

## Article

# DECREASE OF CARBONATION, SULFATE AND CHLORIDE INGRESS DUE TO THE SUBSTITUTION OF CEMENT BY 10% OF NON CALCINED BENTONITE

Carmen Andrade <sup>1</sup>, Ana Martínez-Serrano <sup>2</sup>, Miguel Ángel Sanjuán <sup>3</sup> and Jose A. Tenorio <sup>2</sup>

<sup>1</sup> International Center of Numerical Methods in Engineering (CIMNE)- UPC-Spain

<sup>2</sup> Institute of Construction Sciences "Eduardo Torroja"-CSIC – Spain

<sup>3</sup> Institute of Cement and its Applications (IECA)- Spain

\* Correspondence: tenorio@ietcc.csic.es

**Abstract:** Clinker production is being reduced worldwide in response to the need to drastically lower greenhouse gas emissions. The trend began in the nineteen seventies with the advent of mineral additions to replace clinker. Blast furnace slag and fly ash, industrial by-products that were being stockpiled in waste heaps at the time, have not commonly been included in cements. Supply of these additions is no longer guaranteed, however, due to restrained activity in the source industries for the same reasons as in clinker production. The search is consequently on for other additions that may lower pollutant gas emissions without altering cement performance. In this research bentonite, a very common clay, was used as such an addition directly, with no need for pre-calcination, an still novel approach that has gone little explored to date for reinforced concrete with structural applications. The results of the mechanical strength and chemical resistance (to sulfates, carbonation and chlorides) tests conducted are promising. The carbonation findings proved to be of particular interest, for that is the area where cement with mineral additions tend to be least effective. In the bentonite-bearing material analysed here, however, carbonation resistance was found to be low as or lower than observed in plain Portland cement.

**Keywords:** cement; bentonite; durability; clays

## 1. Introduction

The inordinate rise in the presence of greenhouse gases in the atmosphere is creating a pressing need to lower CO<sub>2</sub> emissions by, among others, reducing the proportion of clinker in cement [1-3]. In the past, clinker content has been replaced with industrial waste such as fly ash, slag or silica fume with no adverse effect on concrete mechanical performance or durability [4]. With abatement of the likewise carbon-intensive source industries, however, the availability of those substitute mineral additions is beginning to wane. Hence the imperative to seek replacements for clinker in nature to broaden the spectrum of alternative materials. The study described hereunder explored the use of non-pre-treated bentonite, a widely available clay, as one such alternative.

As an anionic clay present in nature, bentonite can be obtained at low cost. It is also highly water-absorbent and thixotropic (gel-like when vibrated). It was first discovered in 1988 in the United States and more specifically at Fort Benton, Wyoming [5], after which it is named. Its composition consists primarily in magnesium silicate, montmorillonite and aluminium hydrate, the third in the form of colloid-sized crystallites. Each individual montmorillonite crystal, in turn, comprises an octahedral layer of aluminium sandwiched between two tetrahedral layers of silicon. It carries a negative charge associated with isomorphic substitutions, such as Al<sup>3+</sup> for Mg<sup>2+</sup>, in the crystallite network, which is offset by exchangeable alkaline metal cations [5].

Clay use as a mineral addition in cement is nothing new, for it dates from many years ago, although subject to pre-calcination [6]. A number of studies [7-9] have recently reported promising results around its application to replace more conventionally used additions such as fly ash or slag. Few studies on its non-pre-calcined use have been found in the literature [10-20]. Its use in foundations and for stabilizing the soil [21-23] however is much more common, although for that approach has consistently posed rheological problems. For this last reason, many building codes limit the presence of clay materials in aggregates. Nonetheless, today's admixtures afford fresh concrete properties impossible to attain in the past and modern laboratory techniques now in place can substantially shorten the time needed to design an optimal mix [24-27].

Eluding the extra cost and additional handling involved in calcining clays at temperatures of up to 1000 °C, would carry obvious advantages. The present study consequently aims to explore the physical-mechanical properties and durability of concrete prepared with non-calcined clay as a substitute for clinker at different (wt/wt) replacement ratios.

A review of the literature on the long-term performance of bentonite showed that it has exhibited excellent durability in underground works, where it has been used profusely as permanent formwork in concrete foundations often built long ago [21-23]. And whilst bentonite plays a non-calculated load-bearing role in such cases, none of the studies published report any long-term incompatibility between the two materials. It is likewise used in conjunction with concrete to generate impermeable slurry walls in highly radioactive waste storage facilities (designed to last for thousands of years) [28-30], where the caverns holding the radioactive waste are shotcreted and the encapsulated waste itself lies on a bed of bentonite. The use of such systems has given rise to research on how the alkaline nature of concrete may affect the long-term stability of bentonite clays. Such studies have verified the interaction between cement alkalinity and bentonite phases [28-31] or equivalently, phase reactivity with clinker hydrated phases, with initially promising results from the standpoint of their role as a clinker replacement because of the slow reactivity. This reactivity is due to the high alkalinity of the pore solution which solubilize the silico-aluminates of the bentonite. In terms of radioactive waste such reactivity would be detrimental, however, if it affected the stability of the shotcrete/bentonite interface, given the many thousands of years they are intended to be in contact.

Standardised active additions such as fly ash, natural pozzolans, slag and silica fume, in turn, are known to effectively inhibit chloride and sulfate ingress [32-33], enhancing durability, although their presence in concrete impacts carbonation resistance adversely [7,10,36]. That is significant, for any decline in carbonate resistance is a primary long-term concern because it favours reinforcement corrosion [34-38] and the associated economic loss. The importance of seeking additions that either favour or at least are not detrimental to concrete durability cannot therefore be overstated.

This study constitutes preliminary research on how replacing up to 30 % clinker with non-pre-calcined bentonite may affect mortar mechanical properties and how carbonation depth and chloride and sulfate diffusion may be impacted by the presence of 10 % of the clay with different types of binders already containing mineral additions. The findings are highly promising, particularly as regards carbonation, the weak point observed in other mineral additions. In the tests conducted, carbonation resistance either remained essentially unchanged or improved in the substituted relative to the reference mortar. Plain Portland cement or cement bearing standardised additions was used throughout.

