Chapter

Activated Clays and Their Potential in the Cement Industry

Carlos Hernando Aramburo Varela, Luiz Felipe de Pinho, César Pedrajas Nieto-Márquez and Rafael Talero Morales

Abstract

The thermal activation of clays to produce highly reactive artificial pozzolans on a large scale is one of the most important technologies developed on an industrial scale to reduce CO_2 emissions in cement manufacture. This technical document deals with the scientific basis for the thermal activation of clays to produce an extraordinarily high quality supplementary cementitious material (SCM) based on the contents of its hydraulic factors, reactive silica (SiO_2^{r-}) and reactive alumina ($Al_2O_3^{r-}$). The production process and the optimization of its use in the new cements offers better performance, features and durability. Furthermore, its mixture with Portland cement is much more appropriate when carried out in a blending station after both components, activated clay and Portland cement, are ground separately and not jointly in a single mill.

Keywords: cement, activated clays, calcined clays, pozzolanic additions, low carbon

1. Introduction

Currently, the cement industry is working on the search and use of new SCMs that allow the reduction of the clinker/cement factor in a significant way. The traditionally ones used are mainly blast furnace slags, natural pozzolans and fly ashes. In the case of the latter, and in view of the requirement to reduce "greenhouse-effect" gas emissions, the commitments acquired from COP21, and the forthcoming closure of coal-based electricity generation plants will greatly affect and seriously compromise their availability soon.

In the field of cements, mineral additions are understood to be natural or artificial inorganic materials or products that, added to Portland cement (PC) in certain quantities, improve its normal behavior, and may also sometimes provide some additional and specific positive quality or improve some of the characteristics of PC. As already mentioned before, the traditional mineral additions that are used in the cement and concrete industry, we can mention the pozzolanic additions (natural and artificial) and blast furnace slags, both which are known as active additions, in order to differentiate them of non-active or misnamed inert additions. The latter can be of limestone or siliceous origin and receive the common name of "filler", and none can be considered pozzolanic.

Figure 1 shows the scarce availability of conventional SCMs in relation to the existence of limestone and clays. The availability of thermally activated clays on the

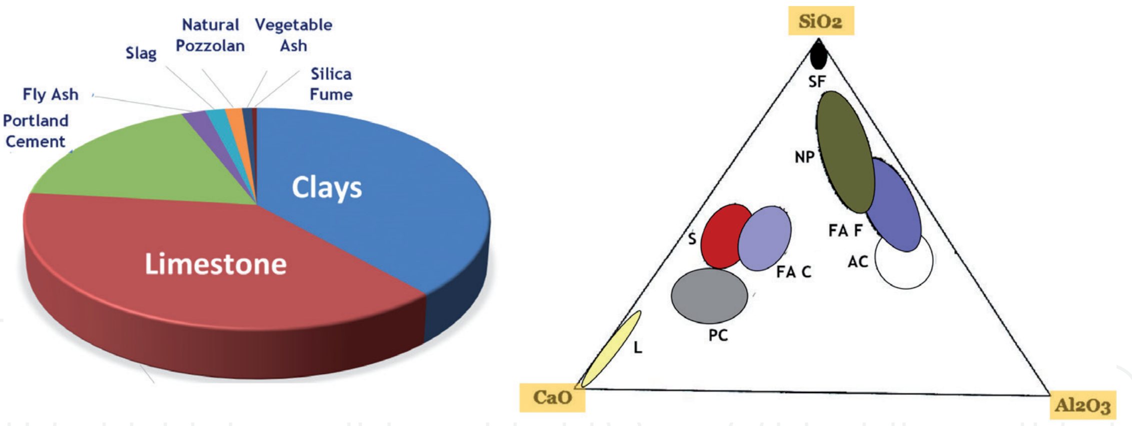

Figure 1.
Availability of MCSs worldwide. Their variability according to their composition.

globe is quite large, giving the SCM the greatest potential in the cement industry, even more so given the future drastic reduction in the supply of fly ash.

The need to activate clays thermally for an industrial scale manufacturing arises also because of its very high pozzolanic reactivity and the high quality that it implies. In addition, the cement producer has the control over production capacity and quality. Here it is necessary to clarify the difference of terms like "calcined clay" and " activated clay". The first term, which is the most frequently used in publications, also includes the calcined clays of the ceramic and brick industry, which have very low pozzolanic activity. The second term, "activated clay" (AC), which is a clay with a much higher pozzolanic activity, therefore it will be the term used instead of "calcined clay" from now on.

The new technology to produce AC implies an industrial development that will bring greater sustainability in the cement industry bringing not only due to the considerable reduction of CO_2 emission levels down to 70% compared to the Portland clinker manufacturing but also resulting in an important reduction in energy consumption.

