Comparative study on porosity and permeability of conventional concrete and concrete with variable proportions of natural zeolite additions

Estudio comparativo de porosidad y permeabilidad de un hormigón convencional frente a hormigones en proporciones variables de adiciones con zeolitas naturales

Juan Carlos de la Cruz (Main Author)
Ibervias Ingenieros S.L. España
jc@ibervias.com

Jose María del Campo (Contact Author)
Universidad Politécnica de Madrid.
Calle Ramiro de MAeztu, 7, 28040 Madrid, España
+34 9133660000
josemaria.delcampo@upm.es

David Colorado
Universidad Alfonso X El Sabio, España
dcoloara@uax.es

Abstract

With the use of special additives, the concrete benefits over its product life increase, both in terms of mechanical properties and durability. Zeolites are used in the field of building work for, thank to their properties, they lend to the concrete enhanced features. This paper explores the physical and mechanical properties improvements of hardened concrete and its permeability. To this aim, on the one hand a concrete of control and another with Zeolite additions between 5% and 10% have been measured out with respect to the weight of cement, while on the other Compressive strength and permeability testing have been carried out through the Mercury intrusion porosimetry test. After these tests, it was possible to obtain concrete with Zeolite proportions of 5% and 10% that showed a suitable workability. With respect to the already analyzed mechanical properties, the inclusion of Zeolites as an additive was an improvement. In that respect, the durable features related to this type of concrete were also similarly improved, being also remarkable the lack of alkali-silica reactions.

Resumen

Con el uso de aditivos especiales, el número de beneficios de hormigón durante su vida útil aumenta, tanto en términos de propiedades mecánicas como de durabilidad. Las zeolitas son utilizadas en el campo de la construcción ya que gracias a sus propiedades confieren al hormigón mejores características. El trabajo ahonda en la mejora de las características físico-mecánicas del hormigón endurecido y en la permeabilidad. Para llevarlo cabo se han dosificado un hormigón de control y otro con adiciones del 5 y 10% de zeolita respecto al peso del cemento y por otro lado un "prototipo de hormigón con adición de zeolita al 5%". Se han realizado ensayos de resistencia a compresión y de permeabilidad usando el ensayo de porosimetría por intrusión de mercurio. Tras todos los ensayos realizados se consiguieron obtener hormigones con proporciones de zeolita del 5% y 10% que presentaron una adecuada trabajabilidad. Por un lado, la incorporación de zeolitas como aditivo produjo una mejora en las propiedades mecánicas estudiadas En otro sentido, las características durables de este tipo de hormigón también se vieron igualmente mejoradas, verificándose además la ausencia de reactividad de tipo álcali-sílice.

Introduction

The countless advantages offered by zeolites can be regarded as a novel product in the construction industry (Nazareno, 2002). The ease of removal, simple location of the deposits of natural zeolite, lack of complexity of their manufacturing process, and reduction of environmental pollution make zeolite a suitable material for the construction industry.

Along with the above mentioned advantages, specifically, zeolite application in cementitious materials such as mortar and concrete contributes to enhancing the mechanical properties of these materials as well to a noticeable increase of their resistance chloride ion diffusion, their freeze-thaw resistance, and overall permeability. (Saltos & Eguez, 2005; Rosell et al., 2011; Castellanos et al., 2014). It also increases their sulfate resistance, enabling them to be used in aggressive environments (Janotka & Stevula 1998).

The International Zeolite Association (IZA) has recognized more than 50 types of natural zeolites. Nonetheless, synthetic zeolites are being studied, characterized, and used in various industrial processes. According to IZA, "a zeolite is characterized by a structure of linked tetrahedrons that contains cavities in the form of channels and boxes commonly occupied by water molecules and cations" (IZA) .The abundance of natural zeolites is given by the great number of combinations of cations, both in nature and disposition (Casals, 1988).

By definition, Zeolites are aluminosilicates of alkali and alkaline earth cations (potassium, calcium and sodium) (Paola, 2004). Their main features are an open structure and their ability to accommodate water and cations within its structure and give them up without changing its structure significantly (Rossel

et al., 2006). As part of the tectosilicate group, they are sedimentary rocks.

The framework contains interconnected channels occupied by cations of sodium, calcium, potassium, and magnesium, among others cations that balance the negative charge of the anionic framework, and by water molecules. These cations are mobile and can be exchanged in varying degrees for other cations (Casals, 1988).

Structurally, they are considered hydrated aluminum tectosilicates where aluminum is replacing silicon (Si) at the center of the structural tetrahedrons, with alkaline and alkaline earth cations forming open structures. The general chemical formula of zeolites is (Fernández, 1989; Hidalgo, 2011):

$$X_aY_bO_2c.nH_2O$$
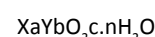
Where: X = Na, Ca, K, Ba, Sr   Y = Si and Al; The Si to Al ratio is < 1 The Si+Al to O ratio is 0.5; n is a variable number which depends on the type of zeolite.