## 2. Materials and Methods

### 2.1. Materials

All the cements listed in Table 1 were used in the carbonation tests, whereas cement CEM I 42,5 R-SR 3 served as the basis for the mechanical strength and sulfate and chloride diffusion trials.

A commercial bentonite (Mapeproof Seal), distributed by Mapei for purposes other than studied here, was used to ensure consistent composition and particle size distribution throughout. According to the vendor’s specifications sheet, the material contained over 95 wt% montmorillonite.

The particle size distribution and volume density curves for the bentonite powder used are graphed in Figure 1. Ninety per cent of the particles were <86 µm, whilst most lay within the 10 µm to 15 µm range (see the volume density curve). Such greater fineness than observed for the cement was initially deemed suitable, although optimisable. Addition fineness plays a significant role in the strength and rheology of composite cements, for the distribution curves for those materials complement the curve for the cement itself. This parameter must consequently be analysed in depth, in the future [39].

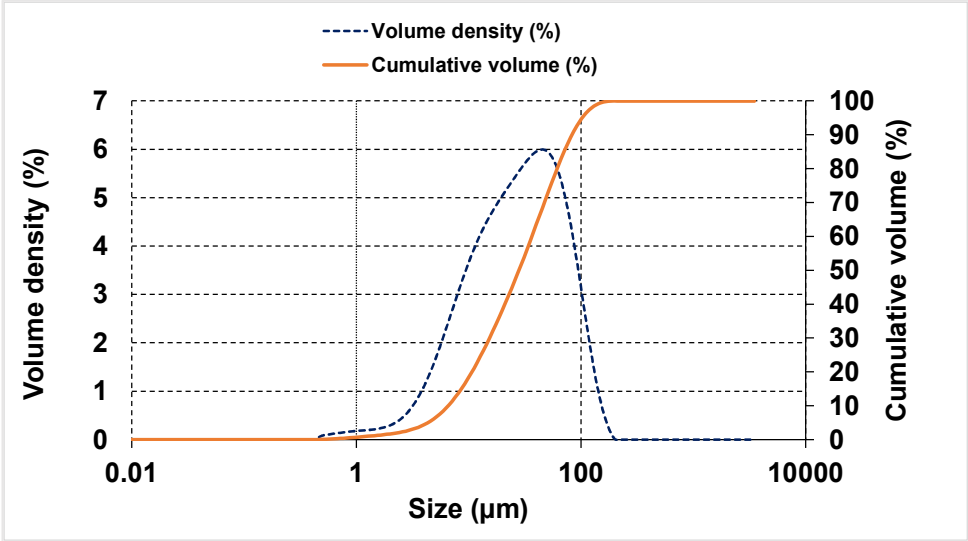


Figure 1. Particle size distribution and volume density plots for bentonite.

Another factor of particular interest in bentonite materials is water demand, affected not only by fineness but also by its sodium content [4]. This property was not a variable in present study.

Table 1. Chemical composition of the cements used in the tests.

Cement	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	LOI	IR	Cl-
CEM I/ 42.5 R	20.24	3.99	2.92	62.88	1.41	3.47	0.08	0.86	2.78	0.10	0.02
CEM I 52.5R – SR 3	21.73	3.67	4.31	66.12	1.32	3.00	0.49	0.57	1.12	0.19	0.01
CEM II/A-P 42.5 R	29.09	5.29	2.98	51.60	1.78	2.82	0.39	0.53	2.94	--	0.06
CEM II/ A-P 42.5 R	28.17	6.20	3.13	52.41	1.32	3.11	0.38	0.67	2.34	--	0.05
CEM II/A-S 42.5 N	23.24	5.74	2.46	61.82	2.29	2.83	0.46	0.59	--	--	0.05
CEM II/ A- V 42.5 R	23.00	6.30	3.50	58.00	1.42	3.22	0.49	0.80	2.30	2.10	0.06
CEM III/A 42.5 N	24.55	6.42	2.14	57.14	3.00	2.80	0.40	0.50	0.91	0.21	0.05

CEM IV/A (V) 42.5 R-SR	27.14	5.25	3.20	53.10	1.58	2.82	0.37	0.49	2.70	---	0.06
IV/A(P) 42.5 R/MR	28.36	4.72	3.17	52.81	2.16	2.59	0.33	0.51	2.43	---	0.04
BL II/B-LL 42.5 R	18.70	3.83	2.64	61.70	1.29	2.97	0.06	0.81	10.86	0.33	0.02

## 2.2. Specimen types

Different types of specimens were prepared. depending on the test.

- For mechanical strength and carbonation resistance testing 10x10x60 mm cement paste specimens bearing 10 %, 20 % or 30 % bentonite additions were prepared at a water/cement ratio of 0.5. They were cured in a climatic chamber at 90 % relative humidity. first in the moulds for 24 h and after removal for 28 d prior to testing.
- For chloride diffusions the 70 cubic mm cement mortar specimens used were prepared with a water/cement ratio of 0.5. They were cured in a climatic chamber at 90 % relative humidity. first in the moulds for 24 h and after removal for 28 d prior to application of an electric current to test for chloride diffusion.

## 2.3. Test methods

### 2.3.1. X-ray diffraction

Cement paste mineralogical composition [40] was determined on a Bruker AXS DB Advance X-ray diffractor configured without a monochromator, fitted with a 3 kW (Cu K $\alpha$ 1.2) copper anode X-ray source and a wolfram cathode. A 30 mA current was applied to the X-ray tube at a voltage of 40 kV. A 0.5 mm fixed divergence slit was used. The instrument was also fitted with a 2.5 rad primary Soller slit and a Lynx-eye X-ray super-speed detector with a 3 mm anti-scatter slit, a 2.50 rad secondary Soller slit and a 0.5 % Ni-K beta filter.

### 2.3.2. Twenty-eight day flexural and compressive strength

Testing for flexural strength [42] consisted in bending the prismatic specimens by applying a force perpendicular to their longitudinal axis. on a Netsch test frame specifically designed for small specimens.

The test was deemed valid only when the specimen failed across the middle.

The two halves of the specimens resulting from the flexural test were subsequently used for compression testing.

Compressive strength was found by exposing the specimens to two axial forces with equal modulus and orientation but coursing in opposite and convergent directions. on an Ibertest Autotest 200/10-SW test frame [40].

