POZZUOLANIC PROPERTIES OF THE NATURAL ZEOLITES OF SOME LATIN AMERICAN DEPOSITS

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ABSTRACT
This paper shows the results of the study of physical, mechanic and chemical behaviour of some natural zeolite types sampled in different outcrops of the world, mainly from Mexico, Cuba and Spain, as well as their incidence in certain practical applications, by means of the utilization of its pozzuolanic properties. Results emphasize that every natural zeolite variety gives different answers in the assays, probably influenced by the subtle variability of their chemical composition.
Key words: zeolites, pozzuolanic, density, geometric, strength

INTRODUCTION
Natural zeolites comprise a wide tectosilicates family, with similar mineralogical, structural and chemical features. They have some properties that convert them in singular minerals, in which emphasizes their ion-exchange capacity.
Currently, the whole known properties of the natural zeolites contribute for a lot of competitive advantages that encourage their exploitation, including their ease extraction, low prices of the primary products, low environmental impact, deposit accessibility and their versatility and profit.
Nevertheless, neither evident, these properties are not constant, but can manifest a high or low quality, depending on the zeolite type. Nowadays, the researchers have defined very well the industrial uses according to certain kinds of natural zeolites.
The purpose of this study is based on the characterization of three zeolite samples through its behavior in various standardized, as well as to obtain relevant conclusions about its influence on the expected results. These natural zeolites (Clinoptilolite-heulandite) have been sampled in the Escalerillas deposit (San Luis Potosi, Mexico), San Andrés deposit (mordenite-clinoptilolite) (Holguin, Cuba) and San Jose-Los Escullos deposit (mordenite-smectite) (Cabo de Gata, Spain) (Costafreda, JL, 2008) (Figure 1), (Novo, R., Martinez, JA, 2009) and (Costafreda, JL, Calvo, B., 2010).

Figure 1 - Partial view of the latin american deposits sampled; a) *Escalerillas*, San Luis Potosi, Mexico; b) *San Jose – Los Escullos*, Cabo de Gata, Almeria, Spain; c) *Loma Blanca*, San Andres, Holguin, Cuba.

METHODS
Three representative samples were researched (ZEO-1, ZEO-2 and ZEO-3). Samples were prepared and grinded for the following essays:

- Geometrical, physical and chemical characterization
- Quality valuation as product of the pozzuolanic cement.

A portland cement with high initial resistance (*CEM I*) has been used in this investigation, to establish a comparison between results.

Geometric, physical and chemical characterization

Geometric characterization

Samples were subjected to geometric reduction to obtain graded aggregates with a maximum size of 10 mm, in order to determine the particle size distribution and fines content by running the test method referenced in the Spanish standard UNE-EN 933-1:1998 and EN 933-1:1998 / A1: 2006.

Physical characterization

Low density is one of the more prominent advantage that natural zeolite has. That is why, in this work it have been taken into consideration the following essays:

- True particles density (porosity is not considered)
- Visible particles density. This parameter is different from before one, given the calculation of the volume occupied by the particles, considering its internal porosity.
- Water absorption.

This procedure was applied on the granulometric fraction bigger than 4 mm (Table 1).

Chemical characterization

With a view to verify the efficiency of the zeolites the SiO_2 + Al_2O_3 + Fe_2O_3 proportions were calculated, while to evaluate its suitability on cements, mortar and concretes. In addition, the total SiO_2 and reactive SiO_2, reactive calcium oxide and insoluble waste contents were calculated too (UNE-EN 196-2: 2006; UNE 80225: 1993 EX y UNE EN 451-1: 2006) (Table 2).
Chemical composition (% oxides in mass) on researched zeolites was calculated through *XRF* technique (Table 3).

