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Pozzolanic reactivity of kaolin clays, a review
Reactividad puzolánica de arcillas caoliníticas, una revisión

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Abstract

Pozzolans have demonstrated to be highly efficient mineral additions in the concrete industry, because they reduce the environmental impact generated by the cement manufacture, improve the physical, chemical and mechanical properties of blends, and reduce costs. Calcined clays have been recognized as very good pozzolans, because they improve the durability and compressive strength of mortars and concretes. However, data reported by different authors show a very high variability that makes its modelling difficult. In the same way, and based on a review of the scientific literature, the relationship between morphologic characteristics, thermal treatments and mineral composition of clays and its pozzolanic reactivity is shown; as well as with the chemical, thermal and mechanical methods for improving that reactivity.

Keywords: *Kaolin clays, calcined clays, pozzolan, metakaolin, supplementary cementitious materials*

Resumen

Las puzolanas han demostrado ser adiciones minerales muy eficientes en la industria del concreto porque ayudan a reducir el impacto ambiental en la fabricación del cemento, mejoran propiedades físicas, químicas y mecánicas de las mezclas y en general ayudan a reducir costos. Las arcillas calcinadas han sido reconocidas como muy buenas puzolanas, ya que estas generan en los morteros y concretos incrementos en la durabilidad y en la resistencia a compresión; sin embargo, los datos reportados por los diferentes autores, muestran una variabilidad tan amplia que hace complejo su modelamiento. En este sentido, a partir de la revisión de literatura científica, se muestra la relación entre las características morfológicas, los tratamientos térmicos y la composición mineralógica de arcillas primarias y secundarias (sedimentarias) con su reactividad puzolánica; así como con los métodos químicos, térmicos y mecánicos que permiten el mejoramiento de dicha reactividad.

Palabras clave: Arcillas calcinadas, puzolana, metacaolín, materiales cementantes suplementarios

1. Introduction

Concrete is one of the most commonly used construction material, with a global consumption rate of approximately 25 GT per year, which is almost 3.8 t per person a year (Petek Gursel et al., 2004).

However, it is also widely recognized that concrete production has a significant impact on the environment. The construction industry is well known as an important source of greenhouse gas emissions (GHG); when considering all the GHG emissions generated by human activities, the cement industry accounts for 5% of these emissions and it also produces approximately 8% of the global CO_2 emissions (Alujas et al., 2015).

Almost half of these emissions are from fossil fuels, since Portland cement is an energy-intensive material that requires 4-5 GJ/t in its manufacturing process (Petek Gursel et al., 2004); and the other half corresponds to the decarbonation of limestone, which releases an average of 0.84 t of CO_2 per ton of clinker to the atmosphere (CSI 2014).

This value may change according to the localization, technology, production efficiency, energy sources for generating electricity and the choice of fuels for the furnace (Petek Gursel et al., 2004). Likewise, it can be affected by the use of alternative raw materials, mineralizers and fluxes minerals, and Supplementary Cementitious Materials (SCMs). A blend of Portland cement and pozzolans has been commonly used to deal with this environmental issue and also to obtain some economic advantages in the production of concrete (Sabir et al., 2001).

Pozzolan is a composite material containing reactive silica or silica-alumina and alumina, which does not have the cementitious properties, but in the presence of water and at room temperature they react with the cement's hydration products (especially the portlandite), in order to form new compounds that have cementitious properties. In the ASTM 593-82 standard, pozzolans are classified in two types: natural pozzolans and synthetic pozzolans. The first ones are the natural material formed by, for example, extrusive igneous rocks formed by volcanic ash or lava containing reactive silica. Biogenic sedimentary rocks like diatomite and radiolarite have also been used (Krajči et al., 2013; Degirmenci and Yilmaz, 2009); or zeolite materials (Özen et al., 2016; Küçükyıldırım and Uzal, 2014).

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As for synthetic pozzolans, many types of waste containing reactive silica have been used, for example, fly ash, rice husk ash, silica fume, blast furnace slags, and others (Nurchasanah, 2013).

One source of pozzolans are calcined clays and their use lies in the availability of materials and the improvement of the concrete's durability (Sabiret al., 2001). The cement industry uses mainly kaolin as a raw material (source of silica and alumina) for producing clinker for, white cement and metakaolin, used as SCM.

Therefore, based on a review of the scientific literature, this paper initially presents the relationship between the physical characteristics and the mineral composition of primary and secondary (sedimentary) kaolin clays and their pozzolanic reactivity; then, it briefly describes some experiences regarding the improvement of this reactivity and, finally, the corresponding conclusions.

Kaolin clays

Clays containing a high percentage of kaolinite ($Al_2O_3.2SiO_2.2H_2O$) are commonly called kaolin.

The properties of clays vary considerably and they strongly depend on their composition and mineral structure. The main characteristic that determines the usefulness of kaolin for a large number of applications is its mineral purity; taking into account the presence of impurities such as quartz, anatase, rutile, pyrite, siderite, feldspar, among others (Mitrović and Zdujić, 2014).

Kaolin clays, both primary and sedimentary, are widely available in the crust of the Earth and its proper thermal treatment leads to the dehydroxilation of the kaolinite's crystal structure and its transformation into metakaolin – MK (Antoni et al., 2012; Fabbri et el., 2013; Elimbi et al., 2011; Castillo et el., 2010; Sabir et al., 2001; Samet et al., 2007). This highly reactive transition phase is an amorphous material with pozzolanic reactivity, which is adequate to be used as SCM (Rashad, 2013).

In the presence of water at room temperature, the calcined kaolin reacts with the calcium hydroxide liberated by the cement hydration in order to form compounds with cementitious properties such as C-S-H (hydrated calcium silicates) and stratlingite (hydrated calcium aluminosilicates) (Tironi et al., 2012).

Characterization of clay and its pozzolanic reactivity

The determination of certain physical properties through the use of characterization techniques and the mineral composition (Table 1) is the starting point for different authors who describe the pozzolanic behavior of kaolin. The following techniques are among the most commonly used: laser grading, specific surface area – BET, thermogravimetric analysis (TGA), differential thermal analysis (DTA), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD).