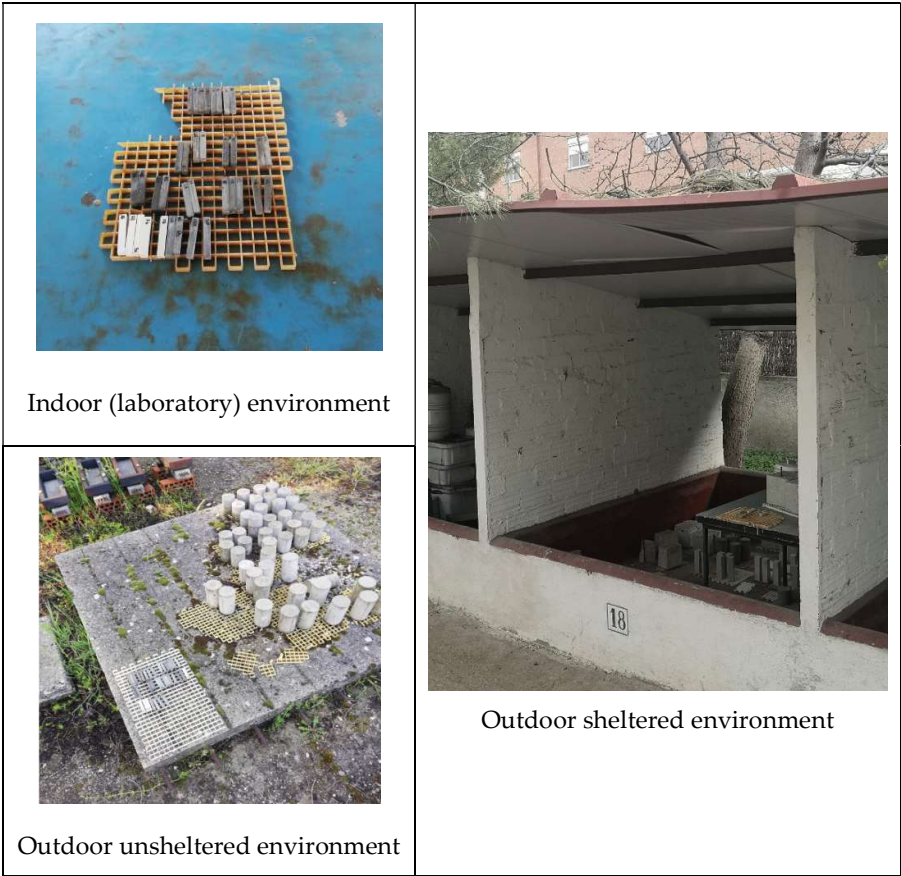
### 2.3.3. Carbonation in natural environments

The 10x10x60 mm specimens were exposed to natural carbonation at the atmospheric CO<sub>2</sub> pressure prevailing in the city of Madrid, in an indoor laboratory environment and two outdoor environments, one sheltered and the other unsheltered from rainfall. i.e.. environments with varying relative humidity and temperatures (Figure 2). The cements tested and their chemical compositions are given in Table 1.

Carbonation depth as found with phenolphthalein, an acid-base indicator. was recorded for the 3 month and 6 month specimens. depicted in the three environments in Figure 2.

**Table 2.** Composition (%) of the cements used in the tests.

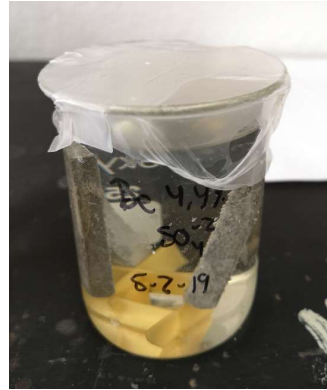
Cement	K	V	L/LL	S	P	Additional component
CEM I/ 42.5 R	95					5
CEM I 52.5R – SR 3	95					5
CEM II/A-P 42.5 R	83				11	6
CEM II/ A-P 42.5 R	80				16	4
CEM II/A-S 42.5 N	83			12		5
CEM II/ A- V 42.5 R	80		15			5
CEM III/A 42.5 N	59			39		2
CEM IV/A (V) 42.5 R-SR	74	23				3
IV/A(P) 42.5 R/MR	87				13	0
BL II/B-LL 42.5 R	74		26			0



**Figure 2.** Exposure to natural carbonation: environments.

#### 2.3.4. Sulfate resistance. Koch – Steinegger method

Cement paste resistance to sulfate ions was tested on 10x10x60 cm specimens further to the Koch-Steinegger method, based on comparing flexural strength in such specimens soaked for 56 d in an aggressive solution (here sodium sulfate at a concentration of 4.4 g/L) to the strength of analogous specimens soaked in water, likewise for 56d (Figure 3). All the specimens had been cured in a humidity chamber for 28 d prior to testing.

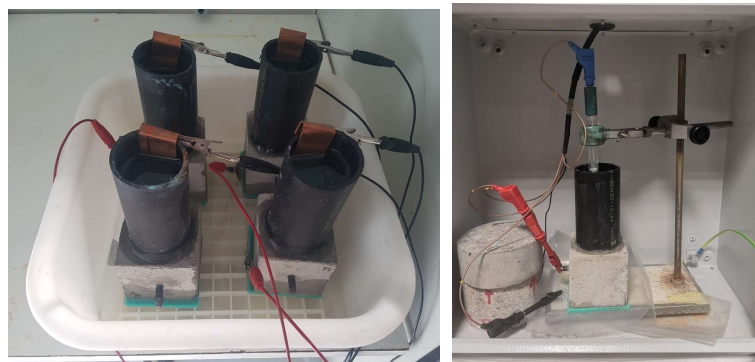


**Figure 3.** Koch- Steinegger exposure to sulfate attack.

#### 2.3.5. Accelerated chloride ingress

The accelerated chloride diffusion test described in Spanish standard UNE 83992-2 EX [36] was conducted on steel bars embedded in 70 cubic mm mortar specimens with 10 % bentonite substitution, comparing their performance to that of reference CEM I 42.5SR specimens of the same dimensions.