Valuation of zeolites as aggregate of cements

Setting and volume stability of cements with zeolites

The setting is a process in which the cement experiments some hardening and resistances in a few days after preparations of the paste. There are two setting times, the first comprise 1-4 hours, and the second one is 3-7 hours (O´Nelly, R. y Hill, R. 2001) (UNE EN 196-3:1996) (Table 4).
A mix of 500 g composed by portland cement an natural zeolites was prepared and mixed with distillate water during 10-15 seconds. The environmental temperature chamber was 19,1 ºC, and 64% of relative humidity (UNE EN 196-3:1996).
Volume stability was determined by *Le Chatelier* method, in the same humidity and temperature conditions above mentioned.

Mechanical strength

In the calculation of the mechanical strength were used hard mortars prism, beforehand prepared with portland cement (75%), natural zeolite (25%), normalized sand and distilled water (UNE-EN 196-1:2005 & UNE-EN 196-3: 2005) (Tables 5 and 6). The calculation of the strength activity index was realized for prescription of *UNE-EN 196-1: 2005; UNE 80303-1:2001 & UNE 80303-2:2001* (Table 7).

RESULTS

(Table 1 - Determination of densities and absorption capacity for using zeolites)

Sample	Fractions		True density of particles	Visible density of particles	Water absorption WA_{24}
	Fraction (di/Di) (mm)	(%)	($Mg.m^{-3}$)	($Mg.m^{-3}$)	(%)
ZEO-MEXICO	4-10	100	2,20	1,27	33,22
ZEO-CUBA	4-10	100	2,31	1,79	12,61
ZEO-SPAIN	4-10	100	2,31	1,57	20,36
AGGREGATE-REF(*)	-		2,62	2,59	0,53
(*) Aggregate of reference. (UNE-EN 1097-6:2001 & UNE-EN 1097-6:2001/A1:2006).					

Table 2 - Chemical analysis results showing the reactive components contents on the natural zeolites samples.

Sample	SiO_2 (Total)	CaO (Total)	Fe_2O_3	Al_2O_3	SiO_2 (Reactive)	CaO (Reactive)	Residuo Insoluble Waste
ZEO-MEXICO	67,57	3,08	2,45	12,84	56,94	2,83	3,01
ZEO-CUBA	65,04	2,92	2,25	11,19	63,31	2,80	3,21
ZEO-SPAIN	67,89	1,57	1,39	11,60	60,18	1,30	2,31
(UNE-EN 196-2: 2006; UNE 80225: 1993 EX & UNE EN 451-1: 2006).							

Table 3- Chemical analysis results (*x ray florescence*) from natural zeolites samples used in this work.

% OXIDES IN MASS							
S_iO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P.P.C.
ZEO-MEXICO							
67,3	12,14	6,77	6,87	1,25	1,27	0,87	11,51
ZEO-CUBA							
65,41	13,15	1,9	4,32	0,36	2,23	0,48	11,68
ZEO-SPAIN							
67,79	12,11	1,46	1,68	1,31	2,6	3,47	11,20

The results of the physical essay (setting and volume stability) obtained from hard mortars prism studies are showed in table 4.

Table 4 - Setting time and volume stability results from analyzed samples.

SAMPLE	Water mass (g)	Water of normal consistence (%)	Start (hour)	Initial setting (min)	Final (hour)	Final setting (min)	Volume stability (Le Chatelier) (mm)
ZEO-MÉXICO	195	39,0	13:05	315	14:10	380	0,0
ZEO-CUBA	168	33,5	13:10	315	14:20	385	1,0
ZEO-ESPAÑA	194	39,0	13:35	325	14:45	395	2,0
AGGREGATE-REF	159	32,0	10:10	95	10:50	135	1,0
Temperature: 19,1 ºC; Relative humidity: 64 %.					*UNE-EN 196-3: 2005*		

Table 5 - Strength results from different ages.

Sample	Age (days)	Strength (Mpa)
ZEO-MEXICO	7	27,9
	28	50,4
	90	59,1
ZEO-CUBA	7	28,5
	28	50,9
	90	62,3
ZEO-SPAIN	7	30,3
	28	43,7
	90	55,5
AGGREGATE-REF	7	41,6
	28	55,2
	90	66,1
UNE-EN 196-1: 2005.		