Table 1. *Clay characterization techniques*

Author	*Material*	*Techniques*
Avet et al. (2016)	*Seven kaolin clays*	*TGA, XRD, Laser Grading, SEM*
Hollanders et al. (2016)	*Four pure kaolin clays*	*X-ray Fluorescence (XRF), XRD, Laser Grading, BET, FTIR*
Saand et al. (2016)	*Kaolin clay*	*EDS, DRX*
Snellings and Scrivener (2015)	*Kaolin clay*	*XRF, XRD, Laser Grading, BET*
Taylor-Lange et al. (2015)	*Commercial kaolin*	*XRF, XRD, Laser Grading, BET*
(Shafiq et al. 2015)	*Commercial kaolin KM40*	*TGA, XRD, Laser Grading, BET, SEM*
Alujas et al. (2015)	*Cuban sedimentary kaolin clay*	*XRF, XRD, FTIR, TGA –DTA, Laser Grading, BET*
Fitos et al. (2015)	*Commercial kaolin, three Greek hydrothermal kaolin*	*Laser Grading, XRD, FTIR, TGA-DTA*
Souri et al. (2015)	*Two Iranian sedimentary kaolins*	*XRF, XRD, SEM*
Tironi et al. (2014)	*Five Argentinian kaolin clays, two primary, two sedimentary*	*FTIR, TGA-DTA, SEM, XRD*
Tironi et al. (2013)	*Five Argentinian kaolinite clays, two bentonite*	*XRD, BET*
Fabbri et al. (2013)	*Three commercial kaolins*	*XRD, ICP-OES, SEM, BET, TGA –DTA*
Fernandez et al. (2011)	*Kaolinite, illite, and standard montmorillonite*	*BET, TGA – DTA, XRD*
Torres et al. (2010)	*Five commercial kaolins*	*FTIR, XRD, SEM, DTA*
Bich et al. (2009)	*Three commercial kaolins*	*Laser Grading, BET, XRD, IR*
Samet et al. (2007)	*Tunisian sedimentary kaolin clay*	*XRD, TGA - DTA*
Torres et al. (2007)	*Sedimentary kaolin, Colombian commercial kaolin*	*XRD, TGA*
Shvarzman et al. (2003)	*Israeli sedimentary kaolin, one commercial*	*SEM, BET, XRD, TGA –DTA*
Kakali et al. (2001)	*Four Greek kaolins, one commercial*	*XRD, IR, TGA - DTA*

Figure 1 presents the average particle diameter (d50) of the studied kaolins. It shows a minimum of 0.26 µm and a maximum of 9 µm and the specific surface area is distributed between 5.8 m²/g and 42 m²/g. The inverse relationship between the particle size and the surface area is evident in the analyzed kaolins; however, in the samples studied by Bich et al. (2009), the most elevated area of 30.5 m²/g corresponds to a d50 of 8 µm, similar to the maximum diameter. This could be explained by MK particles, where the sheets of this phyllosilicate are more separated, thereby increasing their porosity and so their surface area.

On the other hand, Figure 2 presents the mineral composition of the characterized kaolins. Although there are some highly pure ones, in general the kaolinite is found together with other minerals, mainly illite, quartz and feldspar.

Kaolinite contents are distributed between a minimum of 2% and a maximum of 98%; illite contents are lower than 20%, while quartz contents can reach 60%, which shows that not only high purity kaolins have been activated to be used as pozzolans.

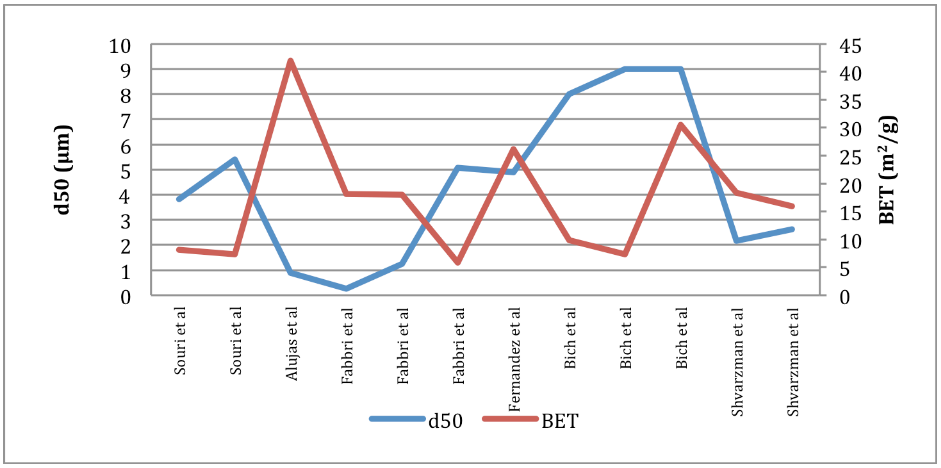

Figure 1. *Specific surface area and d50 for different kaolins*

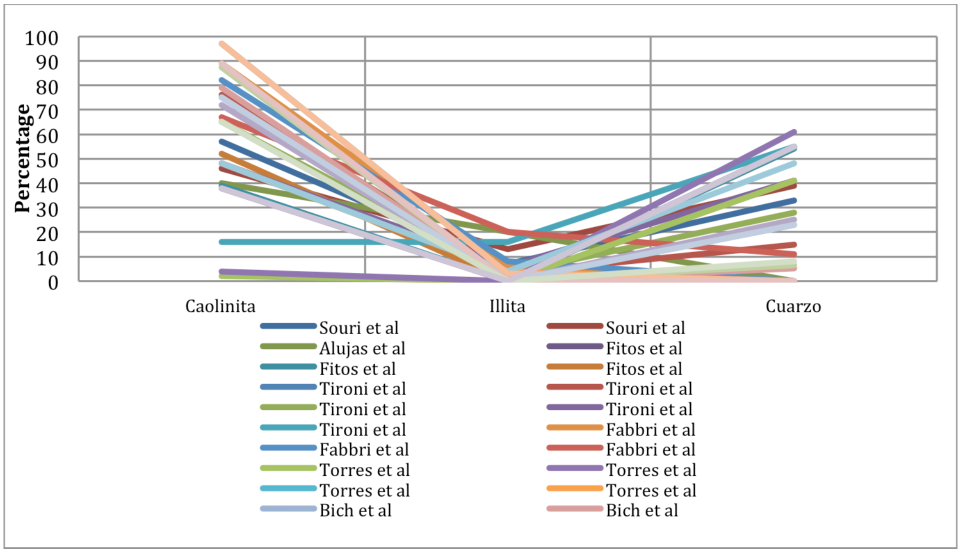

Figure 2. *Mineral composition of different kaolins*

Regarding the thermal processing to transform kaolin into metakaolin (MK), different authors evaluate temperatures of 650, 700 and 850°C, with soaking times of up to 900 minutes at the selected temperature, as shown in Figure 3. The efficiency of the thermal treatment is evaluated based on the XRD spectra and the transformation into metakaolin, the calculation of the dehydroxilation percentage (Tironi et al., 2012 and Taylor-Lange et al., 2015) and the compressive strength (Said-Mansour et al., 2011 and Moodi et al, 2011).

The effect of the thermal treatment assessed according to the dehydroxilation degree shows that the highest percentage (100%) is evidenced at 650°C at 45 and 120 minutes (Fabbri et al., 2013), at 700°C between 4 and 900 minutes, and at 850°C between 30 and 900 minutes (Bich et al., 2009).