The test consisted in connecting specimens made with different types of mortar to an electrical current that accelerated diffusion (migration) across the matrix. Corrosion potential and corrosion rate were monitored in the specimens until corrosion was electrochemically detected in the embedded reinforcement bars (see setup in Figure 4).



**Figure 4.** Accelerated corrosion test setup.

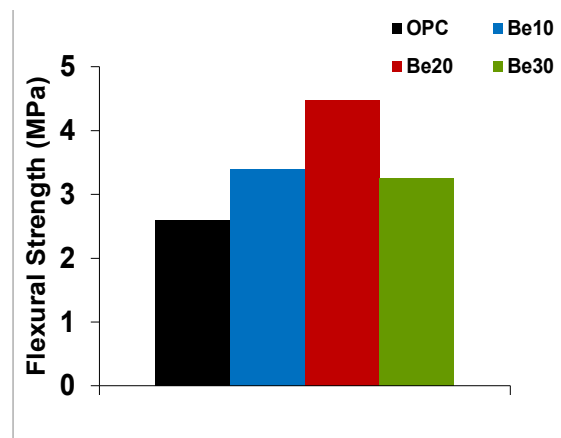
### 3. Results

#### 3.1. Flexural and compressive strength

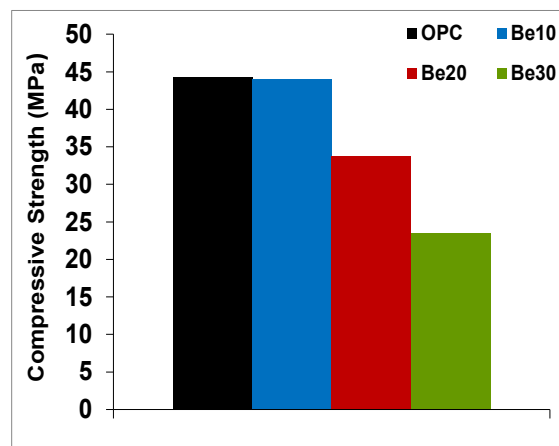
Additions should not alter, except to improve, mix mechanical performance. As Figure 5 shows, substitution of 10 % or 20 % of cement CEM I 52.5R – SR 3 by bentonite raised 28 d flexural strength relative to the reference cement except for 30% substitution. Adding 30 % bentonite also yielded smaller strength than in the reference, but higher when it is the 10 % or 20% of substitution.

While unaffected by bentonite at a replacement ratio of 10 % (Figure 6), compressive strength declined at ratios of 20 % or 30 %. Those findings informed the decision to use only the 10 % bentonite in all the subsequent tests as a conservative proportion.





**Figure 5.** Flexural strength in cement pastes prepared with the reference cement and with blended cement at replacement ratios of 10 %, 20 % and 30 %.



**Figure 6.** Compressive strength in cement pastes prepared with the reference cement and with blended cement at replacement ratios of 10 %, 20 % and 30 %.

### 3.2. X-ray diffraction -based characterisation

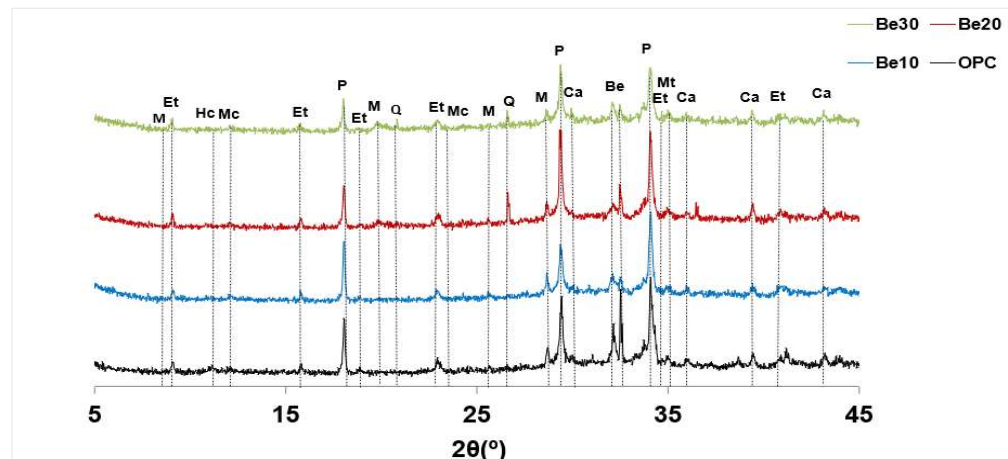
The possible reactivity and stability of bentonite-substituted cement paste were also explored. The diffractograms for 28 d pastes bearing 10 %, 20 % and 30 % bentonite are reproduced in Figure 7, whilst the relative content (counts, in per cent) of the various phases is graphed in Figure 8.

The reflections attributable to bentonite (montmorillonite and quartz) rose in intensity between 10 % and 20 % replacement, although no such rise was visible between 20 % and 30 %.

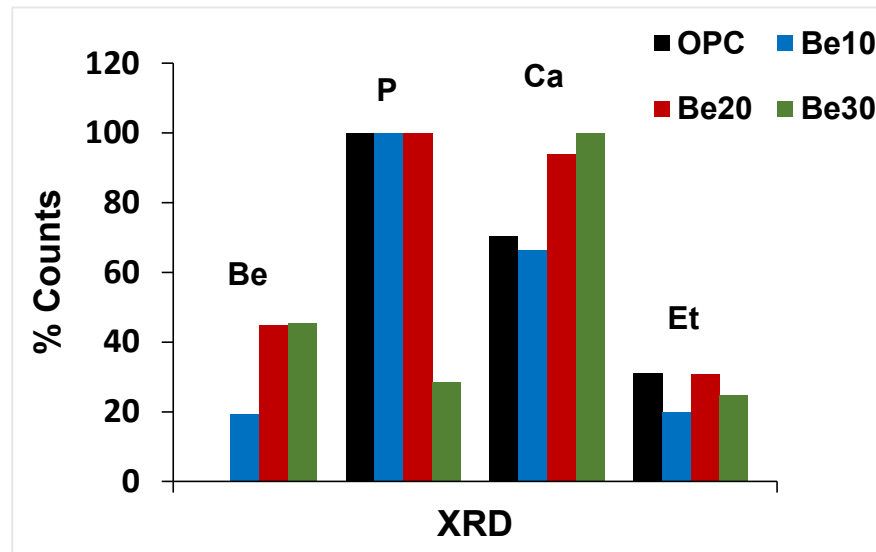
Portlandite content was similar to the reference in the former two mixes, but declined significantly at 30 % replacement. According to [28], that decline might be explained by the formation of a calcium zeolite in the interaction between bentonite and the pore solution in the hydrated cement, confirmation of which premise lies outside the scope of the present study.