The durability of concrete can be defined as its ability to resist actions from the service environment, physical, chemical, and biological attacks, and any process that tends to deteriorate it. Therefore, a healthy and compact concrete refers to a concrete that maintains its original form and its resistance under service in time (Fernández, 1989). Generally, a healthy and compact concrete presents good durability when it is subjected to normal conditions of environment and wear, and, in the case

of reinforced concrete, it also offers high resistance to steel corrosion.

In this study the quality of concrete with zeolites in the presence of such attacks and their mechanical physical behavior is analyzed. To this aim, we have performed an experimental campaign in which we have looked at two dosages: conventional concrete and concrete with addition of zeolites.

Experimental Champaign

Concrete components

Cement: The cement used in the study is as follows: CEM I 52.5 R. According to and using the standard UNE-EN 197-1: 2011.

Aggregates: The origin of the conventional aggregates used is siliceous. Selected with a maximum size of 12 mm, they are considered as a typical value in the manufacture of concrete, which are prefabricated and used in the civil engineering industry. A fine fraction of 0/6 mm was used and a coarse fraction of 6/12 mm.

Additives: The additive selected was CHRYSOFLUID Optima 206, a new generation superplasticizer, based on modified polycarboxylate particularly recommended for ready-mixed concrete and civil works. It is intended to create a strong water reduction and/or an increased workability of concrete. It allows making concrete with longer workability maintenance without affecting the initial strength.

Zeolites: The clinoptilolite type has been chosen among the nine types of natural zeolite that come from sedimentary rocks: chabazite, clinoptilolite, erionite, mordenite, stilbite, ferrierite, phillipsite, huelandita and laumantita. It has been supplied by the company ZeoCat and sent as micronized powder with a particle size between 0-1 mm, with the following chemical composition: SiO_2: 68.15%, Al_2O_3: 12.30%, K_2O: 2.80% CaO: 3.95%, Na_2O: 0.75%, MgO: 0.90%, Fe_2O_3: 1.30%, TiO_2: 0.20%. The choice of natural zeolite versus the synthetic zeolite is due to the difficulty of finding these types of zeolite in Spain.

Formulation for concrete

For the manufacture of concrete with zeolites with corresponding patterns type, it was used a PEMAT PM-250, of annular tray with central cylindrical inner workings with central suspension and propeller engine placed horizontally with a capacity to prepare concrete mixtures of 250 liter volume according to the manufacturer. The chosen type of concrete for manufacture in this project was a HP/30/F/12/IIa.

Mercury intrusion porosimetry test

The mercury intrusion porosimetry was performed with a AutoPore IV 9500 from Micromeritics, concrete samples were previously crushed to obtain pieces with a suitable size to allow introduction into the cell of a penetrometer with a volume of 5 cm3. Samples were previously dried in a heater at 110 °C for 24 hours, then degassed by vacuum to a pressure of 50 µmHg; the penetrometer filled with mercury was performed to 0.5 psia which corresponds to 0.00034 MPa pressure.

Tridistilled mercury, supplied by Scharlab, was used with a surface tension of 0.485 N m-1, the equilibrium time was of 20 sec, and the maximum range intrusion pressure was established at 33000 psia (219 MPa). The working temperature was always around 25 ± 1 °C, which is always taken into account

in correcting the density of mercury that is its main parameter when determining real and apparent densities that allow the calculation of the sample's porosity.

The contact angle between mercury and concrete is only 117º, according to the Kumar and Bhattacharjee (2003), method, with which we determine the pore diameter through the Washburn-Laplace equation (1):

$$Q_a = 0.5 \cdot A_x \cdot \sqrt{f_c \cdot E_c} \leq R_g \cdot R_y \cdot A_x \cdot F_c$$

(1)

Where: P is the pressure to which mercury is exposed within the sample (Pa), γ mercury surface tension (N m-1), θ mercury contact angle and r is the pore radius (µm). By calculating the bulk density (ρb), we are able to determine the subsequent porosity that resulted from equation (2):

$$Q_{se} = 0.37 \cdot \alpha \cdot A_x \cdot \sqrt{f_{ck} \cdot E_c} \leq 0.8 \cdot A_{se} \cdot f_u$$

(2)

Where: mS mass of sample used (g), mP mass of the empty penetrometer (g), mT total mass of the conglomerate formed by the sample, and mercury penetrometer (g), VP the empty penetrometer volume previously calibrated (cm3), and ρHg mercury density at working temperature (g cm-3). The bulk density data along with the real or (ρr) the porosity percentage of the sample was obtained by applying the following equation (3):

$$Q_{rc} = R_p \cdot R_n \cdot R_y \cdot A_x \cdot F_m$$

(3)

Concrete prototype manufacture with 5% addition of zeolite

Table 1. Characteristics of concrete used in the manufacture of the prototype. Own elaboration, 2014.