Thermal treatments reported for the thermal activation of kaolins differ from one author to another with regard to the times and temperatures considered optimal. These temperatures range from 450 to 850°C, and calcination times range from 30 minutes to 3 hours.

These differences are attributed to the kaolin used as raw material, considering the fact that some authors study natural kaolin and non-kaolin clays, while others concentrate on commercial high purity kaolin clays. Likewise, the thermal treatment has an impact on the morphological characteristics. Figure 4 shows the change of the clays' d50 before and after the thermal activation, according to the temperature used.

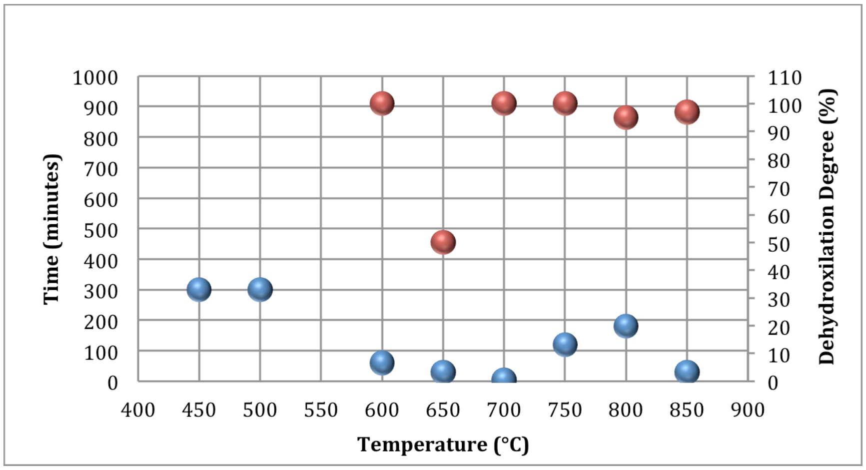

***Figure 3.** Evaluated calcination temperatures and times*

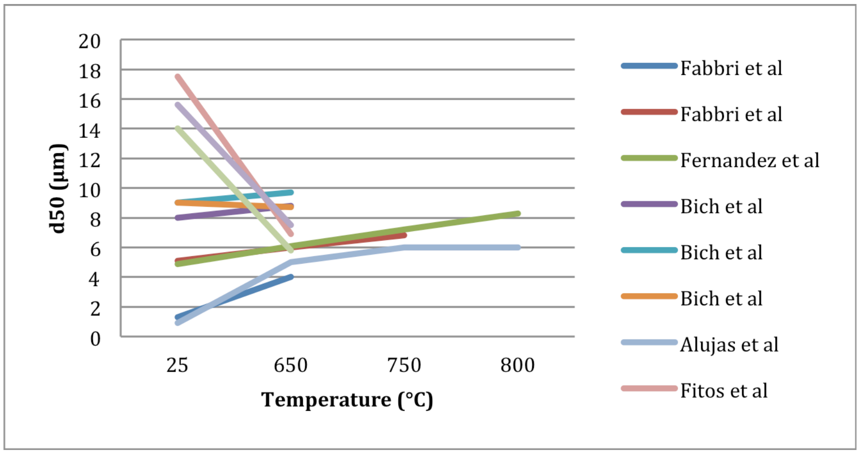

***Figure 4.** Temperature effect on d50*

Results show that the temperature increases the d50 due to the agglomeration of particles. However, in three kaolins of hydrothermal origin studied by Fitos et al. (2015) and one studied by Bich et al. (2009), the temperature reduced the d50, where the particle contraction effect prevails over the aggregation effect.

As for the specific surface area (SSA), Figure 5 shows the effect of the thermal treatment on the surface area of certain kaolins. A trend is observed where the surface area tends to reduce as the temperature increases, although there is no consensus among the authors.

Fabbri et al. (2013) and Bich et al. (2009) find that the SSA increases, where the contraction effect prevails due to the water loss (Souri et al., 2015).

The pozzolanic activity includes all the reactions among the active components of pozzolan, calcium hydroxide (released during the Portland cement (PC) hydration) and water. Two parameters are included in the evaluation of this activity: the maximum amount of calcium hydroxide (CH) with which a pozzolan can be mixed and the speed at which this reaction is produced (Hewlett, 2003).

The tests for evaluating the pozzolanic activity are divided in direct methods measuring the CH consumption (such as the Chapelle test – NF P18-513, the Frattini test – EN 196-5 and the saturated lime test) and indirect methods measuring a property change associated to the pozzolanic reaction (such as the Strength Activity Index – SAI (ASTM C311), the electrical conductivity and the change of the pH of a calcium hydroxide solution, and the heat conduction microcalorimetry (Donatello et al., 2010).

The pozzolanic activity is usually evaluated in CH-MK pastes in a 70-30% proportion; and in mortars at ages between 7 and 90 days. Figure 6 shows the Strength Activity Index (SAI) based on the consumption of calcium hydroxide (CH), for seven of the analyzed studies. A non-linear correlation is observed between the Strength Activity Index (SAI) and the CH consumption, with a stronger pozzolanic activity at late curing ages.

The pozzolanic behavior of thermally treated kaolins is highly variable; the SAI is distributed between 0.6 and 1.5, influenced not only by the different morphological and mineral characteristics, but also by their origin and treatment method.