Table 6 - Mechanical and physical demands for cements according to initial and normal resistances (UNE EN 196-1:2005).

Strength index	Strength Mpa				Setting initial time (min)	Expansion (mm)
	Initial strength		Normal strength			
	2 days	7 days	28 days			
32,5 N	-	≥16,0	≥32,5	≤52,5	≥75	≤10
32,5 R	≥10,0	-				
42,5 N	≥10,0	-	≥42,5	≤62,5	≥60	
42,5 R	≥20,0	-				
52,5 N	≥20,0	-	≥52,5	-	≥45	
52,5 R	≥30,0	-				
UNE EN 196-1:2005 y UNE-EN 196-3: 2005.						

Table 7 - Strength activity index from samples at 28 days.

Sample	strength (28 days) Mpa	IAR (%)
ZEO-MEXICO	50,4	91,3
ZEO-CUBA	50,9	92,2
ZEO-SPAIN	43,7	79,1
AGGREGATE-REF	55,2	-
UNE-EN 196-1: 2005; UNE 80303-1:2001 & UNE 80303-2:2001.		

DISCUSSION

Geometric characterization

Zeolites submitted to study show a regular particle size distribution, with a content in very fine particles from 3% to 4 %. Nevertheless, is evident the different behaviour demonstrated by the Mexican natural zeolite during crushing, showing better granulometric distribution than other samples.

Physical characterization

Results have emphasized that natural zeolites have minor densities than other aggregates used as industrial products (about 0,3 mg/m^3). The mexican zeolites shows minor density than cuban and spanish ones (Figure 2).

On the other hand, the visible density has demonstrated that natural zeolites have major porosity than those conventional materials (this parameter is reduced in a 1 mg/m^3).

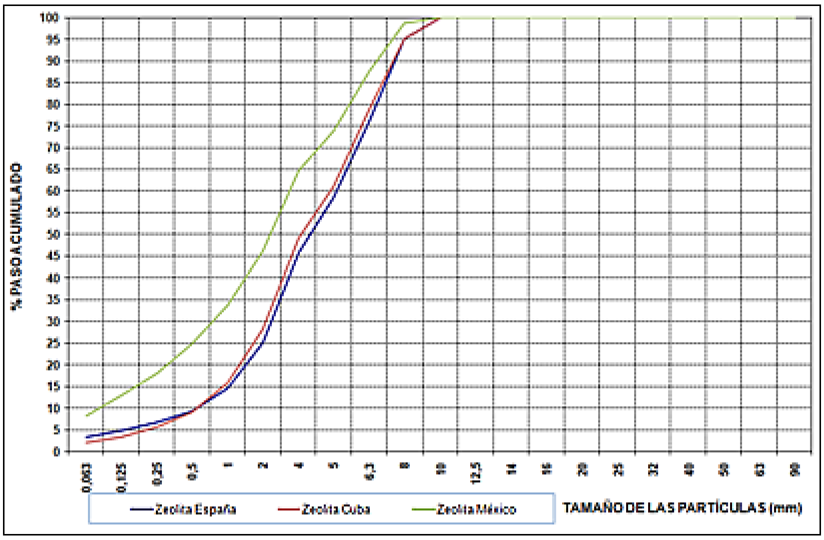

Figure 2 - Particles size distribution from zeolite samples.

According to the previous parameters, the absorption water capacity in studied zeolites is raised, mainly in case of the Mexican sample, whose absorption capacity represent a third of its mass.

Chemical characterization

The zeolites studied exceed the minimum allowable value (70%) (according to ASTM C 618-89 standard.) Also, the Al_2O_3 content are within the standard range (11.6 to 14.7%), this chemical property, linked to the the high pozzolanic reactivity of the zeolite, contributes to increase the strength of cements against the attack of the sulphates (Table 2).