Concrete characteristics	Pattern Concrete	Zeolites' concrete
Cement type *	CEM II A/L 42.5 R	CEM II A/L 42.5 R
Coarse aggregate,		
mm	20	20
Cement,		
Kg/m3	350	350
Zeolites,		
%	-	5
Ratio a/c	0.45	0.44
Additive **	1.0	1.5
Cone cm	6.0	5.0
Type	Weak	Weak

*CEM II A/L 42.5R less resistance than initial cement, (CEM I 52.5 R)
** Plasticizer and water reducer, pozzolanic type supplied supplied by BASF company.

For the development of this prototype, concrete test tubes have been manufactured and they are characterized by exposition IIIb+Qb (marine environment), using 15x 15x60 cm prismatic molds. Two conventional prismatic concrete test tubes used as reference with and without armor in order to perform physico-mechanical tests and two prismatic test tubes with 5% natural zeolite addition with respect to the amount of cement with and without armor for durability testing. The armor consists of three 60 cm long steel rods, with 0.06 cm diameter, that occupy length of the piece longitudinally. Each is spaced equidistantly from the other in height, so that the covered range is approximately between 50-150 mm.

## Results

Hardened concrete results

The physico-mechanical characteristics of hardened concrete depend not only on its nature, but also on its age, conditions of humidity, and temperature to which it has been subjected. The features presented here refer to concrete maintained under the same humidity and temperature conditions, sharing the same ages (7 and 28 days). Thus, the mechanical behaviour was compared presenting concrete added with zeolites with respect to conventional concrete (no additions) used as a reference. Concrete strength is generally understood as the stress point at which it cracks or its ability to withstand stresses without breaking. In order to determine this, the test procedure established by the standard UNE-EN 12390-3: 2009 has been used: For the measurement of compressive strength (Cs), two test tubes were manufactured for each age and used a hydraulic press able to achieve a force equal to 300 tons.

The test procedure to determine the flexural strength (Rf) was the one established by the standard UNE 83305-86. To perform this test, two 15x15x60 cm prismatics have been used. The measurement of the elastic modulus (Rt) was performed on two cylindrical test tubes, according to the standard UNE-EN 12390-13: 2014. The measurement of the elastic modulus (Y) was performed on two cylindrical test tubes, as shown by the standard UNE-EN 12390-13: 2014.

Water permeability and mercury intrusion porosimetry test results

The values shown in Table 8 correspond to the most unfavorable depth measurements obtained from the characterization of the three test tubes that undergone testing. The values of apparent diffusion coefficient and transport rate during 6 and 12 months of exposure in concrete with zeolites (Ctot) corresponds to the average total concentration of chlorides in concrete (Meira, Andrade, Padaratz, Alonso and Borba, 2007), Co is the initial concentration of chlorides prior to exposure and k is the constant that measures the speed of transport of chloride into the concrete (see Table 5). Figures 2 and 3 are a graphic representation of these data.

Figure 1 a. Intrusion curves of concrete with zeolites and b. Distribution of porosity of concrete with zeolites. Own elaboration, 2013.
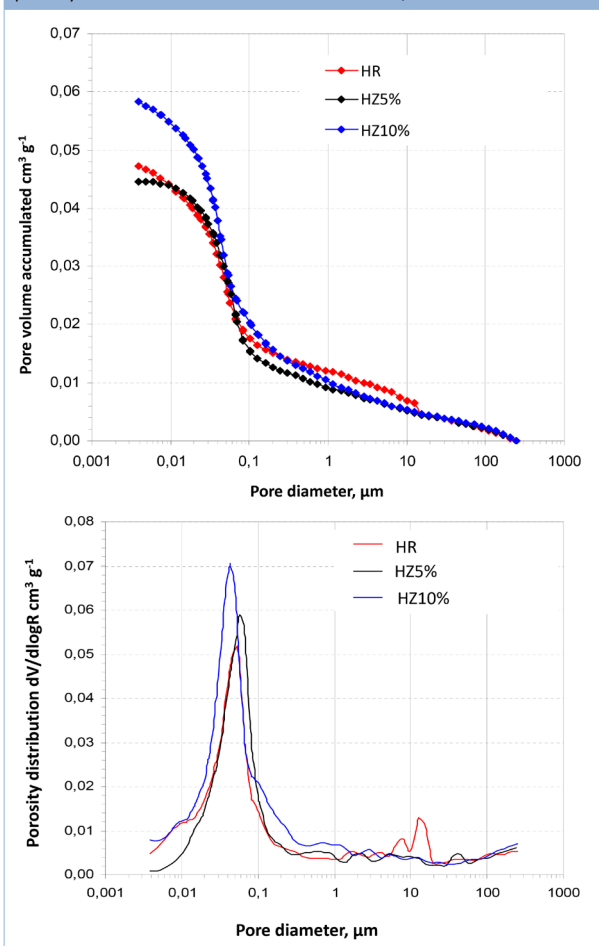
The values shown in Table 8 correspond to the most unfavorable depth measurements obtained from the characterization of the three test tubes that undergone testing. The values of apparent diffusion coefficient and transport rate during 6 and 12 months of exposure in concrete with zeolites (Ctot) corresponds to the average total concentration of chlorides in concrete (Meira, Andrade, Padaratz, Alonso and Borba, 2007), Co is the initial concentration of chlorides prior to exposure and k is the constant that measures the speed of transport of chloride into the concrete (see Table 5). Figures 2 and 3 are a graphic representation of these data.