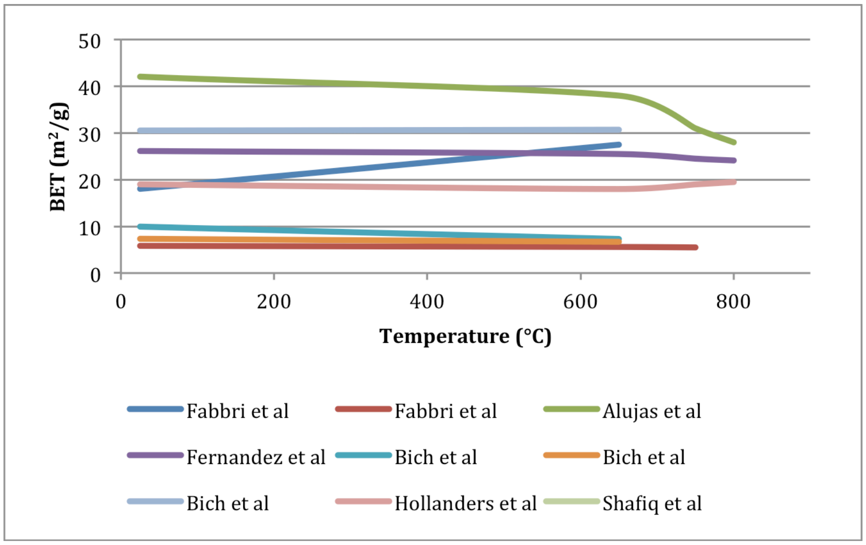

Figure 5. *Temperature effect on the surface area*

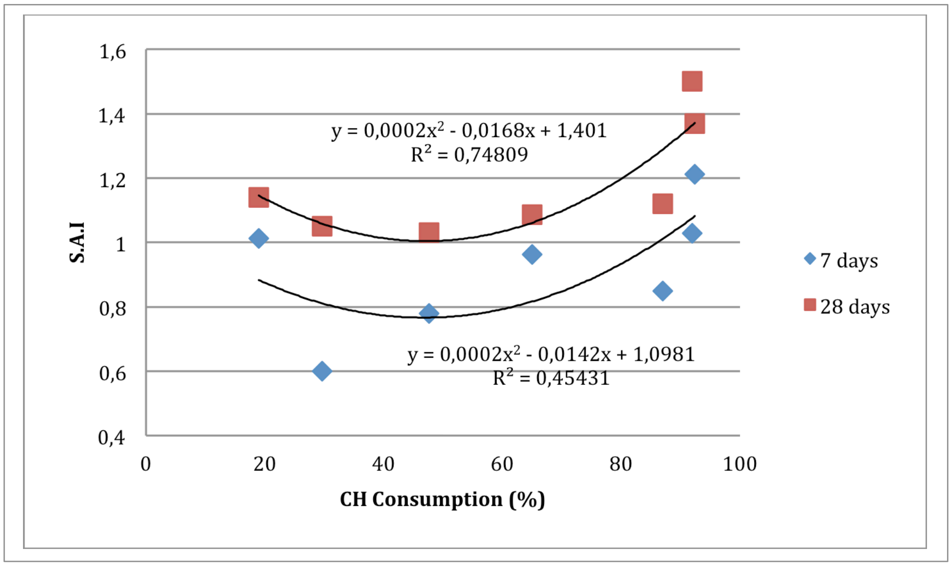

Figure 6. *Relationship between SAI and CH consumption*

The SAI at 7 days for the mixes evaluated in Tironi et al (2014) and Torres et al. (2010) is lower than 0.75 (minimum values stipulated in the ASTM C618 standard for considering that a material is pozzolanic); while the behavior of this index at 28 days shows that all evaluated metakaolin comply with the physical requirement for Class N pozzolans, showing the late activity of these materials.

Likewise, the CH consumption varies between 30% and 92%; it should be noted however that this high variability cannot be solely attributed to the thermal treatment factor. Furthermore, it shows that in these cases, the pozzolanic activity represented by the SAI cannot be solely explained by the chemical activity of the evaluated pozzolan.

Figure 7 relates these variables, in an attempt to explain the pozzolanic behavior (CH consumption) based on the mineral composition (kaolinite %) of raw clay.

Data reported by different authors do not show a good correlation between the kaolinite content of the clay before the thermal treatment and the calcium hydroxide consumption by the resulting metakaolin. Evidence shows that the thermal process modifies all the characteristics of the raw material, thus generating a wide variability in the response of calcined clays, which prevents it from being solely attributable to the initial kaolinite content.

In the same line, Figure 8 relates the CH consumption in PC-MK pastes and mortars at 7 days, based on the specific surface area and the d50 for raw samples.

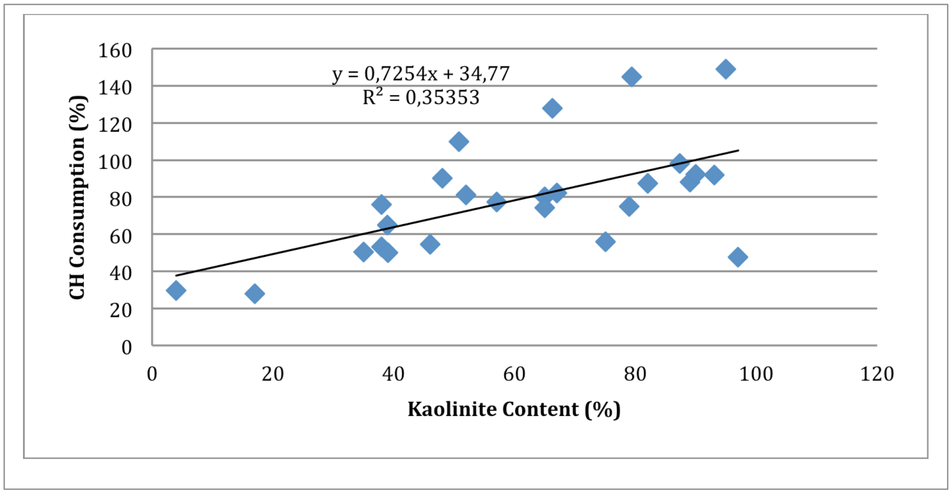

Figure 7. *CH consumption based on the kaolinite content*

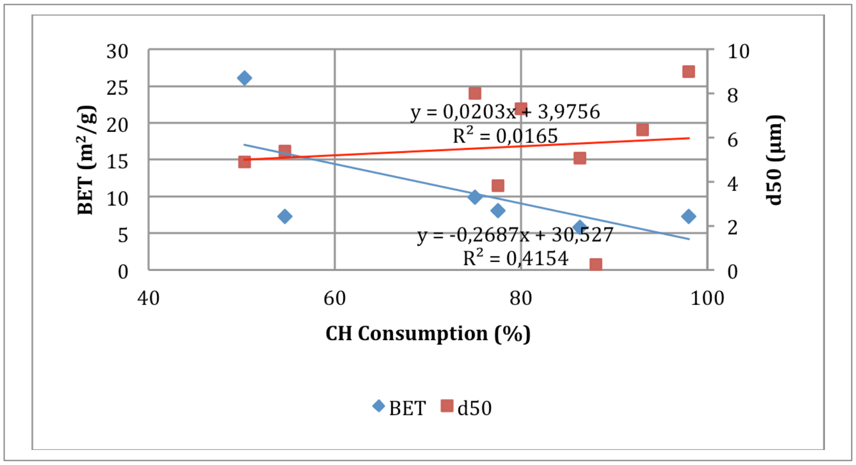

Figure 8. *CH consumption based on d50 and BET*

Data reported by different authors show that simple linear correlation models for explaining the CH consumption based on d50, can only succeed in a small percentage, with a very low correlation coefficient. In the case of the specific surface area measured by the BET analysis, there seems to be even an inverse correlation: the higher the specific surface area the lower the lime fixation. As Snellings and Scrivener (2015) have pointed out, correlations between the BET area of a SCM and its pozzolanic activity have been reported; however, when these correlations are compared in materials of different origins, inconsistencies arise. The absence of a single integrating relationship indicates that the reactivity of a SCM depends on other factors, besides the specific surface.