Al_2O_3 content, detected in the samples, might interfere with the reaction of C_3A into clinker with water and other related compounds in the paste, avoiding the formation of ettringite, however, can contribute to total hydration in those silicate with slow hydraulic reactivity, such as C_2S. This fact, together with the inhibitory action of the zeolite vs portlandite, allows the formation of tobermorite phase (Costafreda, JL, 2008).

Reactive SiO_2 content ranges from 56.94 to 63.31% (Table 2), and exceeds the limit set by the standard (25%). The reactive CaO appears in almost negligible amounts, which would not affect the quality of pozzuolanic cement.

The highest SiO_2 content of zeolite from Spain infer a lower LOI value (Table 3) compared to the other zeolites. It is possible that this fact is related to the crystalline structural stability, however the smectite content, which is in isomorphism with mordenite, could influence the LOI value.

It noted the visible difference between the values of the compounds of Na_2O in zeolites from Cuba and Mexico respect to Spain one´s (Table 3), which reveals a sodic character, with minor CaO, indicating its hydrothermal origin (Costafreda , JL, 2008).

Setting times and volume stability

The values of the start and end times for samples cured with natural zeolites varied in the range of 315 to 325 minutes, while the final values fluctuated between 380 and 395 minutes, with the largest setting times (initial and final) for the spanish zeolites, while cuban and mexican samples have a similar behavior.

The reason for this difference can be found in the complex composition of spanish zeolites, which contain about 19 % of smectite (Costafreda, J.L., 2008). The presence of expansive clays (montmorillonite) also affects the volume stability (Table 1). A sample can be expansive when it is able to separate the two needles ends during the *Le Chatelier* test (approximate distance: 17.5 ± 2.5 mm; standard UNE-EN 196-3: 2005).

However, the UNE-EN 197-1: 2000 standard considers as valid those results which are below 10 (≤ 10 mm) or equal to this value (Table 5).

A normal behavior from the results obtained of the reference cement can be deduced.

Mechanical strength

The mechanical strength values include a normal increase for the analized samples. A significant gap is evident at 7 days in the spanish sample compared with both, mexican and cuban samples, instead, this situation changes dramatically from 28 to 90 days (Tables 5 and 6).

Pozzolanic reactivity of both, mexican and cuban zeolites represents a greater hydraulic efficiency of the reaction in these periods, and is testimony to the influence produced by different chemical compositions (Figure 3).

The test performed at the reference specimen (CEMREF) gives strength values, higher than the remaining samples, and represents a normal situation in this study, however, the strength difference in all samples, in respect to CEMREF, is not excessive, taking into account the slow initial reactivity of the pozzolan.

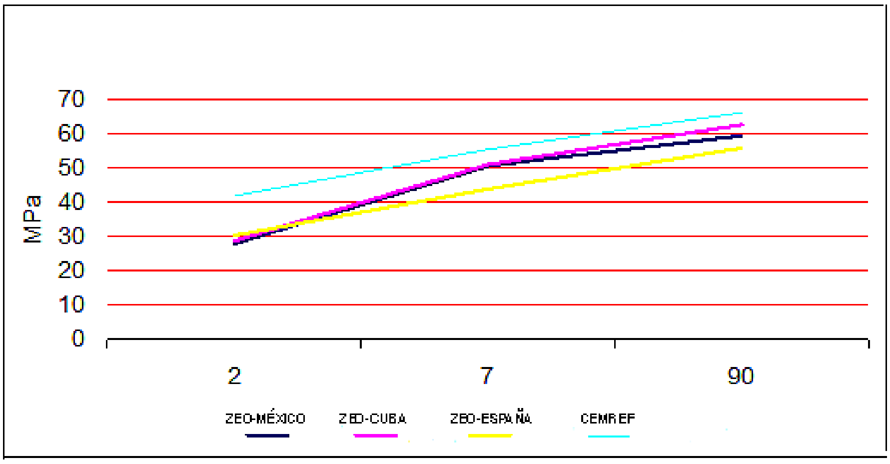

Figure 3 - Evolution of mechanical strength over time.