Table 3. Concrete porosity with zeolites, showing their Rc after 28 days, and hardened concrete density determined by mercury porosimetry (MIP). Own elaboration 2014

Sample	Cs N/mm2	Porosity(%) (MIP)	Density (kg/m3)
HR	56.96	10.60	2246
HZ5%	62.88	10.12	2264
HZ10%	64.12	12.57	2152

Table 2. Cs at the age of 7 an 28 days, Δ Rf at 28, ΔRt at 28 days, and ΔY at 28 days. Own elaboration, 2014

Sample	Cs N/mm2		ΔCs		Rf N/mm2	Rt N/mm2	ΔRt N/mm2	Y	ΔY
	7 days age	28 days age	7 days age	28 days age	28 days age	28 days age	28 days age	28 days age	28 days age
Hf	47.07	56.96	-	-	7.38	3.59	-	44000	
HZ5%	49.83	62.88	5.86	10.39	7.50	4.86	35.38	52500	20.04
HZ10%	50.03	64.12	6.29	12.57	7.41	4.80	33.70	48000	10.14
HZ15%	-	-	-	-					

Table 4. Water penetration depth values and permeability of concrete with zeolites. Own elaboration, 2014

Sample	Water depth (mm) (UNE-EN 12390-8:2009)		Permeability (m2) (MIP
	Maximum	Average	
HR	10	10	2.96 x 10-12
HZ5%	15	10	4.37 x 10-11
HZ10%	25	10	3.11 x 10-12
HZ10%	25	10	3.11 x 10-12

Table 5. Apparent diffusion coefficient values and transport rate at 6 and 12 months of exposure in concrete with zeolites. Own elaboration, 2014

Sample	6 months		12 months		C0, %	k
	Cs, %	Dap x 1012, m2 s-1	Cs, %	Dap x 1012,		
HR	0.952	8.00	0.750	6.40	0.250	0.061
HZ5%	0.612	8.72	1.180	4.51	0.396	0.281
HZ10%	0.560	32.9	0.476	9.88	0.071	0.086

Figure 2. Chloride penetration profiles in concrete with zeolites after 12 months exposure. Own elaboration, 2013.
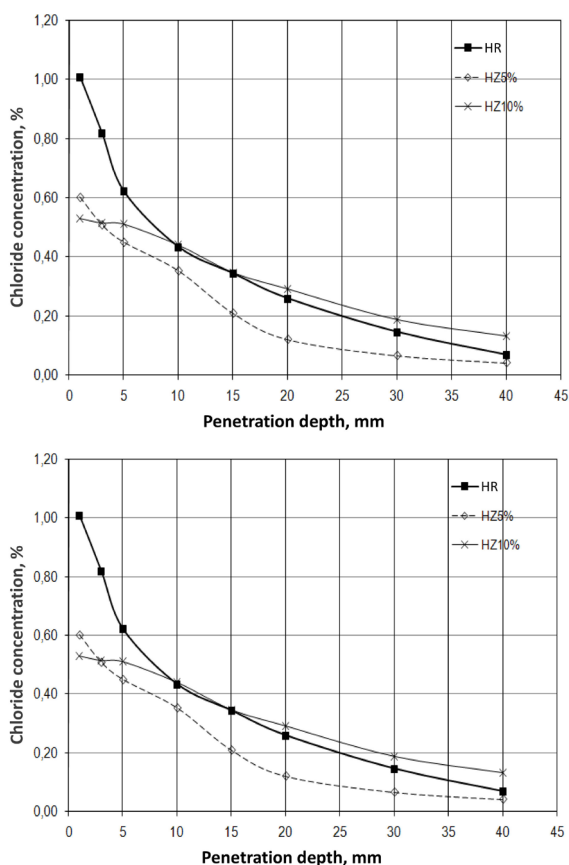
Obtaining the ratio of the average chloride concentration measured in % and the exposure time in months (see Figure 3). The evaluation of concrete's behaviour with zeolites versus the action of the water is done through internal procedure based on a comparative study with conventional concrete and following the Natural Stone standard UNE-EN 12371-02, except when using concrete samples instead of samples of natural stone.