Likewise, in order to describe the pozzolanic behavior of different metakaolins, other simple linear correlation models have been defined, based on the dehydroxilation degree (Bich et al., 2009), the calcination temperature (Moodi et al., 2011) and the fixed lime percentage (Uchima et al., 2015).

Multiple linear correlation models have also been established, such as the general linear model of Güneyisi et al. (2012), which relates the pozzolanic activity index to the type of kaolin and the calcination temperature; and the model of Mermerdaş et al. (2012). Additionally, Tironi et al. (2012) developed a model that relates the compressive strength (CS_t) of mortars mixed with metakaolin at different ages, to the content of initial kaolinite (k), the calcined clays specific surface area – Blaine (SS_{Blaine}) and the inverse of the order/disorder degree of the raw structure ($1/P_0$).

$$CS_t = \alpha_0 + \alpha_1 k + \alpha_2 SS_{Blaine} + \alpha_3 (1/p_0) \qquad \textbf{(1)}$$

Where the α_i are the coefficients obtained by least squares.

Finally, Samet et al. (2007) developed a quadratic model that describes the relationship between the compressive strength at different ages (Y_t) and the calcination temperature (X_1), the BET specific surface (X_2), and the percentage replacement of cement (X_3).

$$y_7 = \propto_0 + \propto_1 x_1 + \propto_2 x_2 - \propto_3 x_3 + \propto_4 x_1^2 + \propto_5 x_2^2 + \propto_6 x_3^2 + \propto_7 x_1 x_2 + \propto_8 x_1 x_3 + \propto_9 x_2 x_3 \qquad \textbf{(2)}$$

The merit of these models lies in the fact that they try to establish the effect of some of the characteristics of raw clay on the development of compressive strength of mortars added with calcined clays, that is, they are multivariable. On the other hand, limitations refer to the fact that most models do not report the adjustments obtained at the time of validating them, and also because they have a linear character; despite the evidence that some variables seem to correlate better in a non-linear way.

Improvement of the pozzolanic reactivity

In an effort to improve the MK reactivity, different authors have proposed methods such as acid activation and thermal and/or mechanical treatments.

***Table 2.** Improvement of the reactivity method*

Author	***Method***	***Material***
Souri et al. (2015)	*Mechanochemical activation, 60, 180, 300 and 350 min*	*Kaolin clays*
Kovářík et al. (2015)	*Recalcination 500 - 1000°C*	*Commercial CM*
Mitrović and Zdujić (2014)	*Mechanochemical activation, 10 - 1200 min*	*Kaolin clay*
Mitrovic and Zdujic (2013)	*Mechanochemical activation, 15 - 150 min*	*Kaolin lay*
Ghorbel and Samet (2013)	*Ferric nitrate addition 0.4 M, 10 – 150 ml*	*Pharmaceutical kaolin*
Taylor-Lange, Riding, and Juenger (2012)	*Addition ZnO - 0.1, 0.5, 1%*	*Natural kaolin*
Vizcayno et al. (2010)	*Mechanochemical activation 15 - 120 min*	*Two natural kaolins– one commercial*
San Cristóbal et al. (2009)	*Acid activation HCl 6M - 90°C – 3 h*	*Kaolin sand – Washed kaolin*
Lenarda et al. (2007)	*Acid activation H_2S0_4 1M - 90°C*	*Natural kaolin*
Belver, Bañares, and Vicente (2004)	*Acid activation HCl 6M - 90°C, 6 – 24h*	*Spanish natural kaolin*
Belver, Bañares, and Vicente (2004)	*Basice activation KOH 5M - 90°C*	*Spanish natural kaolin*

The mechanochemical activation and the acid activation are the most commonly used methods. It has been found that acid activation increases the SSA, while the basice activation reduces the SiO_2 content, as shown in Figure 9.

However, since the different authors do not evaluate the pozzolanic reactivity of the materials after the acid/basice activations, it is just possible to foresee an increase in this reactivity in case there is an SSA increase, without being able to specify its magnitude.

The 2.7% addition of ferric nitrate to a commercial kaolin and its subsequent calcination increases the compressive strength at 7 days, from 16 MPa in the sample of pure cement to 22 MPa in the substituted mix, and from 27 MPa to 48 MPa at 90 days, since the Coulomb forces between the negatively charged surface of the kaolin and the positive charges of iron (Fe^{+3}) generate the deposition of nodules (Ghorbel and Samet, 2013), which are consumed during the hydration, forming ferric ettringite and iron-substituted C-S-H (Samet et al., 2013).

Furthermore, the recalcination at 800°C increased the CH consumption, from 1225 mg/g to 1748 mg/g (Kovarik et al., 2015).

Figure 10 presents the effect of the mechanochemical activation on the pozzolanic reactivity.

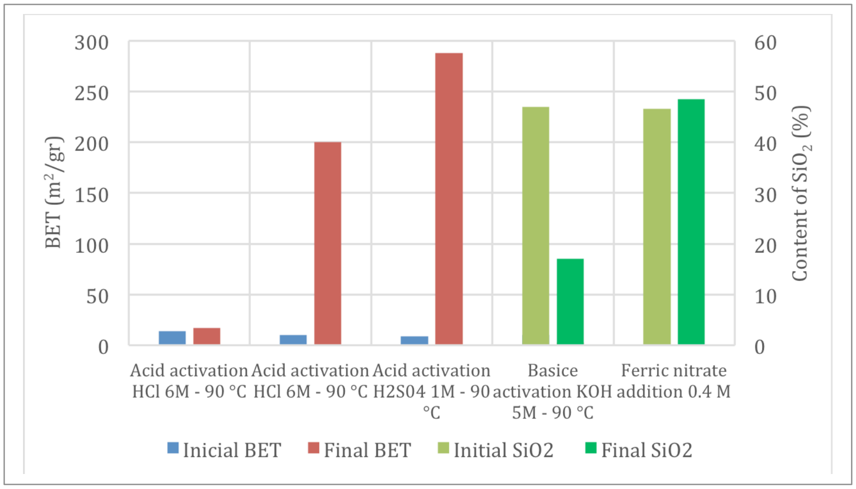

Figure 9. *Effect of chemical activation and inorganic additives on different metakaolins*

