial MK. The improvement in the physical-technical performance of the calcined marl-enriched Portland cement pastes is attributed to calcium silicates present in lower quantities in marl during the calcination as a result of the solid-phase reaction. Calcium silicates are involved in the formation of calcium silicate hydrates during the hydration of Portland cement as well as in the formation of calcium hydrocarboaluminates and solid solutions of calcium hydrocarboaluminates and calcium hydroxoaluminate.

3 Conclusions

Clays, which are in demand by many industries, have recently become an even more valuable mineral resource for the cement industry. Crude clay is not only a key ingredient of the raw material mix for Portland clinker production but also an effective and promising SCM in its thermally treated state for blended Portland cements. This review of recent studies in the field of calcined clays for the production of inorganic binders, oriented on the sustainable development of the cement industry, shows the suitability, for this purpose, of a wide range of clays, including pure and impure mono- and multi-mineral, 1:1 and 2:1 type mineral-based clays, with varying levels of efficiency. Based on an analysis of these studies, the following conclusions can be drawn:

1. Optimal calcination conditions vary for diverse clays owing to varieties in their chemical-mineralogical composition, crystallography, structural order/disorder, structural imperfections, interval between structural disorganisation and recrystallisation of clay minerals, and so on.

2. The chemical reactivity of calcined clays is a disorder/dehydroxylation function. For kaolinite, dehydroxylation is correlated with amorphisation, but there is no direct correlation between dehydroxylation and amorphisation of 2:1 type clay minerals. For non-kaolinite minerals, reactivity is better predicted by the amount of amorphous material than by the dehydroxylation level.

3. Many studies have demonstrated that the chemical reactivity and performance of calcined clays obtained from high-grade kaolin clays can be comparable with those obtained from medium or low-grade kaolin clays and multi-mineral kaolin and non-kaolin clays.

4. The pozzolanic activity of calcined clays is dependent on their chemical composition, notably their SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ content, degree of amorphousness/dehydroxylation, and fineness.

5. The presence of up to 40% of quartz in calcined clays plays a reinforcing role. An impurity of up to 2.7% Fe$_2$O$_3$ in calcined clays has positive effects from both physical and chemical points of view. Calcium carbonate in clays formed during the thermal treatment of calcium silicates beneficially affects the mechanical performance of hardened Portland cement-based materials incorporated with calcined clays.

6. Pozzolans can be produced from not only kaolin clays but also halloysite/kaolinite, kaolinite/montmorillonite, kaolinite/illite, kaolinite/illite/smectite, kaolinite-pyrophillite-illite, smectite-illite, illite, illite/smectite, illite/muscovite, illite-chlorite clays, marl, loamy clay, light loam, and marls.

Further systematic studies dedicated to investigating the relationships between chemical reactivity and quantitative and qualitative chemical and mineralogical compositions of widely available clays
through various modern methods, modelling, and statistical analyses are required for a deeper understanding of the diverse potential of clays. Such further studies are expected to expand the raw materials base for environmentally oriented and technically effective cement production. The determination of the range of the most promising types of clays that are more widespread than kaolin clays, the specification of acceptance criteria for raw clays and calcined products, and studies on the performance of mortars and concretes incorporated with representative samples of these calcined clays would contribute to the sustainability of concrete production.

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