Figure 3. Chloride penetration profiles in concrete with zeolites after 12 months exposure. Own elaboration, 2013.
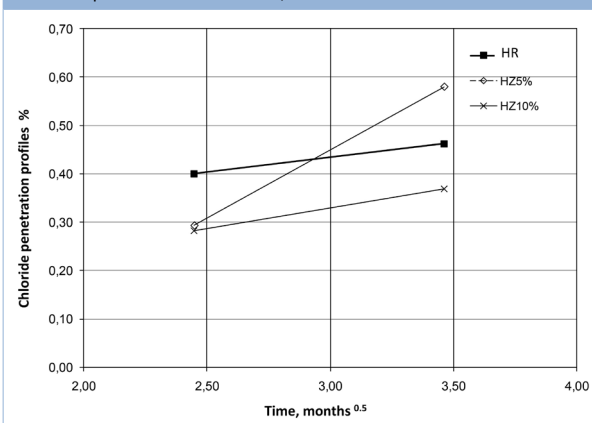
The use of zeolites in mortar and concrete can mitigate, and even completely avoid, certain phenomena that are very significant because of their destructive nature, such as the alkali-silica and the alkali-carbonate reactions, both of which are responsible for the cracking and expansion of concrete structures (Poon et al., 1999; Mertens et al., 2009). However, considering that clinoptilolite crystalline structure consists essentially of aluminosilicates and various ions as sodium and potassium (Armbruster, 2001), resistance to alkali-silica reaction was considered worth studying.

Figure 4. Expansions observed in concretes with zeolites. Own elaboration, 2013.
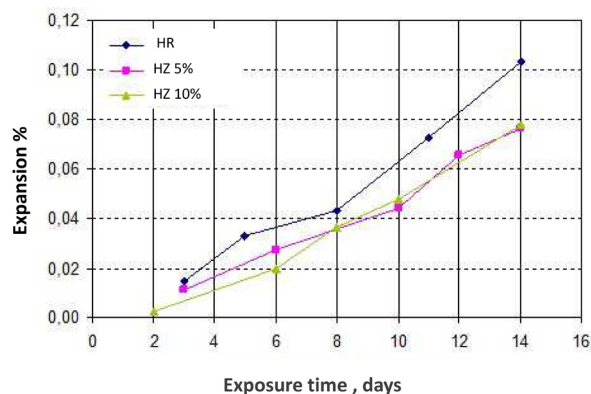
Results of the prototype concrete with 5% zeolite addition tests

The physico-mechanical tests carried out consisted of measuring the Rf and the compressive strength in test tubes prepared according to the procedure established by standards UNE-EN-12390-5: 2001 and UNE-EN-12390-3-2001 (see table 7). For the evaluation of the durable characteristics of the pieces of concrete with zeolites, we have analyzed its behaviour after the chlorides diffusion at the age of 7 days setting time. To this aim, it was made an exposure to a chloride environment by providing pools with a sodium chloride solution according to the available standards for pools (see Table 7).

Discussion

The compression results obtained from each zeolite mixtures highlight that, with respect to HR concrete, there is always an increase of resistance at both 7 and 28 days age, this

being proportional to the content of added zeolite (Table 2). The resistance values after 7 days of HR concrete, HZ5% and HZ10%, showed no excessive difference in their compression values, reaching an average value of 49 MPa. At first, this may suggest the little influence of zeolite used in the resistance of these types of concrete. After 28 days, all of them showed a noticeable increase with greater divergence evident from these results than they were at the age of 7 days.

When working with proportions of 15% zeolite, the concrete obtained had such a dry consistency that made the manufacture of test tubes unfeasible, even by the method of vibration. This indicated that maintaining such constant ratio a/c versus HR decreased the workability of concrete materials. Generally, concrete presents low Rt. This weakness is a frequent cause of cracking; therefore, the lack of cracks is important for the continuity of a concrete structure and, thus, it ensures durability. The results in Table 2 show a decrease in flexural strength as the proportion of zeolite increases. The reason for this decrease in resistance, while the proportion of zeolites increases, creates uncertainties that should be studied further.

In view of the results shown in Table 6, Rt values of concrete with zeolites increase with respect to conventional concrete. However, there is no noticeable enhancement or increase of this property between different concrete with zeolites. The values obtained range between 6% -8%, and it can be said that the behaviour trend towards improvement in concrete with zeolites is similar to that observed in Cs, as expected.