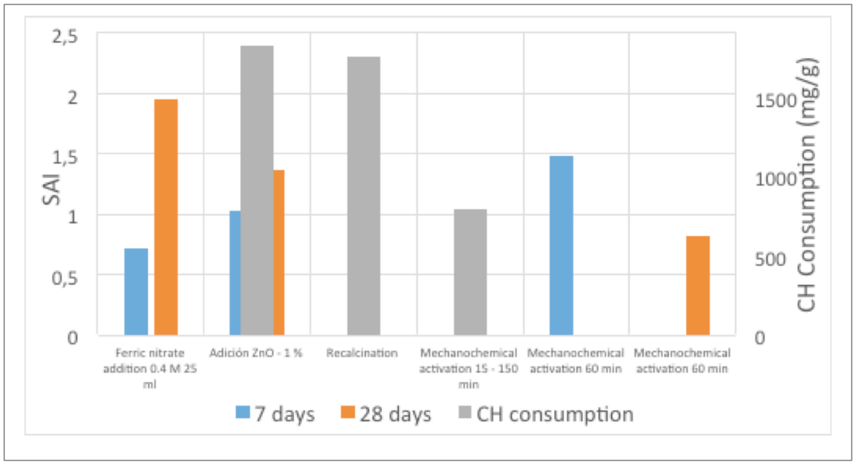

Figure 10. *Effect of the mechanochemical activation on the reactivity*

Mitrovic et al. (2013) grinded a raw kaolin clay, without additives, in a planetary mill during 15, 30, 60, 120 and 300 minutes. They found that the d50 increased from 9.85 to 11.34 μm after 15 minutes, due to the particles' agglomeration. The CH consumption after grinding for 15 minutes was 790 mg, while for the sample grinded for 5 hours it was 760 mg, thus evidencing that grinding for over 15 minutes did not have relevant effects on the pozzolanic activity.

Nevertheless, Mitrovic et al. (2014) treated a raw kaolin clay mechanically in a horizontal ball mill during 10 minutes, thereby reducing the d50 from 23 to 10 μm, while the pozzolanic activity, measured in PC - MK mortars (80-20) at 7 days, showed a continuous increase as the grinding time increased, from 2.9 MPa to 14 MPa after 1200 minutes.

Likewise, Viscayno et al. (2010) mechanically treated two raw kaolins and one industrial kaolin in an oscillating mill at 1420 rpm during 15, 30, 60 and 120 minutes. The resulting d4.3 after 15, 30 and 60 minutes was 30.89, 26.75 and 19.67, respectively. The pozzolanic activity index evaluated in PC – MK industrial mortars (80-20) after 28 days with a grinding time of 60 minutes was 0.79, and 0.85 after 120 minutes. It was shown that longer grinding times produce finer materials with higher SAI, which seems to contradict the results of Mitrovic et al. (2013). It would also be convenient to evaluate if the energy and economic costs of longer grinding times are justified with regard to the benefit obtained in the Pozzolanic Activity Index.

Figure 11 shows the specific surface area – BET and the d50 for mechanically treated samples, based on grinding times evaluated by different authors.

The simple linear correlation reveals that the longer the grinding time, the larger the specific surface area – BET; on the other hand, the d50 shows very disperse values that cannot be properly represented by the same type of correlation, although it seems to have a decreasing tendency.

Figure 12 shows the Strength Activity Index (SAI) based on grinding time.

The compressive strength at 7 days can be explained by the grinding time through a simple linear regression with a good adjustment (R^2 = 0.85); the longer the grinding time, the higher the compressive strength; while for the SAI' regression at 28 days, the coefficient of determination is 0.8.

Thus, the relative efficiency of the methods for improving the pozzolanic reactivity is recognized; although no models are reported nor validated that can properly establish the effect of kaolin clays' morphological characteristics on their response to those methods.

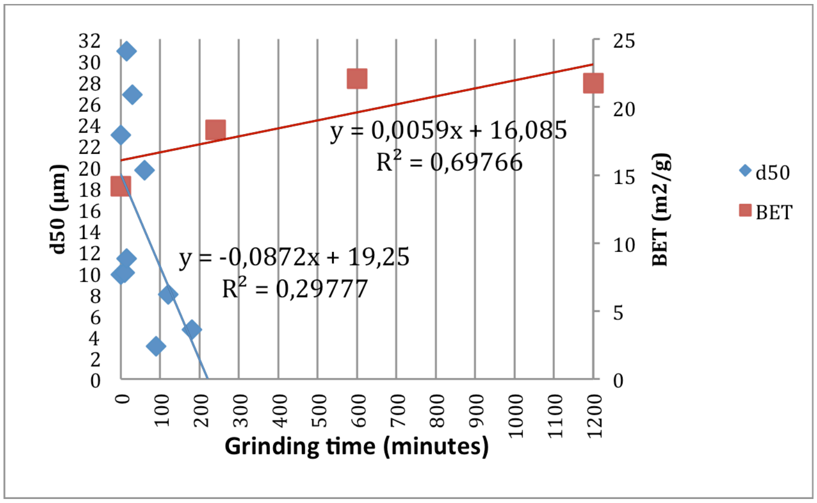

Figure 11. *BET area and d50 based on grinding time*

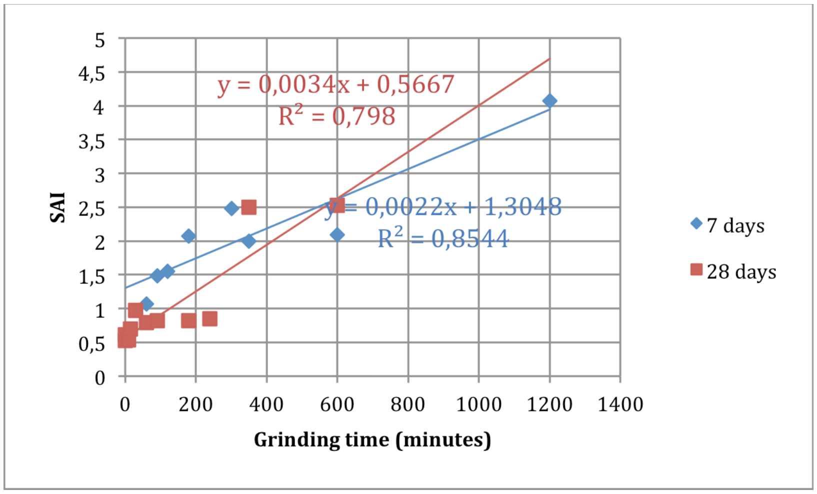

Figure 12. *Pozzolanic activity based on grinding time*

2. Conclusions

Regarding the morphological characteristics, most authors find an inverse relationship between the average particle size (d50) and the studied materials' SSA. Likewise, it was observed that, as a consequence of the thermal treatment of kaolin, transformations occur through the dehydroxilation of kaolinite with aggregation of metakaolin particles and the formation of bigger grains, reflected by a generalized increase of the d50. However, a decrease is observed in the specific surface area as a consequence of the dehydroxilation of clays.

The morphological characteristics and the mineral composition of kaolin clays partially explain its pozzolanic behavior through simple linear correlations; nevertheless, given the coefficients of determination, it is necessary to establish other kinds of correlations that can model the reactivity of this type of materials with a higher level of significance.