Inasmuch as the carbonate phases would have been generated by carbonation occurring during the test, for the time being the rise in intensity with bentonite content need not be attributed to that higher proportion of the clay.

As ettringite content, in turn, followed neither an upward nor a downward pattern, its presence would be due to the cement and can be considered unaffected by the addition.



**Figure 7.** XRD patterns for unadded CEM I 52.5R – SR 3 and the same cement with 10 %, 20 % or 30 % bentonite.

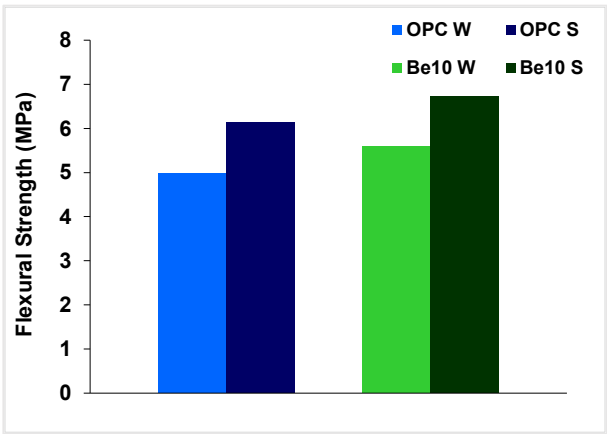


**Figure 8.** Counts in XRD diffractograms of the crystalline phases identified in the mixes cement and bentonite.

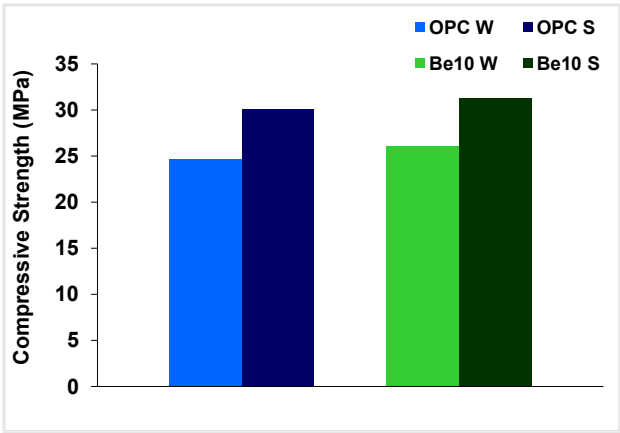
### 3.3. Sulfate attack

The results for this test are deemed acceptable when the strength of the substituted cement is greater than 70 % of the value recorded for the control soaked in distilled water. Further to the flexural and compressive strengths of the reference specimen soaked in water and the specimens bearing 10 % bentonite graphed in Figure 9, strength was higher in both the reference and in the specimen bearing the bentonite presence when soaked in the sulfate solution than when soaked in water. The increase in resistance was attributed to the increase in hydration degree due to the longer age after 56 days of testing with respect to 28 days curing. Comparing reference with bentonite substituted the resistances are very similar. This fact enabled to deduce in this preliminary study that the bentonite is not modifying the performance of the cement in absence of substitution with regards to sulfate attack.





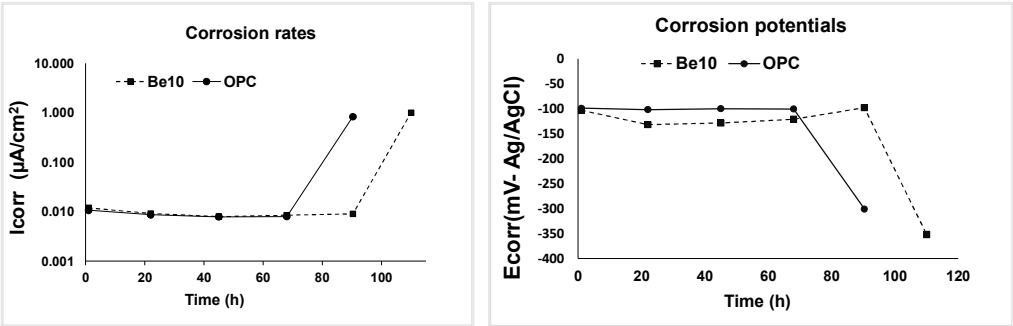
**Figure 9.** Flexural strength in reference specimens and specimens with substitution of 10 % bentonite soaked in distilled water (W) or in sulfate (S).



**Figure 10.** Compressive strength in reference specimens and specimens with substitution of 10 % bentonite soaked in distilled water (W) or in sulfate (S).

3.4. Chloride resistance test

This test aimed to determine the effects of the bentonite addition on chloride transport in the mortar matrix and the chloride ion threshold at which the reinforcing steel began to corrode. Figure 11 shows the trends of the corrosion potential and of the corrosion rate during the experiment until a shift of both is detected and the depassivation occurs.

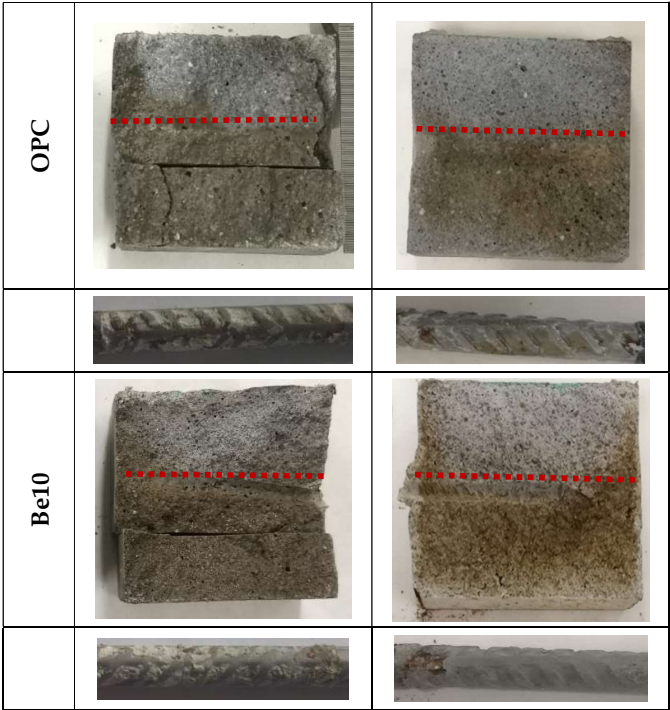


**Figure 11.** Corrosion potential and corrosion rate, measured periodically until an abrupt change in tendency in the variables denoted reinforcement de-passivation.