In all cases, their incorporation boosts Y with respect to conventional concrete (see Table 6). Nevertheless, the added 5% of zeolite produced a greater effect on the module compared to 10% zeolite. The value of the specific module for concrete HZ10% differ from its resistance value to compression (see Table 2), for it should be proportional to it.

Concrete permeability is related to the amount of water or other liquid substances migration from the pores of the material in a certain period of time; thus, we obtain: the composition of the porosity in the concrete paste, hydration or association with the release of heat or hydration heat, and mixing water evaporation, the concrete temperature, and the formation of cavities and plastic shrinkage cracks in the concrete during the setting time.

The concrete pores appoint to environmental exposure and damage of the material from liquids and gases that enter, such as carbon dioxide, water, oxygen, chloride, sulfate, etc.; these elements or compounds originate various chemical reactions, whose most critical effect is the corrosion of steel in the construction element. Hence, the concept of durability in concrete (Castorena et al., 2007) (Valencia et al., 2012) is linked to maintaining their original shape, quality, and good performance when exposed to the atmosphere of service.

Mercury porosimetry allows us to notice the influence of the zeolite inclusion in the porosity of the final concrete. When the percentage of zeolite added was 5%, no difference from the reference concrete was observed, however at a rate of 10%, porosity increased to 12.57% (see Table 3). Normal values for conventional concrete porosity typically range between 9 and 10%, so the porosity obtained for concrete HZ5% may be considered normal for this type of material.

Furthermore, the increase we observed in the porosity, up to 12%, in concrete HZ10% could be explained by a limitation in the degree of reaction that presents this pozzolanic material (Poon, Lam, Kou, and Lin 1999). Some authors have shown an inverse relationship between the porosity of concrete and compressive strength (Kumar and Bhattacharjee, 2003), and by comparing these values to each other it could be observed that in HZ5% the lack of porosity produced a strong increase of the resistance; however, in the concrete HZ10% the effect was the opposite.

The latter can be explained by filling the pores of the concrete with the reaction products resulting from the cement and clinoptilolite, which may lead to a decrease or refining of the pore size resulted in an increase of resistance (Sabir, Wild, and Bay, 2001). When observing the peak of the porosity distributions in Figure 2, we notice a displacement towards an effective and smaller pore size with respect to the other concrete, which may explain its resistance regardless of the value of an increase in porosity (Rübner and Hoffmann, 2006).

The density of hardened concrete is an important parameter to be taken into account, since it depends on the density components that show both its volume and composition. Likewise, these values not only offer an idea of the influence of the ratio a/c in the intrinsic porosity of concrete, but also the contribution of the material included. One of the methods to ensure the durability of concrete against the entry of chemical aggressive species such as chlorides, sulfates, etc., is to obtain a concrete with reduced permeability to guarantee that

Table 6. Data obtained from the freeze-thaw resistance of concrete testing with zeolites.Own elaboration, 2014

Sample	Mass loss (%)	Cs N/mm2			Residual Strength c/r pattern (%)	F	Air porous> 360 $\Box$m (%)
		Initial (28 days age)	Final	Loss of Resistance (%)			
HR	1.27	59.87	53.50	-10.64	-	289	0.04
HZ5%	0.23	64.32	58.25	-9.43	11.41	314	0.15
HZ10%	0.27	68.42	66.20	-3.24	69.52	268	1.25

Table 7. Data obtained from accelerated diffusion testing of concrete with zeolites and from compression flexural strength tests to the reference concrete and the added one with % zeoilte. Own elaboration, 2013

Sample	Accelerated diffusion						Flexural strength	Compression
	24 hours		53 hours		83 Hours			
	x, mm	Dx10-11, m² s-1	x, mm	Prototype (N/mm²)	Prototype (N/mm²)	Dx10-11, m2 s-1	Prototype (N/mm²)	Prototype (N/mm²)
HR	11.73	2.26	19.55	5.36	27.55	1.84	5.36	40.67
HZ5%	7.68	1.19	11.54	5.59	20.06	1.24	5.59	45.23

concrete degradation processes slow down. An experimental verification of the achievement of a porous structure sufficiently impermeable concrete for the environment in which it will be located, can be performed by checking the water impermeability of concrete by the method of determining the depth of penetration of water under pressure, according to the standard UNE-EN-12390-8: 2009 which should be read along with the standard UNE-EN-12390-8: 2009/1M: 2011.

The greater or lesser ease of penetration that may present concrete in an environment with certain humidity is an important factor to take into account since this favors the dissolution and propagation of reactive species into the concrete. The water penetration values in concrete with zeolites, shown in Table 4, we observe that this was greater in cases where concrete contained 10%, no significant differences were observed with respect to the reference concrete in the case of concrete with 5% zeolite. This parameter is undoubtedly related to the porosity of the samples, so that the higher the porosity is, the higher its depth of penetration as in the case of concrete HZ10% with 12.57% porosity.