The strength activity index provided by the samples studied in relation to 75% of the value of compressive strength of reference cement (55.2 MPa) for the age of 28 days, are positive in all cases (Table 7). There is a difference between the zeolites from Mexico and Cuba with regard to Spain, but the results fall comfortably within the range set by the UNE-EN 196-1: 2005, UNE 80303-1:2001 and IEC 80303 - 2:2001 standards.

The weight of the analyzed samples varies within a narrow range for the cases of Mexico and Cuba (567.19 to 572.3 g and 573.32 to 579.27 g) (Table 8). The specimens made from zeolites of Spain have a significantly higher weight, which can be caused by the presence of hydrated smectitic phase at the time of weighing (Figure 3).

Table 8 - Evolution of the weight for mortar specimens at different ages.

SAMPLE	Initial weight (average) (g)	Average weight (7 days) (g)	Average weight (90 days) (g)
ZEO-MEXICO	567,19	572,37	576.33
ZEO-CUBA	573,32	579,27	582,23
ZEO-SPAIN	579,86	581,23	585,83
CEMREF	594,19	596,6	597.92
UNE-EN 196-1: 2005 standard			

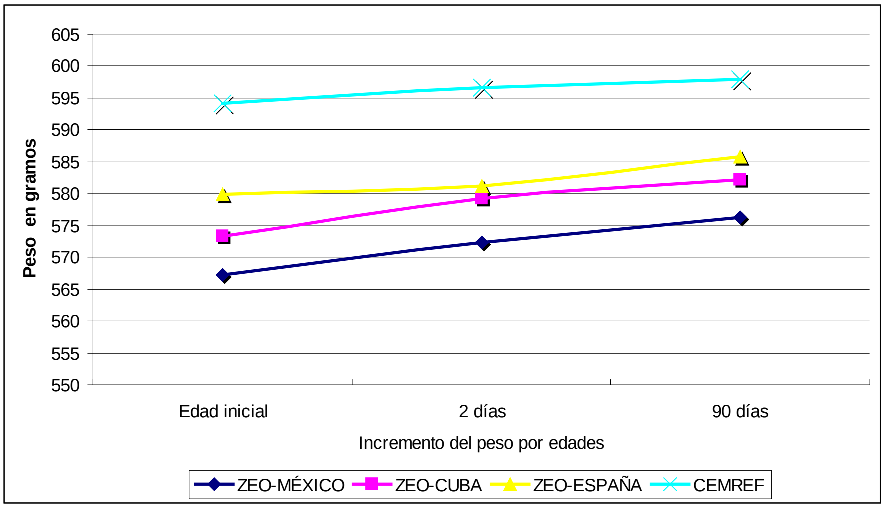

Figure 3 - Increase the weight by age.

The weight of the reference specimen (CEMREF) is the greatest, and exhibits significant differences from other samples.

CONCLUSIONS

It is clear that the physical, chemical and mechanical properties of natural zeolites vary considerably according to species class, within the family mineralogy. This fact is apparent when the zeolites are found in isomorphism with other minerals. In southeastern Spain is common to find phyllosilicates (montmorillonite) as predominant minerals of the smectite group associated with mordenite (Costafreda, J.L., 2008).

In the case of zeolites from Mexico and Cuba, its purity can be inferred from the high volume stability and setting time, also by high mechanical strength obtained from mechanical tests.

This paper confirms that a wide zeolites variety appears to be suitable in certain global applications, such as the manufacture of cement, mortar and concrete. However, it is possible that in other application fields, which requires certain specific and complex parameters, could be not impracticable the global use of all zeolites.

It should be noted the importance of the weight evolution in the prismatic mortar prepared with zeolites in reference to those made with portland cement only, this fact can be focused on the benefits of using natural zeolite mortar and concrete mixtures for very light and durable structures.

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