2. Classification of pozzolanic additions by their chemical character

Classifying and cataloging pozzolans according to their origin or by their total oxide content that is, according to their chemical composition [1, 2], is insufficient and not at all significant for the characterization of their reactivity. Therefore, R. Talero proposed a very different classification based on the results and conclusions of his research carried out with or without other authors [3–15], which is based on its chemical character resulting from its corresponding reactive silica content, SiO_2^{r-}(%), and reactive alumina, $Al_2O_3^{r-}$(%) (Aluminum, Al, tetra- and/or penta-coordinated, which, in the case of the metakaolin is a metastable structure especially similar to the crystalline phase of the χ-alumina [16]). That is, under the same circumstances, capable of providing (depending on its amorphous or vitreous physical state and the average shape and size of its particles), every natural or artificial pozzolanic addition forming part of the cements and/or their derived products: concretes, mortars, pastes and prefabricated products.

Below are the chemical reactions (1)–(4) in which the hydraulic factors (reactive silica SiO_2^{r-}, and reactive alumina $Al_2O_3^{r-}$) of the pozzolans are involved when they react chemically with the portlandite in an aqueous medium at room temperature, much faster with the portlandite of the PC fraction mixed:

$$SiO_2^{r-} + CaO + H_2O = C?S?H + Q \quad (1)$$

$$Al_2O_3^{r-} + CaO + H_2O = C_3AH_6, C_4AH_{13}, C_4AH_{19} + Q \quad (2)$$

$$C_4AH_{13} + H_2O +_{gypsum} = AFm + Q \quad (3)$$

$$AFm + H_2O +_{gypsum} = AFt + Q \quad (4)$$

In this sense, it is very important to know the chemical character of pozzolans through the determination of the content of its hydraulic factors ((SiO_2^{r-}(%) and $Al_2O_3^{r-}$(%)).

Depending on its chemical character, pozzolans will have a very different influence on all the properties, performance and behavior of the PC base materials; starting from its fresh state to the recently hardened and the completely hardened: rheological behavior of its fresh pastes [3], to the heat of hydration [4–6], the mechanical-resistant performance [7] and durability against attack of sulfates [8–11] and chlorides [12–15] and other natural aggressive chemical attacks (sea water - aggregate-alkali reactivity and carbonation) in which the particle shape and average size can influence its nature like in the case of siliceous pozzolans and the silicic ones on its chemical character such as in silica fume and diatoms above all.

3. The clays. Its thermal activation and pozzolanic properties

The term "clay" refers to both a group of phyllosilicates and a granulometric division of the detritic rocks. This term also designates, in a not very precise way, a sediment or a rock constituted, in a great part, by minerals of the clay [17]. From a granulometric point of view, clay is any fraction smaller than 1/125 mm (≈ 4 μm) of a detritic rock, regardless of its composition. Although there is no precise size limit for clay minerals, most do not exceed 2 μm.

This crystalline structure is formed basically by two types of layers: tetrahedrons and octahedrons [18]. The tetrahedral layer has the group Si_2O_5 as basic unit, with

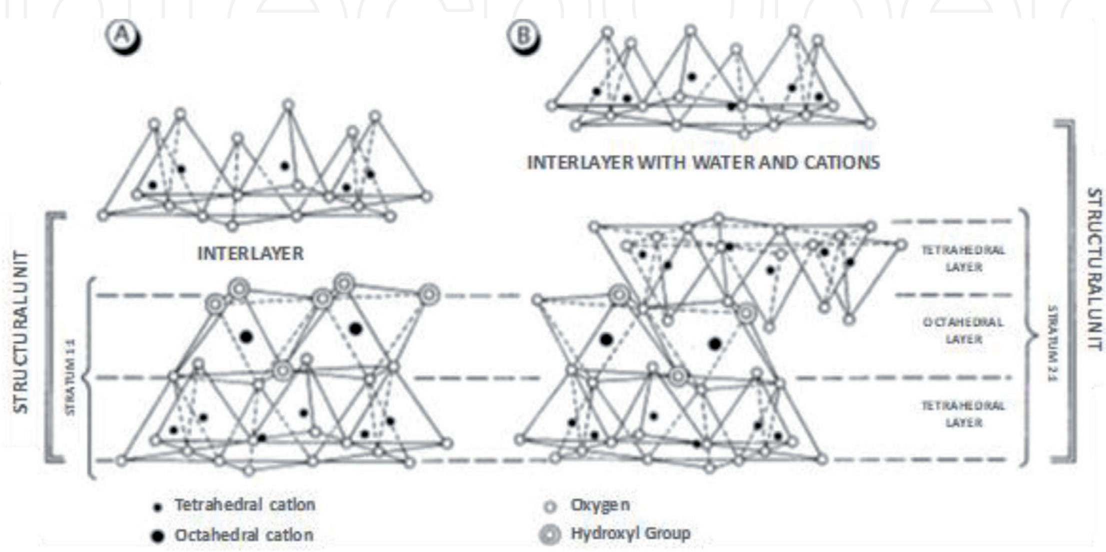

Figure 2.
Structure of the clay minerals. A) Type 1:1 stratum. B) Type 2:1 stratum [18].

the silicon in tetrahedral coordination and three oxygen of each tetrahedron shared with the adjacent ones forming a hexagonal structure (**Figure 2**). A part of the silicon atoms can be replaced by aluminum atoms and, occasionally, by Fe (III).