A few linear correlation models and multiple non-linear models, which also include the calcination temperature and percentage replacement of cement, have succeeded to more reliably establish the significance and magnitude of the effect of these characteristics on the reactivity.

In the same way, different authors have confirmed the improved reactivity of calcined clays in relation to the CH consumption and the compressive strength, when inorganic additives are used and recalcination is carried out. However, the improvement of the pozzolanic behavior has yet to be explained by means of correlation models that evaluate other variables apart from grinding times.

Thus, there is an increasing interest in demonstrating the effectiveness of the treatments for evaluating and improving the reactivity of clays concerning their use as SCM, mainly impure ones of sedimentary origin, thereby explaining its pozzolanic behavior based on the characteristics of raw clays, through simple or multiple correlation models, as in the case of commercial pure metakaolins.

3. References

Alujas Adrian, Rodrigo Fernández, Rafael Quintana, Karen L. Scrivener and Fernando Martirena (2015), "Pozzolanic Reactivity of Low Grade Kaolinitic Clays: Influence of Calcination Temperature and Impact of Calcination Products on OPC Hydration." Applied Clay Science 108 (May): 94–101. doi:10.1016/j.clay.2015.01.028.

Antoni M., J. Rossen, F. Martirena and K. Scrivener (2012), "Cement Substitution by a Combination of Metakaolin and Limestone." Cement and Concrete Research 42 (12): 1579–89. doi:10.1016/j.cemconres.2012.09.006.

Avet Francois, Ruben Snellings, Adrian Alujas Diaz, Mohsen Ben Haha and Karen Scrivener (2016), "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. Elsevier Ltd: 1–11. doi:10.1016/j.cemconres.2016.02.015.

Belver C., M. A. Bañares and M. A. Vicente (2004), "Materiales Con Propiedades Tecnológicas Obtenidos Por Modificación Química de Un Caolín Natural." Boletin de La Sociedad Espanola de Ceramica Y Vidrio 43 (2): 148–54.

Bich Ch., J. Ambroise and J. Péra (2009), "Influence of Degree of Dehydroxylation on the Pozzolanic Activity of Metakaolin." Applied Clay Science 44 (3–4): 194–200. doi:10.1016/j.clay.2009.01.014.

Castillo Rancés, Rodrigo Fernández, Mathieu Antoni, Karen Scrivener, Adrián Alujas and José F Martirena (2010), "Activación de Arcillas de Bajo Grado a Altas Temperaturas." Revista Ingeniería de Construcción 25 (3): 329–52. doi:10.4067/S0718-50732010000300001.

CSI GNR (2014), *Report Final_updated Nov11_LR.pdf.* Accessed November 22. http://www.wbcsdcement.org/pdf/CSI GNR Report final_updated Nov11_LR.pdf.

Degirmenci Nurhayat and Arin Yilmaz (2009), "Use of Diatomite as Partial Replacement for Portland Cement in Cement Mortars." Construction and Building Materials 23 (1): 284–88. doi:10.1016/j.conbuildmat.2007.12.008.

Donatello S., M. Tyrer and C.R. Cheeseman (2010), "Comparison of Test Methods to Assess Pozzolanic Activity." Cement and Concrete Composites 32 (2): 121–27. doi:10.1016/j.cemconcomp.2009.10.008.

Elimbi A., H.K. Tchakoute and D. Njopwouo (2011), "Effects of Calcination Temperature of Kaolinite Clays on the Properties of Geopolymer Cements." Construction and Building Materials 25 (6): 2805–12. doi:10.1016/j.conbuildmat.2010.12.055.

Fabbri B., S. Gualtieri and C. Leonardi (2013) "Modifications Induced by the Thermal Treatment of Kaolin and Determination of Reactivity of Metakaolin." Applied Clay Science 73 (March). Elsevier B.V.: 2–10. doi:10.1016/j.clay.2012.09.019.

Fitos Michalis, Efstratios G. Badogiannis, Sotirios G. Tsivilis and Maria Perraki (2015), "Pozzolanic Activity of Thermally and Mechanically Treated Kaolins of Hydrothermal Origin." Applied Clay Science 116–117 (November): 182–92. doi:10.1016/j.clay.2015.08.028.

Ghorbel Halima and Basma Samet (2013), "Effect of Iron on Pozzolanic Activity of Kaolin." Construction and Building Materials 44 (July): 185–91. doi:10.1016/j.conbuildmat.2013.02.068.

Güneyisi Erhan, Mehmet Gesoğlu, Turan Özturan and Kasım Mermerdaş (2012), "Microstructural Properties and Pozzolanic Activity of Calcined Kaolins as Supplementary Cementing Materials." Canadian Journal of Civil Engineering 39 (12): 1274–84. doi:10.1139/cjce-2011-0586.

Hewlett Peter (2003), Lea's Chemistry of Cement and Concrete. Vol. 2003.

Hollanders Sofie, Rieko Adriaens, Jørgen Skibsted, Özlem Cizer and Jan Elsen (2016), "Pozzolanic Reactivity of Pure Calcined Clays." Applied Clay Science 132: 552–60. doi:10.1016/j.clay.2016.08.003.

Kovářík T., P. Bělský, P. Novotný, J. Říha, J. Savková, R. Medlín, D. Rieger and P. Holba (2015), "Structural and Physical Changes of Re-Calcined Metakaolin Regarding Its Reactivity." Construction and Building Materials 80: 98–104. doi:10.1016/j.conbuildmat.2014.12.062.

Krajči Ľudovít, Marta Kuliffayová, and Ivan Janotka (2013), "Ternary Cement Composites with Metakaolin Sand and Calcined Clayey Diatomite." Procedia Engineering 65: 7–13. doi:10.1016/j.proeng.2013.09.003.

Küçükyıldırım E. and B. Uzal (2014) "Characteristics of Calcined Natural Zeolites for Use in High-Performance Pozzolan Blended Cements." Construction and Building Materials 73 (December): 229–34. doi:10.1016/j.conbuildmat.2014.09.081.

Lenarda M, L. Storaro, A. Talon, E. Moretti and P. Riello (2007), "Solid Acid Catalysts from Clays: Preparation of Mesoporous Catalysts by Chemical Activation of Metakaolin under Acid Conditions." Journal of Colloid and Interface Science 311 (2): 537–43. doi:10.1016/j.jcis.2007.03.015.

Mermerdaş Kasım, Mehmet Gesoğlu, Erhan Güneyisi and Turan Özturan (2012), "Strength Development of Concretes Incorporated with Metakaolin and Different Types of Calcined Kaolins." Construction and Building Materials 37 (December): 766–74. doi:10.1016/j.conbuildmat.2012.07.077.

Mitrovic Aleksandra and Miodrag Zdujic (2013), "Mechanochemical Treatment of Serbian Kaolin Clay to Obtain High Reactive Pozzolana." Journal of the Serbian Chemical Society 78 (4): 579–90. doi:10.2298/JSC120829107M.