The chloride diffusion coefficients are listed in Table 2. They are calculated from the penetration depth of the colorimetric front depicted in Figure 12. Those of the mortar with the 10% substitution of bentonite are much smaller. Rather than penetration depth per se (figure 12-red line), that decrease is derived from the test times as the depassivation happens before in the reference mortar than in that with the bentonite. In other words, it took much longer to reach the penetration shown in the figures in the bentonite-bearing than in the reference specimens, denoting higher electrical resistivity in the former.

**Table 3.** Chloride non-steady-state non steady-state diffusion coefficient ( $D_{ns}$ ) in reference (OPC) and with substitution of 10 % bentonite-bearing specimens.

Sample	Test time (h)	Maximum penetration (mm)		Mean penetration (mm)	$D_{ns}$ diffusion coefficient (cm <sup>2</sup> /s)
OPC - 1	110	34.04	33.03	33.535	$17 \cdot 10^{-12}$
OPC - 2	110	33.94	33.14	33.54	$15 \cdot 10^{-12}$
Be10 - 1	90	34.12	34.06	21.015	$4.75 \cdot 10^{-12}$
Be10 - 2	90	33.92	33.89	33.91	$4.6 \cdot 10^{-12}$



**Figure 12.** Chloride penetration front at the end of the experiment when corrosion initiation is detected.

The values of the chloride content are given in table 3. The surface concentration is higher in the case of presence of bentonite but opposite, the chloride threshold is lower with the bentonite. This allows to deduce that confirm that it is the transport phase expressed in the diffusion coefficient which controls the better behaviour of the mortar with bentonite.

**Table 3.** Concentration of chlorides in the surface of the specimen at the end of the experiment and in the surface of the steel bar.

	Bar in Reference	Bar in Be10
Chloride Surface concentration	1.10	1.64
Chloride threshold (% mass mortar)	0.35	0.13

3.5. Natural carbonation

The photographs in Table 3 depict the phenolphthalein staining in the specimens from which carbonation depth was deduced. Generally speaking, the shallowest depths were observed in the laboratory, intermediate penetration under outdoor sheltered conditions and the deepest in the specimens exposed to rainfall. That order of environmental aggressiveness is diametrically opposed to earlier reports. According to those data, penetration was deepest in specimens exposed to indoor environments or sheltered outdoor conditions, whilst carbonation was least intense in those exposed to rainfall, due to their higher or nearly optimal moisture content. The present findings were deemed accurate, however, for they were qualitatively identical in the 3 month and 6 month specimens. In this study, the specimens exposed 6 months were tested also during the summer under high temperature, low RH conditions. In other seasons with higher RH and more rain the order may have differed. That is scantily relevant, however, for inasmuch as carbonation was intense in all the samples, the findings sufficed for the aim pursued, namely to compare the behaviour in the various cements.

**Table 3.** Phenolphthalein staining in the cements studied to determine carbonation depth.

CEMENT	3 MONTHS						6 MONTHS					
	INDOORS		OUTDOORS UNSHELTERED		OUTDOORS SHELTERED		INDOORS		OUTDOORS UNSHELTERED		OUTDOORS SHELTERED	
	OPC	Be10	OPC	Be10	OPC	Be10	OPC	Be10	OPC	Be10	OPC	Be10
CEM I 42,5R												
CEM I 42,5SR												
CEMII/AS42,5N												
CEMII/A-P(16) 42,5R												
CEMII/A-P(13) 42,5R												
CEMII/AV42,5R												
CEMIII/A42,5N												
CEMIV/A(V) 42,5R SR												
IV/A(P) 42,5R/MR												
BLII/B-LL42,5R												

Figure 13 plots the 3 month carbonation depths in the specimens bearing 10 % bentonite against the respective references and Figure 14 the same parameters in the 6 month samples. After 3 months carbonation was less intense in a larger number of 10 % bentonite than of reference specimens. The gap was smaller after 6 months, although carbonation is in some cases greater in the substituted cement than in the reference specimens.

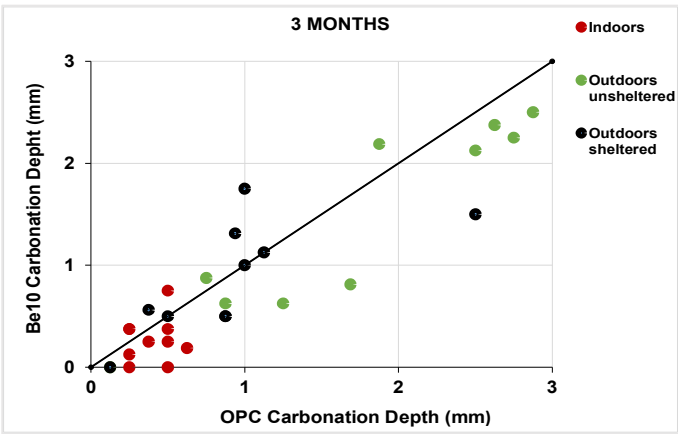


Figure 13. Comparison of Carbonation depth in 3 months specimens between reference and with a substitution of 10% of bentonite.