On the other hand, the octahedral layer has a cation, generally Al, Mg, Fe (II) or Fe (III), in octahedral coordination with oxygen or hydroxyl ions. The smallest tetrahedral structural unit of the octahedral layer consists of three octahedral and depending on the degree of occupation of the octahedral positions, the layers can be dioctahedral or trioctahedral. Dioctahedral minerals are those in which only two of the three octahedral of the structural unit have a cation in the center. When all the octahedral positions are taken, the minerals are called trioctahedral, and the cations occupying the octahedral positions are divalent (Mg, Fe (II)), while in the dioctahedral minerals the octahedral positions are occupied by trivalent cations (Al, Fe (III)).

The stacking of the layers and the substitutions of the ions determine different types of minerals in the clay. According to the layer stacking, they are divided in two big groups: those constituted by a tetrahedral layer and another octahedral layer, which share oxygen atoms (type 1:1) and those formed by two tetrahedral layers separated by an octahedral one (type 2:1).

Kaolinite, montmorillonite and illite clays, when undergoing adequate heating, can be activated as a result of a dihydroxylation process or loss of OH^- groups from their crystalline network, through the following chemical reaction:

$$-OH^- + -OH^- \xrightarrow{\uparrow Q} H_2O\uparrow + O^{2-} \qquad (5)$$

The optimal temperature for this purpose usually ranges from 600–800°C, depending on the clay mineral composition itself. In synthesis, the clay thermal decomposition begins at 120°C with the loss of humidity (hygroscopic, colloidal and hydration water physically adsorbed, or absorbed in the material pores). As the process temperature increases, the hydroxyl groups begin to separate from the crystalline network (dihydroxylation stage). The increase in the vibration energy reaches a thermal agitation value adequate to enable the union with a nearby proton and form a water molecule that goes to the atmosphere to finally separate from the crystalline structure leaving it in an amorphous state that is not vitreous like that of fly ashes. At temperatures above 920° C, the AC becomes very unstable making the formation of spinel, pseudo-mullite or pre-mullite and even mullite possible [19]. **Figure 3** shows the thermal behavior of the most common clays [19]. The temperature values here given correspond to kaolinitic clays.

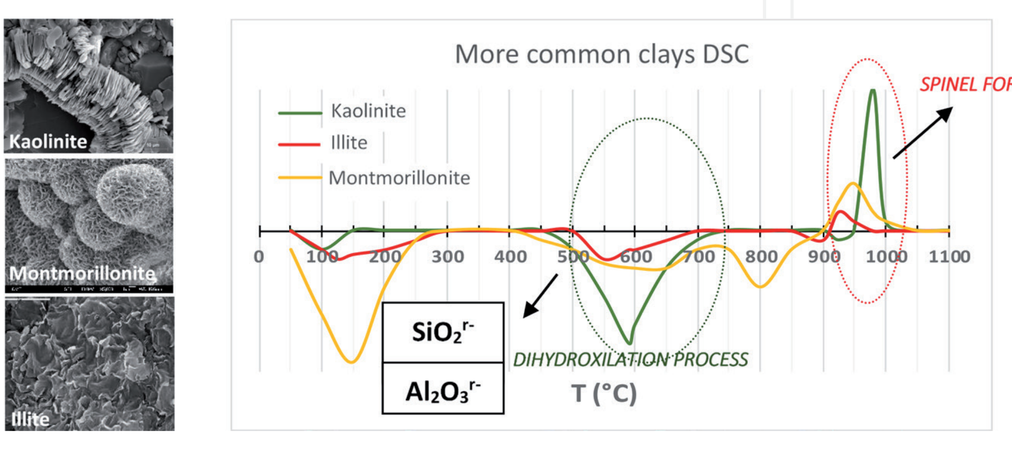

Figure 3.
Thermal behavior of the most common clays and its consequences for their resulting final pozzolanicity at each temperature.