The permeability calculation through mercury porosimetry confirmed this different behavior. In this case, a clear increase in the permeability of concrete with higher proportions of zeolite and a slight decrease in HZ5% were also observed with respect to that of the reference. In Table 5, the parameters calculated with the porosity of the samples have been compared, observing that the apparent diffusion coefficient presented magnitudes of the same type but still significant differences between them. They show a direct relationship with the porosity obtained by mercury porosimetry. Thus, the higher the porosity of the concrete is, the higher the diffusion coefficient. It can be said that in this type of concrete, the diffusion process is mainly controlled by the porosity and the chloride concentration gradients in the different zones of these materials.

The higher velocity value can be found in concrete HZ5%, while HZ10% shows values of the same type regarding their reference concrete (Figures 2 and 3). These differences suggest that, apart from porosity, other factors such as the average pore diameter and, especially, the critical pore size can control the diffusion process, since in many cases they are the ones that give access to a more or less interconnected network of pores that may favor the diffusion process and, thus, ions penetration velocity.

Residual strength values, shown in Table 6, grow with respect to the concrete pattern in proportion to the content of zeolite. Freeze-thaw resistance data, F, determined by mercury porosimetry in some cases differ with experimental values. While concrete HZ5% had an F value of 314, indicating that this is a very resistant concrete to freeze-thaw processes, concrete HZ10% with a value of 268 would be considered slightly resistant in these conditions.

When interpreting these results, we should take into account the influence of the factors contributing to a greater or lesser extent to the strength of these concretes, such as materials used in manufacture: type of cement, aggregate, etc. However, one factor that plays a significant role in resistance to freeze-thaw resistance of concrete is the content of occluded air (Aïtcin, 2003; Rübner & Hoffmann, 2006). The mercury intrusion technique cannot determine pores whose size exceeds 360 µm (Webb and Orr 1997); as these pores are formed by a low additional occluded air additional volume which falls in the calculation of resistance factor F; that is why the determined values are not well-balanced with those obtained experimentally. Indirectly, it could be said that in

these types of concrete there is occluded air that grows over the percentage of added zeolite, which affects the improvement of its properties when facing sudden temperature changes. Indirectly, we can determine pore air content over µm 360 with the difference of the density data of hardened concrete. As shown, the occluded air content is higher according to the increased content of zeolite.

The final interpretation of these results may be explained through two key factors: the existence of occluded air pores, as a result of the manufacturing process and the addition of zeolite that favors freeze-thaw resistance which, on the other hand, generates this addition more resistant microstructure resulting from sudden temperature changes. According to the standard UNE 146508: 1999 EX, it is considered that an aggregate is potentially harmful when its expansion is higher than 0.2% of the initial length of the test tube, in this case in mortars with zeolite in its composition were not detected expansions greater than 0.08%, as in both these proportions were always lower than the corresponding reference to the specimen which is not considered reactive. This indicates that the zeolite certainly improves the properties of siliceous aggregate used making it less reactive.

In the case of "prototypes" (Table 7) after 28 days curing proceeded to break the prisms. Rf experienced a slight decrease, however the compressive strength experienced an increase with the addition of zeolite. The values obtained in this case were slightly lower compared to the first concrete produced, these differences are due to the type of cement used, because while it was initially a CEM I 52.5R at laboratory scale, in the pieces of the prototype it has been used a less resistant CEM II A/L 42.5R. The decrease of the diffusion coefficient showed a clear increase in the resistance to chloride diffusion with the addition of zeolite, almost twice compared to conventional concrete (Table 5).

Conclusions

The obtained results lead us to the following conclusions: The awful workability of concrete with additions of 15% or higher is a drawback when attempting to obtain concrete with a high proportion of zeolite, except when using partial replacement of cement and/or varying the consistency by adding water or additive. Thus, it could provoke a conflict between strength and workability.

With respect to the addition of natural clinoptilolite, it was possible to obtain concrete with zeolite proportions of 5% and 10% which showed an adequate workability. On the one hand, the addition of this additive was an improvement in the already analyzed mechanical properties. Cs, Rt, and Y increased in proportion to the content of zeolite with respect to conventional concrete. Conversely, Rf decreased higher proportions of zeolite, showing a reverse behavior from the observed one with respect to the rest of the properties studied. In other words, the durable characteristics of this type of concrete were also similarly improved. Resistance to chloride diffusion in concrete increased 5%, as resistance to freeze-thaw did. Furthermore, the absence of reactivity of alkali-silica type in the presence of zeolite concrete was analyzed. The low increase of Rf, at the same time the proportion of zeolites increase, should be studied further.