Mitrović Aleksandra and Miodrag Zdujić (2014), "Preparation of Pozzolanic Addition by Mechanical Treatment of Kaolin Clay." International Journal of Mineral Processing 132 (November): 59–66. doi:10.1016/j.minpro.2014.09.004.

Moodi F., A. A. Ramezanianpour and A.Sh. Safavizadeh (2011), "Evaluation of the Optimal Process of Thermal Activation of Kaolins." Scientia Iranica 18 (4): 906–12. doi:10.1016/j.scient.2011.07.011.

Nurchasanah Yenny (2013), "Characteristic of 'Tulakan' Soil as Natural Pozzolan to Substitute Portland Cement as Construction Material." Procedia Engineering 54. Elsevier B.V.: 764–73. doi:10.1016/j.proeng.2013.03.070.

Özen S., M.C. Göncüoğlu, B. Liguori, B. de Gennaro, P. Cappelletti, G.D. Gatta, F. Iucolano and C. Colella (2016), "A Comprehensive Evaluation of Sedimentary Zeolites from Turkey as Pozzolanic Addition of Cement- and Lime-Based Binders." Construction and Building Materials 105 (February): 46–61. doi:10.1016/j.conbuildmat.2015.12.055.

Petek Gursel A., Eric Masanet, Arpad Horvath and Alex Stadel (2014), "Life-Cycle Inventory Analysis of Concrete Production: A Critical Review." Cement and Concrete Composites 51 (August): 38–48. doi:10.1016/j.cemconcomp.2014.03.005.

Rashad Alaa M. (2013), "Metakaolin as Cementitious Material: History, Scours, Production and Composition – A Comprehensive Overview." Construction and Building Materials 41 (April): 303–18. doi:10.1016/j.conbuildmat.2012.12.001.

Saand Abdullah, Manthar Ali Keerio, Daddan Khan Bangwar and Muhammad Kashif Samo (2016), "Development of Metakaolin as a Pozzolanic Material from Local Natural Material, Soorh." Arabian Journal for Science and Engineering 41 (12): 4937–44. doi:10.1007/s13369-016-2216-1.

Sabir B. B., S. Wild and J. Bai (2001), "Metakaolin and Calcined Clays as Pozzolans for Concrete: A Review." Cement and Concrete Composites 23 (6): 441–454.

Said-Mansour Mohamed, El-Hadj Kadri, Said Kenai, Mohamed Ghrici and Rachid Bennaceur (2011), "Influence of Calcined Kaolin on Mortar Properties." Construction and Building Materials 25 (5): 2275–82. doi:10.1016/j.conbuildmat.2010.11.017.

Samet B., T. Mnif and M. Chaabouni (2007), "Use of a Kaolinitic Clay as a Pozzolanic Material for Cements: Formulation of Blended Cement." Cement and Concrete Composites 29 (10): 741–49. doi:10.1016/j.cemconcomp.2007.04.012.

Samet Basma, Ahlem Chakchouk, G. M. Sadiqul Islam, Samir Bouaziz, Ahlem Chakchouk and Basma Samet (2013), "Discussion: Difference in Pozzolanic Behaviour of Tunisian Clays with Lime and Cement." Advances in Cement Research 24 (1): 119–119. doi:10.1680/adcr.2012.24.1.11.

San Cristóbal, Ana G., Ricardo Castelló, M. Angeles Martín Luengo and Carmen Vizcayno (2009), "Acid Activation of Mechanically and Thermally Modified Kaolins." Materials Research Bulletin 44 (11): 2103–11. doi:10.1016/j.materresbull.2009.07.016.

Shafiq Nasir, Muhd Fadhil Nuruddin, Sadaqat Ullah Khan and Tehmina Ayub (2015), "Calcined Kaolin as Cement Replacing Material and Its Use in High Strength Concrete." Construction and Building Materials 81: 313–23. doi:10.1016/j.conbuildmat.2015.02.050.

Snellings Ruben and Karen L. Scrivener (2015), "Rapid Screening Tests for Supplementary Cementitious Materials: Past and Future." Materials and Structures 49 (8): 1–15. doi:10.1617/s11527-015-0718-z.

Souri Alireza, Hadi Kazemi-Kamyab, Ruben Snellings, Rahim Naghizadeh, Farhad Golestani-Fard and Karen Scrivener (2015), "Pozzolanic Activity of Mechanochemically and Thermally Activated Kaolins in Cement." Cement and Concrete Research 77. Elsevier Ltd: 47–59. doi:10.1016/j.cemconres.2015.04.017.

Taylor-Lange, Sarah C., Emily L. Lamon, Kyle A. Riding and Maria C.G. Juenger (2015), "Calcined Kaolinite–bentonite Clay Blends as Supplementary Cementitious Materials." Applied Clay Science 108 (May): 84–93. doi:10.1016/j.clay.2015.01.025.

Taylor-Lange, Sarah C., Kyle A. Riding and Maria C. G. Juenger (2012), "Increasing the Reactivity of Metakaolin-Cement Blends Using Zinc Oxide." Cement and Concrete Composites 34 (7). Elsevier Ltd: 835–47. doi:10.1016/j.cemconcomp.2012.03.004.

Tironi A., M.A. Trezza, E.F. Irassar and A.N. Scian (2012), "Thermal Treatment of Kaolin: Effect on the Pozzolanic Activity." Procedia Materials Science 1 (January): 343–50. doi:10.1016/j.mspro.2012.06.046.

Tironi Alejandra, Monica A. Trezza, Alberto N. Scian and Edgardo F. Irassar (2014), "Potential Use of Argentine Kaolinitic Clays as Pozzolanic Material." Applied Clay Science 101 (November): 468–76. doi:10.1016/j.clay.2014.09.009.

Tironi Alejandra, Mónica A. Trezza, Alberto N. Scian and Edgardo F. Irassar (2012), "Kaolinitic Calcined Clays: Factors Affecting Its Performance as Pozzolans." Construction and Building Materials 28 (1): 276–81. doi:10.1016/j.conbuildmat.2011.08.064.

Uchima Juan S., Oscar J. Restrepo and Jorge I. Tobón (2015), "Pozzolanicity of the Material Obtained in the Simultaneous Calcination of Biomass and Kaolinitic Clay." Construction and Building Materials 95. Elsevier Ltd: 414–20. doi:10.1016/j.conbuildmat.2015.07.104.

Vizcayno C., R.M. de Gutiérrez, R. Castello, E. Rodriguez and C.E. Guerrero (2010), "Pozzolan Obtained by Mechanochemical and Thermal Treatments of Kaolin." Applied Clay Science 49 (4): 405–13. doi:10.1016/j.clay.2009.09.008.