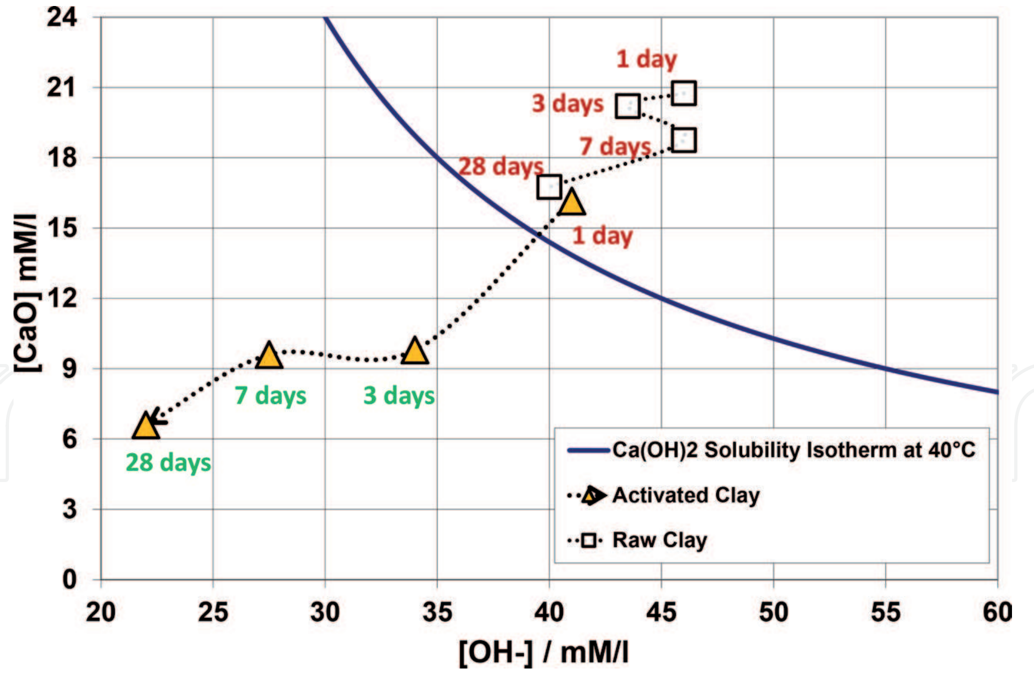

Figure 4.
Increased pozzolanic properties of clay after thermal activation. Frattini test [20]. Results. Ages: 1, 2, 7 and 28 days.

The thermal activation process of the clays produces an artificial pozzolan with an aluminic chemical character, according to R. Talero [3–15]. The chemically combined water of the clay released to the atmosphere acts on the coordination index of Al_2O_3 which was 6 [19]. After this thermal process, in optimum conditions (in coordination 4 or 5 [16]) it reacts chemically and very quickly with the portlandite of the liquid phase of the PC from the very first ages of its hydration. The physical state is amorphous and not vitreous like that of fly ash. On the other hand, the pozzolanic reaction of the latter, in the same circumstances and on an equal footing with everything else, is necessarily much slower.

Therefore, although kaolinitic clays have a higher content of Al_2O_3, a priori, it should not be a restriction as to which clay to use to produce an artificial pozzolan through thermal activation. Although finally and in any case, the suitability must be evaluated according to the content of SiO_2^{r-} (%) and $Al_2O_3^{r-}$ (%) in each mixture of clays that is possible to generate during its thermal activation process.

Figure 4 shows the pozzolanic activity of a kaolinitic clay, determined by the EN 196–5 standard [20] before and after its optimal thermal activation.

4. Pyro process technology

First, the clay must go through the drying, activation, and cooling processes. If the clay to be activated has a high content of iron (greater than 4%), it is important to ensure the change of color of the clay to gray during the thermal activation process to generate pozzolanic characteristics and thus promote its mixing with the PC.

The main parameters to obtain thermally AC and to guarantee its color change are the precise control of the adequate calcination temperature and the concentration of oxygen in the gases in the drying, activation, and cooling equipment.

The technology used for the combustion system of the drying and thermal activation processes allows operation with solid fuel, ensuring the stability of the flame even in a process with lower temperatures (less than 900°C).

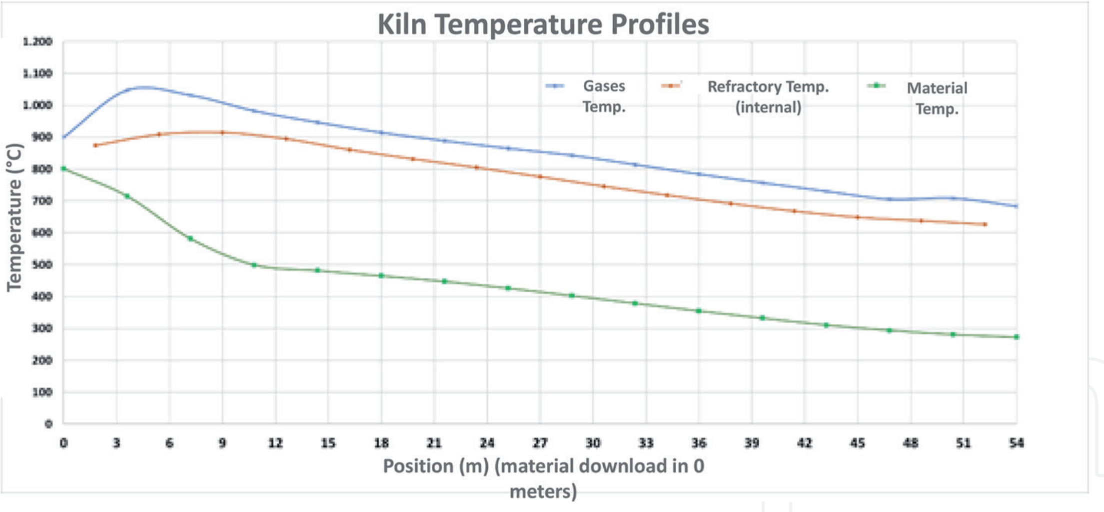

Figure 5.
T-profiles of gases, material bed and refractory.