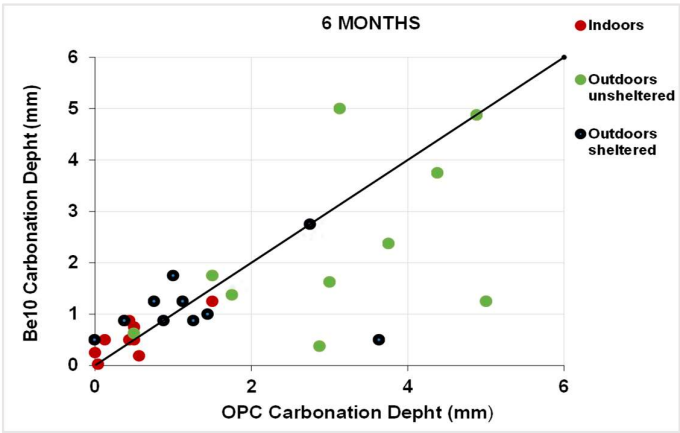


Figure 14. Comparison of Carbonation depth in 6 months specimens between reference and with a substitution of 10% of bentonite.

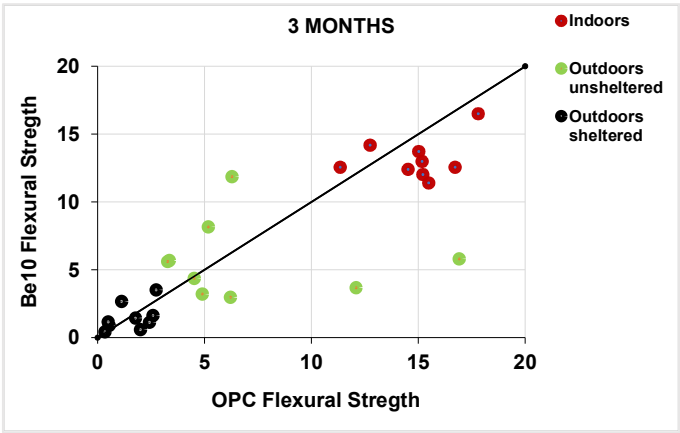


Figure 15. Comparison of Flexural strength in 3 months specimens.

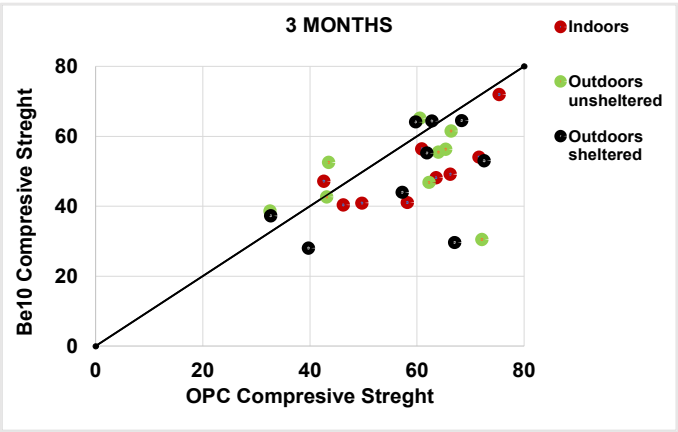


Figure 16. Comparison of Compressive strength in 3 months specimens.

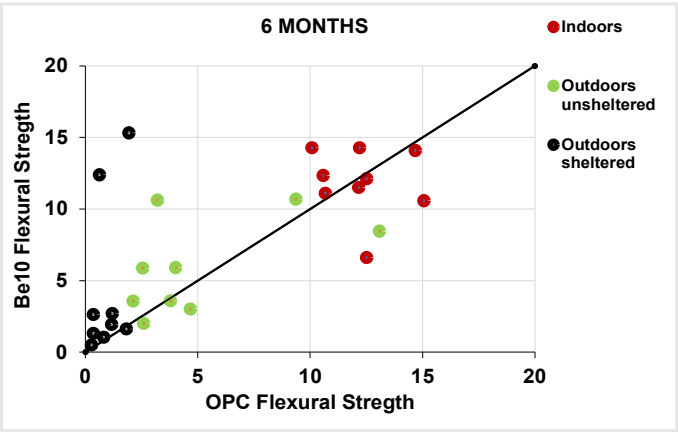


Figure 17. Flexural strength in 6 months specimens.

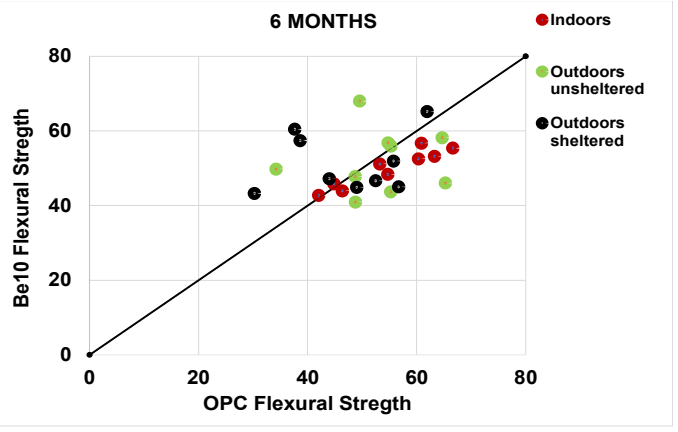


Figure 18. Comparison of Compressive strength in 6 months specimens.

As a rule, the flexural strengths were fairly similar in the reference and substituted samples. The compressive strength values were even closer in the two types of mortars. Inasmuch as the experiment was designed for purposes of comparison, the inference drawn from these findings is that substituting 10 % bentonite to the cement mix had no consistent effect on mortar behaviour.

#### 4. Discussion

Rising to the challenge posed by the need to reduce the cement industry's carbon footprint may involve, they may be either large-scale technological change based on research into new manufacturing methods, or adopting a more direct and technologically simple approach consisting in lowering the proportion of clinker in cements without altering their essential properties [1-3]. Replacing clinker with non-CO<sub>2</sub>-emitting materials is the most immediate alternative open to the industry.

By-products such as blast furnace slag, that are in themselves cementitious, have long been deployed to reduce clinker content [1], as have acid materials (pozzolans and more recently fly ash and silica fume) that react with the calcium hydroxide released in cement hydration. The use of natural pozzolans began to decline in the wake of their depletion in some natural reserves or because of the adverse impact of quarrying on the environment. In contrast, as an industrial by-product fly ash was much less costly, for it did not have to be mined and the enormous stockpiles of coal industry waste had to be pared down. At around the same time, the nineteen seventies oil crisis raised the price of the fuel used to manufacture clinker. That combination of factors led to the general trend of addition of minerals to the clinker which, depending on the commercial and legislative conditions prevailing in any given country, were either milled directly with the clinker or added at concrete plants.