In view of these results, it can be said that the zeolite is a new addition to be taken into consideration within the group of materials including EHE (silica fume and fly ash). According to this standard, additions can be defined as pozzolanic additions with latent hydraulicity or inorganic materials, being finely divided, can be added to concrete in order to improve some

of its properties or confer special properties. The zeolite meets these characteristics; it also presents the advantage of being a natural product, thus contributing to environmental sustainability.

Acknowledgment

References

Armbruster, T. (2001). Clinoptilotite-heulandite: applications and basic research. Studies in Surface Science and Catalysis, 135, 13-27.

Aïtcin, P.C. (2003). The durability characteristics of high performance concrete: a review, Cement & Concrete Composites, (25), 409–420.

Casals, C. (1988). Las zeolitas mineral del siglo XX. Usos y aplicaciones. Ediciones Publicigraf.

Castellanos, N. T., García, S. I., Agredo, J. T., & de Gutiérrez, R. M. (2014). Resistance of blended concrete containing an industrial petrochemical residue to chloride ion penetration and carbonation. Ingeniería e Investigación, 34(1), 11-16.

Castorena, J., Pérez, J. L., Borunda, A., Gaona, C., Torres-Acosta, A., Velázquez, I. & Almeraya, F. (2007). Modelación con elementos finitos del agrietamiento en el hormigón por corrosión localizada en la armadura. Revista ingeniería de construcción, 22(1), 35-42

Fernández, M. (1989). Hormigón. Ed. Colegio de Ingenieros de Caminos, Canales y Puertos.

Hidalgo, J. R. (2011). Estructura química de las zeolitas así como sus aplicaciones industriales. Revista Digital innovación y experiencias educativas, 45. ISSN 1988-6047.

Janotka, I., & Stevula, L. (1998). Effect of bentonite and zeolite on the durability of the cement suspension under sulphate attack. ACI Materials Journal, 96(6), 710-715 .

Kumar, R., & Bhattacharjee, B. (2003). Porosity, pore size distribution and in situ strength of concrete. Cement and Concrete Research, 33(1), 155-164.

Meira, G.R., Andrade, C., Padaratz , I.J., Alonso, C. & Borba Jr, J.C.(2007) Chloride penetration into concrete structures in themarine atmosphere zone – Relationship between deposition ofchlorides on the wet candle and chlorides accumulated into concrete, Cement & Concrete Composites, (29), 667–676.

Mertens, G., Snellings, R., Van Balen, K., Bicer-Simsir, B., Verlooy, P. & Elsen, J. (2009). Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity, Cement and Concrete Research, (39), 233–240.

Nazareno Coloma, J. A., & Peña Carpio, E. (2002). Gestión del movimiento de tierras y aprovechamiento de las zeolitas naturales existentes en el parque tecnológico del campus-espol.

Paola, R. E. (2004). El uso de la Zeolita como una adición mineral para producir Cemento Puzolánico. ESPOL, Guayaquil.

Poon, C.S., Lam, L., Kou, S.C. & Lin, Z.S. (1999) A study on the hydration rate of natural zeolite blended cement pastes, Construction and Building Materials, 13, 427-432.

Rodríguez-Camacho, R.E. & Uribe-Afif, R. (2002). Importance of using the natural pozzolans on concrete durability, Cement and Concrete Research, (32), 1851–1858.

Rosell Lam, M., Costafreda Mustelier, J. L., Parra y Alfaro, J. L., & Calvo Pérez, B. (2011). Influencia de la adicion de zeolita en las propiedades micro y macroestructurales en pastas y morteros. Minas

Rosell, M., Galloso, R., & Calvo, B. (2006). Zeolita como aditivo mineral activo en hormigones de altas prestaciones. Boletín Geológico y Minero, 117(4), 783-792.

Rübner, K. & Hoffmann, D. (2006). Characterization of mineral building materials by mercury-intrusion porosimetry, Part. Syst. Charact, (23), 20-28.

Sabir, B., Wild, S., Bay, J. (2001). Metakaolin and calcined clays as pozzolans for concrete: a review. Cement and Concrete Composites, (23), 441-454

Saltos Arteaga, C. O., & Eguez Alava, H. (2005). Efectos De La Adición De La Zeolita En Las Propiedades Mecánicas De Un Hormigón Convencional De Cemento Pórtland Tipo I.

Valencia, G., Mejía de Gutiérrez, R., Barrera, J., & Delvasto, S. (2012). Estudio de durabilidad y corrosión en morteros armados adicionados con toba volcánica y ceniza de bagazo de caña de azúcar. Revista de la construcción, 11(2), 112-122.

Webb, P.A. & Orr, C., (1997) Analytical methods in fine particle technology, Micromeritics instrument corporation Asociación Internacional de Zeolitas (http://www.iza-online.org/)[16/09/2014]