The drying and thermal activation of the clays can be carried out by means of rotary kilns or with "flash technology". In the case of the use of rotary kilns, it is possible to reuse existing kilns in cement factories that are already out of service to adapt them, in any case, to their new condition of adequate heating of the clays for their activation.

Figure 5 shows the temperature profiles of the gases, the material bed and the refractory lining of a mathematical model developed for the simulation of rotary kilns for the thermal activation of clays. In this case, the material fed into the kiln has already been dried at ≈ 250°C.

The flash technology is based on the dragging of small solid particles by a concurrent flow of hot gases to obtain high coefficients of heat and mass transfer in a more compact equipment. This technology can be used for the drying or activation process. In the case of applying a flash calciner, the process must be staged in several stages in a cyclone tower to ensure the proper residence time of the material in the temperature range of 750 to 850°C or "transit time", necessary for the activation to take place.

The experience in rotary kilns at an industrial level is extensive in Brazil with kilns of up to 1,100 Tm/day. And at the present time in Colombia with a kiln with a capacity of 1,500 Tm/day. Its operation is relatively simple and easy to understand by control room operators. Its operation control, in terms of adjusting the activation temperatures according to the quality control variables hour by hour, is relatively easy to handle, even though the short activation range in terms of temperature makes this control very demanding in order to obtain an AC of high pozzolanic activity. Therefore, it is important to say that the experience of thermal activation of clays with rotary kilns has already been several decades and there is not, nowadays, an industrial activation in "flash calciner" of such an important industrial size.

Finally, after having achieved the thermal activation of the clayey material, it is necessary to cool it. In this last stage and in the case of clays with a high Fe_2O_3 (%) content, it is also important to control the atmosphere to avoid that the material at high temperatures comes into contact with high air flows and thus avoid that the gray color obtained in the previous heating stages is maintained and not lost by the oxidation of the new thermally activated material. A technology that is perfectly suited to these two objectives (cooling the material and maintaining its gray color) is the rotary cooler.

5. Process control and verification variables

One of the aspects that takes on an extraordinary importance in the process of thermal activation of clays, is how to assure the quality of these after having them thermally activated because there is still no analytical method or mechanical test that determines the pozzolanic activity in a direct and immediate way as soon as the AC has left the rotary kiln or the flash Calciner.

Therefore, the clay thermal activation must be determined in an indirect way to guarantee the highest possible content of $Al_2O_3^{r-}$ (%) [21] and SiO_2^{r-} (%) [22] after the process of thermal activation of the kiln by quick kiln adjustments in case it will be necessary. This will undoubtedly translate into a higher pozzolanic activity of the same [20], as mentioned above.

During this stage, and for the same reason, it is highly recommended to determine parameters such as Loss of Ignition (LOI), content of Kaolinite (%) before and after this calcination process and also its Pozzolanic Activity Index (PAI) after the calcination process. All these analyses must be correlated previously.

On this previous stage it is so important to determine the hydraulic factor contents of $Al_2O_3^{r-}$ (%) [21] and SiO_2^{r-} (%) [22] on the AC, in order to find the optimum temperature of every different clay available in the quarry.

In that sense, the activation temperature at which the highest contents of $Al_2O_3^{r-}$ (%) [21] are obtained in the AC, will be the optimum temperature. Therefore, in this way it will also be possible to determine the upper and lower activation ranges, which indicate whether this optimal thermal activation temperature is exceeded to a certain extent, in such case, a recrystallization of the *amorphous* structure of the AC obtained will be produced, losing its activation level and, therefore, pozzolanic activity. And if, on the contrary, the temperature is very low, the needed dihydroxylation will not be achieved and its pozzolanic activity will be also very poor because it still has remains of raw clay without thermal activation. Either from kaolinite and/or from illite and/or from montmorillonite or from a random mixture of all three or only two of them. This will undoubtedly result in a lower degree of replacement of Portland clinker in the cement to be designed, dosed and finally produced.

With all this information obtained through the analysis and verification tests that must necessarily be carried out at laboratory level, it is possible to clearly identify and determine the ranges in which these variables move according to the highest pozzolanic activity to be reached, since the mentioned analysis and tests must also be used in the quality control of AC at an industrial scale in the cement factory.

6. Inter-grinding

The most common operation in the cement factories is the inter grinding in a single mill, of the Portland clinker, its setting regulator (natural gypsum stone) and the active and/or non-active mineral additions incorporated in each case, where the reduction in particle size occurs. For this reason, it is especially important to know the hardness indexes of the different materials to be grinded, their humidity, their proportions and granulometric feeding, in order to, with this information, design the load of grinding balls that each grinding chamber must carry, also according to the typology and physical quality of the cement to be produced.