As noted in the introduction, the evidence of climate change and the gradual reduction of the stock of such by-products have driven a return to former paradigms, including the use of additions other than slag or fly ash, such as pre-calcined clays [6]. Even with the investment involved in pre-calcination, clay has become competitive due to the rising cost of emissions [8]. Indisputably, however, the initial cost would be even more competitive if cement performance could be ensured with no need for pre-calcination.

That process of precalcination entails, among others, the loss of the bound water in the constituent minerals present in clay [5-8], which is recovered during hydration. Such thermal dehydration affects clay reactivity, i.e., cement hydration kinetics, but should not in principle impact component stability, for the compounds at issue are the same as they would be if the clay were used without pre-calcination. That is one of the many matters in connection with the use of non-pre-dehydrated natural clays, bentonite among them, in need of more thorough research.

In light of its vast diversity and fairly widespread geographic availability, clay is just one more local raw material deployed in cement manufacture. The very same clays used in clinker kilns might, in certain proportions, constitute compatible additions to lower milling-related CO<sub>2</sub> emissions (since milling clay is less energy-intensive than grinding clinker). That reasoning informed the initiative to undertake preliminary, exploratory research along those lines, part of the results of which are described hereunder.

Surprisingly, very few studies [10-20] on the subject were found in the literature other than reports of the widespread joint use of cement and bentonite in underground works [22-23], such as the nuclear waste storage [28-32], soil stabilisation or impermeable slurry wall construction [21].

To be compatible with cement and usable in concrete, additions must meet a series of short- and long-term requisites, summarised below.

- They must be inert or at least not induce expansion or degenerative reactions.
- They must improve or at least not alter volumetric stability of concrete (in terms of shrinkage and creep especially) [44].
- They must improve or at least not alter mechanical performance.
- They must lengthen or at least not shorten concrete or steel durability.



Despite the very preliminary nature of this study, which addresses some but not all of those factors, the findings are deemed sufficiently promising to be made public, acknowledging however that the use of non-pre-calcined clays will call for considerable research, in light of their enormous variety.

The following paragraphs discuss the more or less basic features of the use of non-pre-calcined clays analysed here, i.e., the effect on mechanical strength, the nature of the hydration products forming and the impact of bentonites on resistance to sulfates, chloride ingress and carbonation.

Be it said from the outset in connection with flexural and compressive strength that bentonite thixotropy necessitates adjusting admixtures and the w/c ratio to ensure suitable mix workability [25-26]. Such thixotropy, which has not been studied in depth, may be either a drawback or an advantage in terms of workability, depending on the intended application (such as precasting) of the concrete at issue of 3D manufacturing [43]. In this study carboxylate admixtures [25-26] were the simplest choice to avoid mixing problems.

One of the most prominent findings of this research was the rise in flexural strength with the proportion of bentonite. In the absence of supplementary testing, no reasons for such a rise can be ventured at this time. Although compressive strength was observed to decline, that development was readily attributable to the lower clinker content.

The XRD findings for the hydrated pastes revealed that at the ages studied the cement barely reacted with bentonite. Further to reports on underground structures, for the nuclear industry in particular, high cement alkalinity induces the formation of a certain proportion of calcium silicate hydrates and calcium zeolites [29-30]. At ambient temperatures, however, that reaction is apparently slow enough to deem bentonite a nearly inert substance.

Although the results of the Koch-Steinegger sulfate resistance tests might be dismissed for their failure to represent actual conditions, they are nonetheless indicative of relatively short-term anomalous and expansive reactions. Longer-term tests using different solutions would be required to confirm the present initially promising results in this regard.

The lower diffusion coefficient measured for chloride ingress, in turn, was attributable to the timing differences between the tests conducted with the reference and with bentonite. As the clay retards chloride penetration significantly, its use as an addition would be beneficial, although further research is called for to determine the reasons for this behaviour. One possibility might be the reduction of porosity (parameter not measured here), whereas any reaction between bentonite and chlorides would be all but ruled out in light of the negative charge in the clay's interlayers, which would accommodate cations but not anions.

The effect of bentonite on carbonation depth must be assessed in the realisation that its action supplemented the action of other additions present in the cement. In other words, at least two additions were in place in the tests conducted here, accounting in some cases for a substantial fraction of the total. In the two additioned CEM I cements used, carbonation was the same or even lower than when no bentonite was present. Of the other cements, the ones bearing natural pozzolans appeared to perform better than those carrying fly ash or slag. In neither case did the use of bentonite induce clearly poorer performance than already observed in those cements, however. Such behaviour cannot be attributed to a reaction between the clay and carbon dioxide, for as noted above, bentonite cannot accommodate anions in its interlayers.

This feature, the reduction or at least non-alteration of carbonation depth, is deemed to be the most relevant finding of this study, for the opposite, lower carbonate resistance, is one of the shortcomings identified in mineral additions in general. Bentonite could consequently be used to advantage instead of the 5 % of inert matter or the up to 10 % of limestone routinely added to clinker, it may improve one or several properties of the end product. Confirmation of the foregoing will nonetheless call for much more testing, in particular to detect possible adverse effects on shrinkage or creep.

## 5. Conclusions

This article describes exploratory experimentation on some of the properties of pastes and mortars made with different proportions of bentonite. The conclusions that may be drawn from the findings include the following.

1. At the replacement ratios tested, bentonite up to 20% substitution improved the flexural strength and at up to 10 % on compressive strength.
2. At 10 % the addition induces no change in cement crystalline hydration products or in the components of bentonite itself (>95 % montmorillonite further to supplier specifications).
3. Substituting 10 % of cement by bentonite:
  - a. In a sulfate solution for 56 d raised cement paste mechanical strength relative to the same materials stored in distilled water. attributed to greater age in the absence of expansive reactions
  - b. Lowers the chloride diffusion coefficient significantly
  - c. Reduces or maintains the carbonation depth observed in the reference material, deemed to be a very promising development.

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