The AC has a very high fineness. It could be said that 85% of its mass passes through the 1 mm mesh sieve, although, this value will depend on the type of clay, its mineralogical composition, and its quartz content. As an example, we can mention that the Bond hardness index for limestone can vary from 10 to 13 Kwh/Tm, for an AC from 13 to 15 Kwh/Tm and for Portland clinker from 16 to 18 Kwh/Tm. The ranges may vary depending on the mineralogical composition, quartz content, origin, etc.

In some cases, the quartz content in the raw clayey material fed to the kiln can vary from 25 to 50%. This factor must be considered, therefore, in an inter-grinding. The AC has an intermediate hardness, although it is closer to that of limestone, having a very fine granulometric feeding so that it will be much easier to grind than limestone, leaving the first chamber of the mill quite empty. To obtain a performance of the same order of magnitude that the traditional cements, with security it will be possible to work with the specifications of a greater retained in the sieve N. ° 325, although its Blaine fineness will be also greater. As an example, for a "General Use", with a performance of ≈ 26 MPa at 28 days, it will be possible to work with a retention in screen No. 325 between 4 to 7% and a Blaine fineness between 4500 to 5500 cm^2/g.

In addition, quartz, although hard to grind, does not usually present a large size so that in this type of grinding it can play the role of "grinding admixture", also producing a cleaning effect of the balls and the lining of the mill, helping the grinding, thus being able to reduce or avoid the chemical admixture that improves the grinding itself. On the other hand, and due to the very low granulometry of the AC, the possibility of feeding it directly into the separator can also be studied. The physical aspects dealt with here make sense for replacement levels above 12%, but, however, with a low feed, its changes will not be much noticed. And as far as pozzolanic activity is concerned, this will become important with replacement levels above 8% depending on its $Al_2O_3^{r-}$ (%) content.

As for the dosage of the cements with this pozzolan, the optimal relationship between all the components, Portland clinker, AC, other SCMs and gypsum, will depend on multiple factors. Therefore, each dosage must be studied and analyzed separately and exclusively, depending on the following premises or conditions: the mineralogical composition of Portland clinker, the reactivity of the AC produced (its contents of $Al_2O_3^{r-}$ (%) and SiO_2^{r-} (%)) and the optimum content of SO_3, among others.

As an example, **Figure 6** shows the mechanical performances [23] obtained with two different types of PCs, with the same dosage of clinker, AC and limestone filler, and with the same grinding fineness, respectively. In this trial, two AC with different content of $Al_2O_3^{r-}$ (%) and different proportion of gypsum added as setting regulator were used.

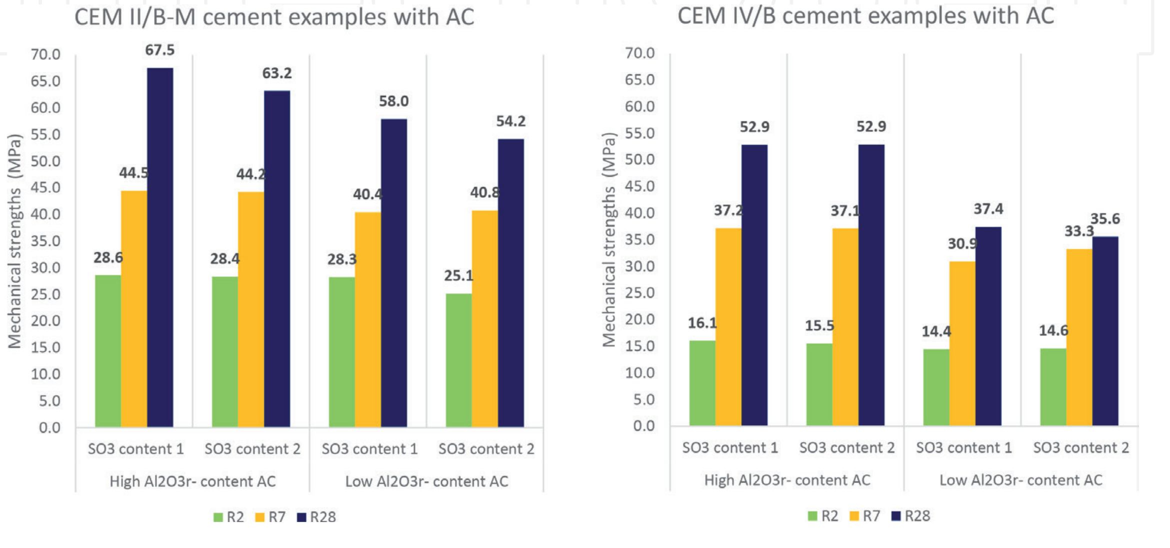

Figure 6.
Performance obtained in the dosage of different cements according to the European normativity [23].

Finally, it is also important to consider the very low granulometry of AC and its rheological behavior when it is so dry, in the transport systems, hoppers and dispensers because avalanches may occur in the hoppers and the control in the dosage may become somewhat difficult.

7. Separate grinding and blending stations

Without a doubt the best grinding option to manufacture cements with several SCMs is separate grinding. From the point of view of particle grinding, the ideal is to grind materials of similar hardness because this ensures a more controlled and efficient grinding. In a inter grinding, the grinding is conducted by the harder material and this will define the retained in the sieve No. 325 and the Blaine fineness, therefore, the softer materials will be "over grinded" and these will affect the final particle size distribution of the product. Logically, the viability of this system will depend on the availability of equipment: two mills and their production capacities.

Separate grinding offers significant savings by eliminating the time required to prepare different products when changing from one product to another. These preparation times represent economical losses and inefficiencies when having to wait for the quality conditions of the new product in the mill to be able to make the changeover to the corresponding silo. An example of this is when changing from a product with a low clinker/cement factor to one with a higher clinker/cement factor. This cement with a higher production cost is "lost" when having to go to the silo with a lower specification.

On the other hand, separate grinding allows to gain in flexibility and grinding efficiencies by specializing the mills in a base product and not a type of cement. The different types of cement will be produced in the Blending Stations. The Control Room operator will be able to specialize his mill in a single "base product" and achieve better efficiencies, stability, and productivity in the grinding process by not having to make product changes and only adjusting improve production and quality.

Another great advantage in specializing the mills is that the room operators will not have to change mill settings and their operation will be easier to perform and carry out.

Separate grinding allows you to have two "intermediate products": the first one, a "base cement" and the second one, a "mix" containing the easiest materials to be ground. The base cement can be formed by the Portland clinker and setting regulator only and/or by some additional SCM, depending on the types of cement to be produced. The mix will be formed, instead, by the AC, the rest of the SCMs and the adequate amount of setting regulator according to its composition. The mixing percentages of each of the intermediate products will depend on the quality of their components and the qualities or types of cement to be produced.

The separate grinding of the mix allows a better control in terms of the Blaine fineness and the desired retained, being in this case of the AC, materials easier to grind than Portland clinker. Depending on the materials to be ground in this mix, a "coarser" grinding can be sought in terms of the retained in sieve No. 325, which could well be in a range between 10 to 15% and the Blaine fineness would be a resultant. This physical aspect will have great importance in the final fineness and in the conformation of the pore system in the final structure of the produced cement paste which will be, with all certainty, more compact than the one reached in the inter grinding. This will undoubtedly also result in greater mechanical resistance and durability of the cements to be produced in separate grinding with blending stations.

Finally, and as we have seen, separate grinding requires the assembly of blending stations, which are simple in their operation and design but at the same time, very demanding in terms of the Dosing systems to be used, therefore that is where the success of the latter lies. A blending station is equivalent to having a new high capacity and very high efficiency mill. Moreover, it does not need preparation times and only needs to introduce the corresponding mixture of the two intermediate products mentioned: the “base cement” and the “mix”. The gain in terms of operation flexibility, dispatch logistics and customer service are unquestionable. For this technology it is essential to have a high-quality dosing and mixing equipment. Its capacity design will be determined by the dispatch and storage conditions.

8. Conclusions and outlook

- Certainly, AC is just beginning to establish itself as the SCM of greater potential than fly ash and any other natural or artificial pozzolans. They are siliceous and aluminous artificial pozzolans in nature, according to the ASTM C618–19 standard [1], and *aluminous* in chemical character, according to R. Talero [3–15], from high to very high quality, according to their reactive chemical composition (SiO_2^{r-} (%) and $Al_2O_3^{r-}$ (%) contents above all and very specially controllable in their manufacture and sustainability with the environment, reducing CO_2 emissions to a 75% in their production, compared with Portland clinker.

- The clays that can be activated are not only kaolinitic but also illitic and montmorillonite (smectitic) clays. But, in any case, their viability of use depends fundamentally, as it has just been said, on the content of SiO_2^{r-} (%) and $Al_2O_3^{r-}$ (%) above all and very specially, that we are able to generate during the process of their thermal activation on an industrial scale.

- The process control of its thermal activation, in terms of maintaining the optimum temperature of calcination in the kiln, is fundamental, since it will guarantee the highest pozzolanic activity of the AC. Therefore, it is of vital importance to permanently control the process variables and the quality parameters of the recently manufactured AC in order to correlate them with the chemical and mechanical parameters of verification of best quality and with the performance variables.

- The separate grinding and blending station are the best option for grinding in terms of quality, particle size distribution, milling efficiency and economic cost.

- The use of activates clays such as SCM to reduce the clinker content in cements is one of the most innovative initiatives that is currently being implemented in the cement sector to achieve the objectives of the European Green Deal to make Europe the first continent climate neutral in 2050. This is a very ambitious goal, but reachable. Through this technology, important emission reductions that will allow the cement and concrete value chain be climate neutral by 2050. This will allow our society to have a sustainable building material.

Author details

Carlos Hernando Aramburo Varela[1], Luiz Felipe de Pinho[2],
César Pedrajas Nieto-Márquez[3]* and Rafael Talero Morales[4]

1 Carlos Aramburo Consultant, Cali, Colombia

2 Dynamis, Sao Paulo, Brazil

3 Cementos Argos, Medellín, Colombia

4 SACACH S.L, Madrid, Spain

*Address all correspondence to: cpedrajas@argos.com.co

References

[1] ASTM C 618-19 Standard. "Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete". ANNUAL BOOK OF ASTM STANDARDS, Section 4 Construction, Vol. 04.02 Concrete and Aggregates.

[2] UNE EN 197-1:2011 Standard. "Cement -Part1: Composition, specifications and conformity criteria for common cements". AENOR. Spain.

[3] Aramburo, C., Pedrajas, C., Rahhal, V., González, M., Talero, R.: "Calcined clays for low carbon cement: Rheological behavior in fresh Portland cement pastes". Materials Letters 239, pp. 24-28, 2019.

[4] Talero R, Rahhal V "Influence of aluminic pozzolans, quartz and gypsum additions on Portland cement hydration". 12th Intern. Congress on the Chemistry of Cement, Proceedings, Montreal, Canada, 8-13 july 2007.

[5] Rahhal V, Talero R. "Calorimetry of Portland Cement with Metakaolins, Quartz and Gypsum Additions". J Therm Anal Cal, 91 (3). p. 825-834, 2008.

[6] Talero, R., Rahhal, V.: "Calorimetric comparison of Portland cement containing silica fume and metakaolin: Is silica fume, like metakaolin, characterized by pozzolanic activity that is more specific than generic?". J. Therm. Anal. Cal., 96 (2), pp. 383-93, 2009.

[7] Talero R, Bollati M.R., Hernández-Olivares F. "Manufacturing non-traditional mortars and concretes by OPC, metacaolin and gypsum (15,05%)". Mater Construcc, 49 (256). p. 29-41, 1999.

[8] Talero, R.: "Performance of metakaolin and Portland cements in ettringite formation as determined by Le Chatelier-Ansttet test: Kinetic and morphological differences and new specification". Sil. Ind. 72 (11-12), pp.191– 204, 2007.

[9] Talero R. "Expansive synergic effect of ettringite from pozzolan (metacaolin) and from OPC, co-precipitating in a common plaster-bearing solution, Part II: Fundamentals, explanation and justification". Constr Build Mater. 25, p. 1139-1158, 2011.

[10] Talero, R.: "Gypsum attack: performance of silicic pozzolans and Portland cements as determined by ASTM C 452-68". Adv.in Cem. Res. 24 (1), pp. 1-15, 2012.

[11] Arámburo C, Pedrajas C, Talero R. "Portland cements with high contents of calcined clay. Mechanical strength and sulfatic attack behaviors". Materials 2020, 13, 4206, 2020.

[12] Lannegrand R., Ramos G., Talero R. "Condition of knowledge about the Friedel's salt". Mater Construcc 51 (262), abr./may. / jun. 2001.

[13] Jones M.R., Macphee D.E., Chudek J.A., Hunter G., Lannegrand R., Talero R., Scrimeneour, S. N. "Studies using 27Al MAS RMN of AFm and AFt phases and the formation of Friedel's salt". Cem Concr Res, 33, p. 177-182 (2003).

[14] Mejía R, Delvasto S, Talero R. "Chloride diffusion measured by a modified permeability test in normal and blended cements". Adv Cem Res, Vol. 15, n°3, p. 113-118 (2003).

[15] Talero R. "Synergic effect of Friedel's salt from pozzolan and from OPC co-precipitating in a chloride solution". Constr Build Mater, 33, p. 164-180 (2012).

[16] Trusilewicz L, Fernández-Martínez F, Rahhal V,

Talero R. "TEM and SAED Characterization of Metacaolin, Pozzolanic Activity". J Amer Ceram Soc, 95 (9), p. 2989-2996, 2012.

[17] Álvarez-Pérez A, Prada-Pérez JL. "Atlas de asociaciones minerales en lámina delgada". Vol. I Caps. 12 y 29: ASOCIACIONES MINERALES EN PROCESOS CERÁMICOS". Fundación Folch. Univ. de Barcelona – España. First Edition: UB 1997.

[18] Grim R.F. "Clay Mineralogy". Mc Graw-Hill, Nueva Tork, pp. 596, 1968.

[19] Grimshaw R.W. "The Chemistry and Physics of Clays and Allied Ceramic Materials", 4th Edition Revised, Ernes Benn Limited, London. 1971.

[20] UNE-EN 196-5:2006 Standard. "Methods of testing cement. Pozzolanicity test for pozzolanic cements". AENOR.

[21] UNE 80-225:2012 Standard: "Métodos de Ensayo de Cementos. Análisis Químico: Determinación del Dioxido de Silicio (SiO_2) Reactivo en los Cementos, en las Puzolanas y en las Cenizas Volantes" AENOR.

[22] Talero, R. New method of wet chemical analysis to determine reactive alumina content in natural and artificial pozzolans. Priv. Communed. 2014.

[23] Norma UNE-EN 196-2: 2014. "Método de ensayo de cementos. Parte 2. Análisis químico de cementos". AENOR.